P–V–T BEHAVIOUR OF HARD BODY FLUIDS. THEORY AND EXPERIMENT

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Received December 22nd, 1985

All available numerical data on virial coefficients along with simulation results for the compressibility factors of hard body fluids and their mixtures have been compiled. Practically all relevant theories for these fluids (lattice theories, specific methods for discontinuous potentials, integral and integro-differential theories, expansion and resummation techniques, as well as perturbation and conformal theories) are reviewed and their results are compared with the data. The individual methods are critically assessed and their advantages and limits are discussed.

1. INTRODUCTION

Accurate description of the equilibrium behaviour of fluids – the aggregate state between solid (modelled by the perfectly ordered crystal) and the perfect gas (a completely disordered system with negligible intermolecular interactions) – from the first principles has been one of the most challenging tasks of contemporary physics and chemistry viewed by many as "the last frontier" in the quest for real understanding of properties of matter. From the practical point of view, the knowledge of an equation of state enables one to evaluate all the equilibrium properties of liquids and gases and their mixtures; these properties are essential for design and control of the majority of chemical process equipments.

First relationships, employed in the classical physical chemistry and chemical engineering, were formulated already in the second half of the last century (van der Waals equation) and at the beginning of this century (virial expansions) and reflected simple views on intermolecular forces. Further impulse came in the thirties and forties when more realistic models of the intermolecular intractions were used in combination with lattice theories of liquids. However, due to the assumption of highly ordered structure (common to the original lattice theories) the obtained equations of state did not find wider applications.

A completely new approach to the formulation of the equation of state of real non-associated fluids stems from the results of an analysis of the effect of repulsive and attractive forces on the structure of fluids. The fact that harsh repulsive forces have a dominant effect on the structure has stimulated studies of hard body (HB) systems, *i.e.* the systems where the repulsive forces are modelled in the simplest way and the attractive forces are neglected completely. The simplicity of the interaction potential made it possible to find either an analytical or a numerical solution of equations for functions characterizing the fluid structure, the exact determination of several lowest virial coefficients and the development of equations of state for such systems. Enormous progress in obtaining pseudoexperimental data has become possible by the use of computers. The knowledge of a HB equation of state has enabled then to apply perturbation methods to determine thermodynamic functions of pure compounds and mixtures at a broad range of conditions. Expressions for the HB compressibility factor form now the "exact" term of modern semiempirical equations of state, the so called augmented van der Waals equations, which begin to show their usefulness in solving practical chemical-engineering problems. All these achievements only underline the importance of the knowledge of the HB fluid properties not only for understanding the behaviour and developing a theory of dense fluids, but also for their direct practical applicability.

Because of their simplicity, the HB systems serve frequently as first testing systems for theories. Vast original literature therefore exists on applications of different theories to these systems as well as on simulation studies. Since the monograph by Hirschfelder and coworkers[1], a number of books dealing with liquids has been published but these focus mainly on basic ideas and methods and not on results for specific systems. Further, all monographs with the only exception[2] deal with simple liquids while molecular liquids (*i.e.* the systems with orientational dependent intermolecular interactions) are only briefly touched, if at all. Review articles[3–10] better reflect recent developments in the field of chemical physics of non-associated molecular fluids but they again focus rather on methods, properties, and results than on systems. An exception may be an article by Boublík[11], reviewing certain methods and results for virial coefficients and equations of state of HB fluids. Partial summaries about structural properties of these fluids and methods describing them may be found in the review articles by Streett and Gubbins[5] and Smith and Nezbeda[9].

The goal of the present paper is therefore to review in detail the contemporary state of our knowledge about the equilibrium properties of the HB fluids. Because of the large amount of material to deal with we confine our considerations to the pressure–volume–temperature (P–V–T) behaviour only. We compile and assess all methods used, and compile and critically evaluate all existing data of both the virial coefficients and compressibility factors. The article is organized as follows: In Section 2 the considered HB models are defined and basic geometric relations are given. Section 3 is devoted to virial coefficients of pure fluids: The basic relations are given first, followed by exact analytical results, numerical results, and approximate analytical results. Tables listing all the virial coefficients known to date are presented. Section 4 deals with equations of state for one-component systems. Basic routes to obtain them are followed by a sketch of the simulation methods and details relevant to hard body fluids, and by a complete, to our best knowledge, collection of the P–V–T data. Various methods are then outlined and comparison of their predictions with simulation data takes up the rest of the section. Section 5 deals with hard body fluid mixtures, both virial coefficients and equations of state, and its structure is similar to that of Sections 3 and 4. Concluding remarks are given in Section 6.

2. HARD BODY SYSTEMS

Hard bodies model in the simplest way the steep repulsive forces between real molecules and should thus copy, at least approximately, their size and shape. Regardless of the model considered, the HB potential, u, takes on two values only:

$$u(1,2) = \begin{matrix} +\infty & \text{if particles 1 and 2 overlap} \\ 0 & \text{otherwise}\,. \end{matrix} \qquad (2.1)$$

All geometric considerations reduce therefore to the problem of determining overlap/nonoverlap for a given configuration defined by a set of parameters. This set usually consists of a distance, r, between two fixed points (reference points), one within each molecule, and of a set of angles, ω_1, ω_2, defining the orientation of the molecules.

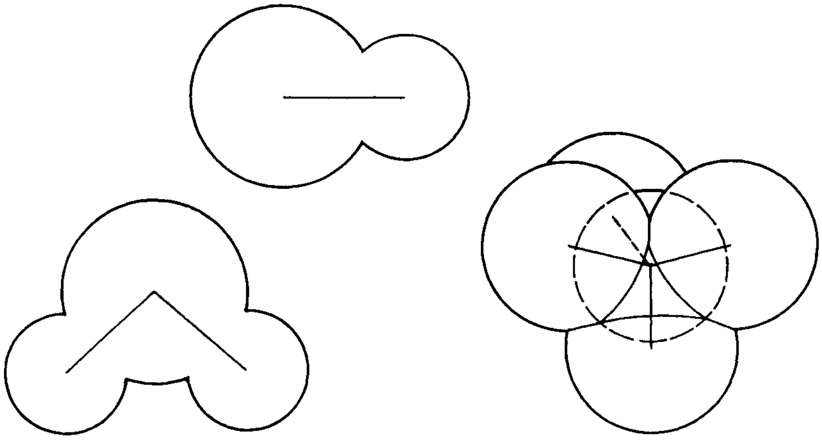
In the case of spherically symmetric molecules (*e.g.* of rare gases), pair interactions depend only on the centre-to-centre distance. The corresponding HB is a sphere (HS) of a diameter σ defining the closest possible approach of two particles. For polyatomic molecules there are, in principle, two possibilities how to describe their shape: by a fused-hard-sphere (FHS) model which is a special case of a more general interaction site (IS) model, or by a convex body (CB) model.

The IS model views a molecule as a system of interaction sites (usually coinciding with individual atoms forming the molecule) which interact with the interaction sites of the other molecule,

$$u(1,2) = \sum u_{\alpha\beta}(r_{\alpha\beta})\,. \qquad (2.2)$$

If the interaction sites are represented by hard spheres, $u_{\alpha\beta} = u_{HS}$, the FHS model is recovered. The FHS models investigated to date are depicted in Figs 1*a* and 1*b*. These are homo- and hetero-nuclear diatomics (dumbells), linear and nonlinear triatomics (both homo- and hetero-nuclear), and tetrahedral penta-atomics (a model of CCl_4). Throughout the paper the diameter of a larger sphere for diatomics, σ_A, and of a central sphere for polyatomics, σ_C, are set to unity.

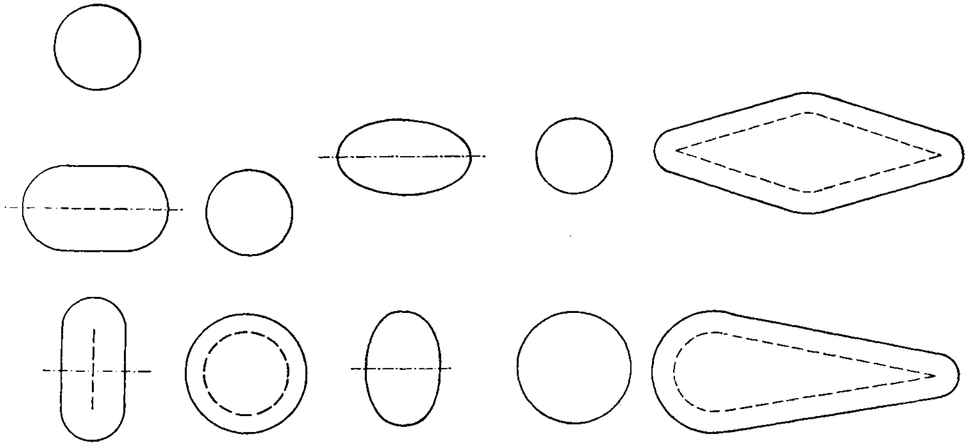
The other group of models, the CB models, was introduced by Kihara[12]. He models the entire molecule or its core by a CB in accordance with the actual molecular structure. In a general case of realistic interactions the pair potential is then assumed to depend explicitly only on the shortest surface-to-surface distance, s, between the CB. Variety of up to date considered shapes represented by CB is somewhat larger in comparison with the FHS models. The models are shown in Figs 2*a*, *b*, *c* and comprise prolate and oblate spherocylinders, prolate and oblate ellipsoids (spheroids), droplet, diamond (double cone), and cube. The breadth of CB is always set to unity and the length is denoted by γ.



1*a* 1*b*

FIG. 1

Fused hard sphere models: *a* general diatomics and symmetric triatomics; *b* tetrahedral pentaatomics



2*a* 2*b* 2*c*

FIG. 2

Convex body models: *a* sphere and prolate and oblate spherocylinders; *b* prolate and oblate ellipsoids; *c* diamond and drop

One advantage of the CB models over the FHS models is that geometry of CB is well developed and makes it possible to treat different CB in a unique way regardless of their actual shape. A convex body may be characterized by three geometric quantities: volume, $\mathscr{V}$, surface area, $\mathscr{S}$, and the $(1/4\pi)$-multiple of the mean curvature integral, $\mathscr{R}$. These three geometric functionals can be simply expressed in terms of two polar angles, ϑ and φ, that determine a tangent plane (or more generally, a supporting plane) of the CB[12]:

$$\mathscr{V} = \frac{1}{3}\iint \mathbf{r}\left(\frac{\partial \mathbf{r}}{\partial \vartheta} \times \frac{\partial \mathbf{r}}{\partial \varphi}\right) \mathrm{d}\vartheta\, \mathrm{d}\varphi \tag{2.3}$$

$$\mathscr{S} = \iint \mathbf{v}\left(\frac{\partial \mathbf{r}}{\partial \vartheta} \times \frac{\partial \mathbf{r}}{\partial \varphi}\right) \mathrm{d}\vartheta\, \mathrm{d}\varphi \tag{2.4}$$

$$\mathscr{R} = \frac{1}{4\pi}\iint \mathbf{r}\left(\frac{\partial \mathbf{v}}{\partial \vartheta} \times \frac{\partial \mathbf{v}}{\partial \varphi}\right) \mathrm{d}\vartheta\, \mathrm{d}\varphi = \frac{1}{4\pi}\iint (\mathbf{r}\,.\,\mathbf{v}) \sin \vartheta\, \mathrm{d}\vartheta\, \mathrm{d}\varphi\,. \tag{2.5}$$

In these expressions $\mathbf{r}(\theta, \varphi)$ is the vector from a reference point (any fixed point within the body) to the contact point of the CB with the tangent plane and $\mathbf{v}$ is the unit vector in the direction of the normal of this plane (see Fig. 3*a*). For convenience we give in Table I expressions of the three basic geometric functionals (in terms of parameters defining individual CB) for frequently employed CB.

Many convex bodies can be viewed as a parallel body to a simpler core, *e.g.* the prolate spherocylinder is the parallel body to a rod. The knowledge of $\mathscr{V}_c$, $\mathscr{S}_c$, and $\mathscr{R}_c$ of the core enables one to evaluate[13] the geometric functionals $\mathscr{V}_{c+\xi}$, $\mathscr{S}_{c+\xi}$, and $\mathscr{R}_{c+\xi}$ of a parallel convex body $c + \xi$ of thickness ξ (the so called Steiner's formulas):

$$\mathscr{R}_{c+\xi} = \mathscr{R}_c + \xi \tag{2.6}$$

$$\mathscr{S}_{c+\xi} = \mathscr{S}_c + 8\pi\mathscr{R}_c\xi + 4\pi\xi^2 \tag{2.7}$$

$$\mathscr{V}_{c+\xi} = \mathscr{V}_c + \mathscr{S}_c\xi + 4\pi\mathscr{R}_c\xi^2 + \tfrac{4}{3}\pi\xi^3\,. \tag{2.8}$$

Two convex bodies 1 and 2 do not overlap if the shortest distance between their cores, l_c, is greater than the common thickness, $l_c > \xi_1 + \xi_2 = \sigma$. Then the shortest distance s between two convex surfaces is a well-defined function, $s = l_c - \sigma$, and is non-negative. Variables associated with s are the direction $\mathbf{v}$, $\mathbf{v} = \mathbf{v}(\vartheta, \varphi)$, and the orientation of both bodies, $\boldsymbol{\omega}_i$ (see Fig. 3*b*). For the transformation of a volume element $\mathrm{d}\mathbf{r}_{12}$ then it holds[14]:

$$\mathrm{d}\mathbf{r}_{12} = \mathbf{v}\left(\frac{\partial \mathbf{r}_{12}}{\partial \vartheta} \times \frac{\partial \mathbf{r}_{12}}{\partial \varphi}\right) \mathrm{d}s\, \mathrm{d}\vartheta\, \mathrm{d}\varphi = \mathrm{d}\mathscr{S}_{1+s+2}(\boldsymbol{\omega}_{12})\, \mathrm{d}s\,, \tag{2.9}$$

where $d\mathcal{S}$ denotes an element of a surface created by bodies 1 and 2 at separation s and at given orientations ω_i. If this surface element is integrated (at s = const.) over orientations, we get the average surface area of a body $1 + s + 2$, which can be expressed through the surface areas of the indiviual bodies:

$$\mathcal{S}_{1+s+2} = \mathcal{S}_{1+2} + 8\pi\mathcal{R}_{1+2}s + 4\pi s^2 \,, \tag{2.10}$$

where

$$\mathcal{S}_{1+2} = \mathcal{S}_1 + \mathcal{S}_2 + 8\pi\mathcal{R}_1\mathcal{R}_2 \tag{2.11}$$

$$\mathcal{R}_{1+2} = \mathcal{R}_1 + \mathcal{R}_2 \,. \tag{2.12}$$

For completeness we also give here expressions for the mean curvature and average volume of body $1 + s + 2$:

$$\begin{aligned} \mathcal{R}_{1+s+2} &= \mathcal{R}_{1+2} + s \\ \mathcal{V}_{1+s+2} &= \mathcal{V}_{1+2} + \mathcal{S}_{1+2}\,s + 4\pi\mathcal{R}_{1+2}\,s^2 + \tfrac{4}{3}\pi s^3 \,, \end{aligned} \tag{2.13}$$

where

$$\mathcal{V}_{1+2} = \mathcal{V}_1 + \mathcal{V}_2 + \mathcal{S}_1\mathcal{R}_2 + \mathcal{S}_2\mathcal{R}_1 \tag{2.14}$$

and $\mathcal{V}_i$ is the volume of body i.

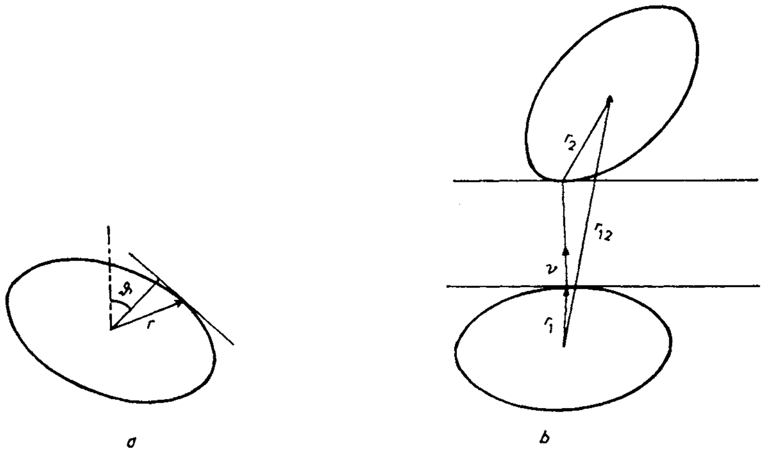


FIG. 3

Definition of basic quantities for a single particle (*a*) and a pair of convex bodies (*b*)

TABLE I

Geometric functionals — volume, $\mathscr{V}$, surface area, $\mathscr{S}$, and $(1/4\pi)$-multiple of the mean curvature integral, $\mathscr{R}$ — of hard convex bodies. σ denotes breadth of bodies and γ the ratio maximum length/breadth; λ denotes the ratio of axis of ellipsoids, R is the radius of circumscribed sphere, a and h denote edges and height, respectively, and φ_i are complements of angles formed by faces

Body	Parameter(s)	$\mathscr{R}$	$\mathscr{S}$	$\mathscr{V}$
Point	—	0	0	0
Rod	l	$\frac{1}{4}l$	0	0
Infinitely thin disc (circle)	σ	$\frac{1}{8}\pi\sigma$	$\frac{1}{2}\pi\sigma^2$	0
Infinitely thin rectangular slab	a, b	$(a + b)/4$	$2ab$	0
Sphere	σ	$\frac{1}{2}\sigma$	$\pi\sigma^2$	$\frac{1}{6}\pi\sigma^3$
Cylinder	γ, σ	$\frac{1}{4}(\gamma + \pi/2)\,\sigma$	$\pi\sigma^2(\frac{1}{2} + \gamma)$	$\frac{1}{4}\pi\gamma\sigma^3$
Prolate spherocylinder	γ, σ	$\frac{1}{4}(\gamma + 1)\,\sigma$	$\gamma\,\pi\sigma^2$	$(3\gamma - 1)\,\pi\sigma^3/12$
Oblate spherocylinder	$\varphi(= \gamma - 1), \sigma$	$\frac{1}{2}(\pi\varphi/4 + 1)\,\sigma$	$\frac{1}{2}(\varphi^2 + \pi\varphi + 2)\,\pi\sigma^2$	$(6\varphi^2 + 3\pi\varphi + 4)\,\pi\sigma^3/24$

Prolate ellipsoid of revolution	$\lambda > 1, \sigma$	$\frac{1}{4}\left\{\lambda + \frac{\ln[\lambda + \sqrt{(\lambda^2 - 1)}]}{\sqrt{(\lambda^2 - 1)}}\right\}\sigma$	$\frac{1}{2}\left[1 + \frac{\lambda^2 \arccos \lambda^{-1}}{\sqrt{(\lambda^2 - 1)}}\right]\pi\sigma^2$	$\pi\lambda\sigma^3/6$
Oblate ellipsoid of revolution	$\lambda < 1, \sigma$	$\frac{1}{4}\left[\lambda + \frac{\arccos \lambda}{\sqrt{(1 - \lambda^2)}}\right]\sigma$	$\frac{1}{2}\left\{1 + \frac{\lambda^2}{\sqrt{(1 - \lambda^2)}} \cdot\right.$ $\left. . \ln\left[\frac{1 + \sqrt{(1 - \lambda^2)}}{\lambda}\right]\right\}\pi\sigma^2$	$\pi\lambda\sigma^3/6$
Spherocone (core of droplet)	γ, σ	$\frac{1}{8}\left(2\gamma + 1 + \frac{1}{2\gamma - 1}\right)\sigma$	$\frac{1}{4}\left(2\gamma + 1 + \frac{1}{2\gamma - 1}\right)\pi\sigma^2$	$\left(2\gamma + 1 + \frac{1}{2\gamma - 1}\right)\frac{\pi\sigma^3}{24}$
Doublecone (core of diamond)	γ, σ	$\frac{1}{4}\left(\gamma + \frac{1}{\gamma}\right)\sigma$	$\frac{1}{2}\left(\gamma + \frac{1}{\gamma}\right)\pi\sigma^2$	$\left(\gamma + \frac{1}{\gamma}\right)\frac{\pi\sigma^3}{12}$
Cube	a	$3a/4$	$6a^2$	a^3
Tetrahedron	R	$(\sqrt{6}/2\pi) \arccos(-\frac{1}{3})\, R$	$8\sqrt{3}R^2/3$	$8\sqrt{3}R^3/27$
Octahedron	R	$(3\sqrt{6}/2\pi) \arccos(\frac{1}{3})\, R$	$4\sqrt{3}R^2$	$4R^3/3$
Regular angular pyramid	$a, h, \varphi_1, \varphi_2$	$3[a\varphi_1 + \varphi_2 \sqrt{(h^2 + \frac{1}{3}a^2)}]/8\pi$	$\frac{1}{2}[\frac{1}{2} a^2 \sqrt{3} + 3a \sqrt{(h^2 +}$ $+ a^2/12)]$	$a^2h/4\sqrt{3}$

In majority of papers dealing with the FHS models the centre of mass (CM) has been traditionally used as a reference point which causes mathematics to become very complex. Reasons for that are easily understood from examining Fig. 4, where we show two arrangements for homonuclear diatomics. To perform the integration over orientations in the CM system means to change positions of all spheres and, consequently, all four pairs must be taken into account in geometrical considerations. Much more suitable seems therefore a system which is linked with an interaction site (site-centered system, SC). From Fig. 4 it is seen that two α-spheres are automatically out of game and positions of only the β-spheres are changed making so the geometry transparent. Such a system was first used by Nezbeda[15] in connection with an approximate treatment of homonuclear diatomics. Later on Nezbeda and Smith[16] and Tildesley and coworkers[17,18] showed that also general expressions for the thermodynamic and correlation functions assume a much simpler form in the SC coordinate system.

3. VIRIAL COEFFICIENTS

3.1. *Virial Expansion*

The virial expansion,

$$\beta P/\varrho \equiv z = 1 + B_2\varrho + B_3\varrho^2 + \ldots \qquad (3.1)$$

was first suggested by Kamerlingh Onnes[19] already in 1901 as an empirical correction to the ideal gas equation of state. In Eq. (*3.1*) $\beta = (kT)^{-1}$, T is the absolute temperature, P is the pressure, ϱ is the number-density, $\varrho = N/V$, and B_i are the virial coeffi-

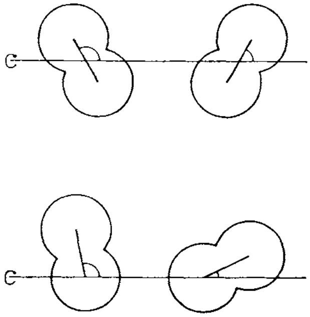


FIG. 4

Two different coordinate systems for FHS models: the centre-of-mass system (upper arrangement) and the site-centred system (lower arrangement) cients. For years the application of Eq. (*3.1*) was confined to the low density region only where it accounts for gas non-ideality. Application of such techniques as Padé approximants or a perturbed virial expansion extends the practical utility of the expansion to much higher densities. The virial expansion provides also a low density limit of any fluid equation of state and must be therefore considered as an integral part of a theoretical description of the P–V–T behaviour of fluids.

Both the canonical and grand-canonical ensembles can be used to derive basic relations for a fluid system and the derivation of Eq. (*3.1*) can be found in nearly every textbook on statistical mechanics[20–23]. In the following we briefly outline the derivation using the grand-canonical ensemble.

Let us consider an open system of classical molecules confined to a volume V at a temperature T. The potential energy of an N-particle system, U_N, is generally given as a sum of pair, triplet, ... *etc.* interactions,

$$U_N = \Sigma u_{ij}(i, j) + \Sigma u_{ijk}(i, j, k) + \ldots, \tag{3.2}$$

where arguments $(i, \ldots)$ denote dependence on positions and orientations of particles $i, \ldots$. The N-particle configuration integral is given by

$$Z_N = \int \ldots \int \exp\left[-\beta U_N\right] \mathrm{d}(1)\, \mathrm{d}(2) \ldots \mathrm{d}(N)\,. \tag{3.3}$$

Since the grand-canonical partition function is given by

$$\Xi = \Sigma \frac{1}{N!} Z_N(V, T)\, z_0^N\,, \tag{3.4}$$

where z_0 is the absolute activity, then, using standard thermodynamic relations and some algebra, it is easy to find the relations between B_i and Z_i (for details see *e.g.* refs[20,22]):

$$B_2(T) = -(1/2V)(Z_2 - Z_1^2) \tag{3.5}$$

$$B_3(T) = -(1/3V)(Z_3 - 3Z_2^2/Z_1 + 3Z_2 Z_1 - Z_1^3) \tag{3.6}$$

$$\vdots$$

etc.

Inserting appropriate expressions for Z_i into (*3.5*) we get

$$B_2(T) = -(1/2V) \int \{\exp\left[-\beta u_{12}\right] - 1\}\, \mathrm{d}(1)\, \mathrm{d}(2) =$$

$$= -(1/2V)\int f_{12}(1, 2)\,\mathrm{d}(1)\,\mathrm{d}(2)\,, \tag{3.7}$$

where f_{12} is the so called Mayer function. For potentials of a finite range, $u = 0$ for $r > r_{\mathrm{range}}$, the f-function is also identically equal to zero beyond that range. For spherical particles Eq. (3.7) assumes then a very simple form

$$B_2(T) = -2\pi \int_0^{r_{\mathrm{range}}} f_{12}(r_{12})\, r_{12}^2\, \mathrm{d}r_{12}\,, \tag{3.8}$$

where r_{12} denotes the centre-centre separation. For non-spherical particles we have

$$B_2(T) = -2\pi \int \{\exp\left[-\beta u(r_{12}, \omega_1, \omega_2)\right] - 1\}\, r_{12}^2\, \mathrm{d}r_{12}\, \mathrm{d}\omega_1\, \mathrm{d}\omega_2 =$$
$$= -2\pi \int_0^{r_{\mathrm{range}}} [\langle e \rangle - 1]\, r^2\, \mathrm{d}r\,, \tag{3.9}$$

where $\langle e(1, 2)\rangle$ is the average Boltzmann factor,

$$\langle e(1, 2)\rangle = \int \exp\left[-\beta u(r, \omega_1, \omega_2)\right] \mathrm{d}\omega_1\, \mathrm{d}\omega_2 \tag{3.10}$$

and

$$\int \mathrm{d}\omega_i = 1\,.$$

The expressions for the higher virial coefficients will contain non-additive energy terms $u_{ijk}, \ldots$. It is known that neglecting all these terms provides usually quite a good approximation for real systems. For the third virial coefficient we thus can get

$$B_3 = -(1/3V)\int f_{12}(1, 2) f_{13}(1, 3) f_{23}(2, 3)\, \mathrm{d}(1)\, \mathrm{d}(2)\, \mathrm{d}(3)\,. \tag{3.11}$$

For spherical particles this integral can be simplified by introducing bipolar coordinates, but this is useless for non-spherical particles due to the integration over orientations.

Expressions for the higher virial coefficients become soon very complex. To make these expressions more transparent, a graphical representation of the integrals is usually used. The first four virial coefficients are shown in Fig. 5, where the black circles denote integration variables associated with a particle, the bonds denote the

Mayer function and the open circle denotes a particle with which a coordinate system is fixed. In evaluation of these diagrams any labelling of the black circles can be used.

A mathematical technique has also been developed allowing one to perform mathematical operations directly with the graphs instead of working with integrals. Details about the diagrammatic technique can be found *e.g.* in refs[24,25]. Instead of denoting the virial coefficients as B_i, a sequence of capital letters B, C, ... has also been often used. The latter notation has given rise to the labelling of individual diagrams according to the number of f-bonds. Thus, for instance, $C3$ stands for the only diagram of B_3, $D4$, $D5$, and $D6$ for diagrams contributing to B_4, *etc.* (see Fig. 5).

Using the graphs with f-bonds only (Mayer representation), the fourth virial coefficient is given by 3 diagrams, the fifth one already by 10 diagrams and the sixth virial coefficient by as many as 56 diagrams. These numbers can be reduced by considering both f- and e-bonds (Ree–Hoover representation[26]). In any graph every pair of points not connected by a line may be considered as being connected by the unit function. Writing

$$1 = e_{ij} - f_{ij} \tag{3.12}$$

the graphs decompose into those with f-bonds only and those with e- and f-bonds, with many cancellations taking place. The result is demonstrated for B_4 in the fourth row of Fig. 5. The reduction is more striking for higher coefficients. The ten Mayer graphs for B_5 reduce to only five and 56 diagrams for B_6 reduce to 23.

Another representation, the so-called two point representation, of the virial coefficients of hard body fluids is based on the fact that the derivative of the hard body pair potential is proportional to the Dirac δ-function. Starting from the expression

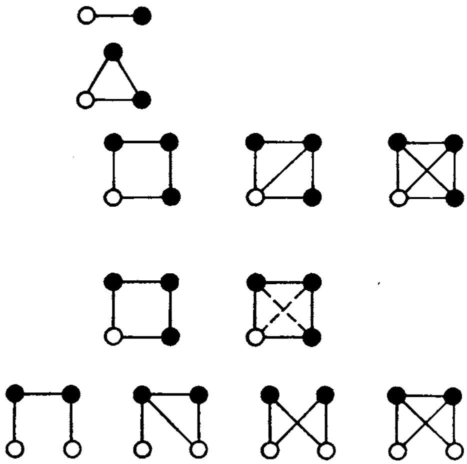
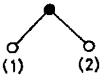


FIG. 5

Diagrams contributing to the virial coefficients B_2 through B_4. The third through fifth rows show different representations of B_4: Mayer representation with f-bonds (——) only (3rd row); Ree–Hoover representation with both f- and e-bonds (----; 4th row); two-point representation (last row) for the compressibility factor in terms of the pair correlation function (see Section 4.1), one can perform integration over dr_{12} which means that all terms are evaluated under the constraint that particles 1 and 2 are in contact. Thus, for instance,

$B_3 = B_2 \times$  $= B_2 c(1,2)$ (3.13)

and $r_{12} = \sigma$ for hard spheres. Further details about this virial series representation may be found *e.g.* in ref.[27]. As an example, the two-point graphs contributing to B_4 are shown in the last row of Fig. 5.

3.2. *Virial Coefficients: Exact Results*

Evaluation of the lowest virial coefficients for hard spheres had been an object of interest long time before the exact formulas for these coefficients were derived, with such names as van der Waals, van Laar, and Boltzmann involved.

The integration in Eqs (*3.9*), (*3.11*), ... is simplest for the hard sphere fluid and has been performed analytically up to B_4. Due to a greater number of integration variables for nonspherical molecules, mathematical complexity has not allowed to get a closed analytical result for these models beyond B_2. Specifically, the analytical results are available for all convex bodies[12], for fused diatomics[28,29] and a special model of linear triatomics[29]. In all remaining cases we have to resort to a numerical integration.

The exact (analytical or numerical) virial coefficients are known at present up to B_7 for hard spheres[30]; for nonspherical models the most frequently computed and reported coefficients are B_2, B_3, and B_4 although for some models also B_5 has been evaluated. The virial coefficients reported in the literature up to 1984 have been compiled by Malijevský and Labík[31].

3.2.1. Numerical Integration

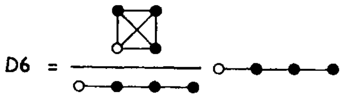
It is well-known that, in general, common quadrature technique becomes ineffective for fourfold integrals. To compute B_2 for a nonspherical model we have to handle with at least a fivefold integral and in the case of B_5 of hard spheres with a 12-fold integral. For these reasons the Monte Carlo (MC) integration is often applied.

For determining the virial coefficients, the MC method is used in two different ways. The "classical" MC integration, *i.e.* the determination of a fraction of a multidimensional volume by the uniform sampling of the total volume, is useful only for B_2. For higher coefficients the fraction becomes very small which makes the method inaccurate.

The other MC method for hard bodies is based on the fact that all graphs defining the virial coefficients contain an open chain, *e.g.* ○—●—●—● for B_4, which is related directly to the second virial coefficient:

$$\circ\!-\!\bullet\!-\!\bullet\!-\!\bullet = [\circ\!-\!\bullet]^3 \qquad (3.14)$$

Since we can write, for instance,



(3.15)

this coefficient may be evaluated as the ratio of $D6$ to the appropriate power of B_2. It means that we must generate first a chain (*3.14*) which will then represent a trial configuration[32]. Having a chain, a check is made whether bond 1 – 4 exists and, in turn, whether bonds 1 – 3 and 2 – 4 exist, too. (We use labelling of points which starts at the open circle and goes counter-clockwise). All graphs can be evaluated in this way including those with e-bonds (*cf.* Fig. 5). It is evident that for the application of this method B_2 must be known very accurately.

In early applications only several tens of thousands of trial configurations were generated to evaluate B_i for linear models and for oblate spherocylinders. It seems nowadays that at least several hundreds of thousands of configurations must be generated for good statistics and in some cases, depending on the model in hand, a million or even more configurations[33,34] are necessary. Accuracy of the results is, according to our experience, 0·25 – 0·75 per cent for B_3 and 0·8 – 2·0 percent for B_4. These uncertainties account for various effects including also an algorithm dependence, while the much higher accuracy specified sometimes in original papers seems to correspond only to reproducibility of the results obtained by using the same program and the same machine configuration.

In the above method a new trial configuration is generated independently of the previous configurations. There exists a third method of evaluating the virial coefficients using the Metropolis-like sampling (with f bonds instead of e-bonds) to generate a trial configuration: If a trial configuration exists, the next one may be obtained by performing a restricted random walk of the individual particles forming the chain. Such an approach was employed *e.g.* by Mulder and Frenkel[35] for ellipsoids.

Quite recently Lado[36] proposed a method to calculate numerically (by employing the spherical harmonic expansion, see Section 4.1.) the convolution integral $c(1, 2)$ (Eq. (*3.13*) with arbitrary r_{12} distance) for molecular fluids. Integral of $c(1, 2)$ over all its variables is directly related to B_3 and this way may be therefore used either to get B_3 as a by-product of computations or as a check of the MC results and *vice versa*.

3.2.2. Hard Spheres

The second virial coefficient equals, from Eq. (*3.8*), one half of the excluded volume around a sphere,

$$B_2 = \tfrac{2}{3}\pi\sigma^3 = 4\mathcal{V}\,, \tag{3.16}$$

where $\mathcal{V}$ is the volume of a sphere.

The third virial coefficient can be simply evaluated by calculating first the convolution integral,

$$c(r_{12}) = \int f(r_{13})\,f(r_{23})\,\mathrm{d}\mathbf{r}_3 \tag{3.17}$$

which is just the excluded volume common to two spheres separated by a distance r_{12}:

$$\begin{aligned} c(r_{12}) &= \tfrac{4}{3}\pi\left[1 - \tfrac{3}{4}(r_{12}/\sigma) + \tfrac{1}{16}(r_{12}/\sigma)^3\right]\sigma^3\,, \quad r_{12} < 2\sigma \\ &= 0\,, \quad r_{12} > 2\sigma\,. \end{aligned} \tag{3.18}$$

Since,

$$C3 = \int f(r_{12})\,c(r_{12})\,\mathrm{d}\mathbf{r}_{12} = -\tfrac{5}{6}\,(\pi\sigma^3)^2 \tag{3.19}$$

we get

$$B_3/\mathcal{V}^2 = 10 \quad \text{or} \quad B_3/B_2^2 = 5/8\,. \tag{3.20}$$

For evaluating B_4 the result for $c(r_{12})$ is also useful:

$$D4 = \int [c(r_{12})]^2\,\mathrm{d}\mathbf{r}_{12} = \frac{17\,408}{105}\,\mathcal{V}^3 \tag{3.21}$$

$$D5 = \int f(r_{12})\,[c(r_{12})]^2\,\mathrm{d}\mathbf{r}_{12} = \frac{406\,208}{3\,360}\,\mathcal{V}^3\,. \tag{3.22}$$

The most difficult term is the fully connected graph *D6*. First calculations of this graph were performed by van Laar[37] and Boltzmann[38] in 1899 by using an extremely complicated algebra. More than fifty years elapsed until their results were verified in 1952 by Nijboer and van Hove[39] who used the two-point graph formulation. Another approach was later used by Rowlinson[40] and Powell[41]. The final total result is

$$B_4/\mathcal{V}^3 = \frac{2\,707}{70} + \frac{438\sqrt{2} - 4\,131\,\arccos{(1/3)}}{70\pi}\,, \tag{3.23}$$

i.e.

$$B_4 = 18{\cdot}3648\mathscr{V}^3 \quad \text{or} \quad B_4/B_2^3 = 0{\cdot}286950\,. \tag{3.24}$$

The fifth virial coefficient is given by a sum of ten diagrams, seven of which were calculated analytically[42,43]. From the remaining three clusters the most difficult is, as usual, the complete star *E10* which was calculated by several authors using different methods[26,43–46]. Kratky[30] re-examined in detail all these results and came to the value

$$B_5/B_2^4 = 0{\cdot}110252 \pm 0{\cdot}000001\,. \tag{3.25}$$

He also re-analysed and then corrected Ree and Hoover's results[26] for B_6 and B_7. All these results along with the approximate values for B_8, B_9, and B_{10} are given in Table II.

Concerning the higher virial coefficients, one may find claims in the literature[26,27] that some of them may be negative. Using approximate theories to find lower and upper bounds to B_n for arbitrary n, Kratky[30] has come to the conclusion that all virial coefficients remain positive.

3.2.3. Convex Body Models

An advantage of the convex body models is that geometry of a single convex object and of a pair of such objects is quite well developed – *cf.* Section 2. Consequently, the second virial coefficient can be expressed analytically for any convex body model.

TABLE II

Virial coefficients of hard spheres (ref.[30])

n	B_n/B_2^{n-1}	$B_n/\mathscr{V}^{n-1}$
2	1·0	4·0
3	0·6250	10·0
4	0·286950	18·3648
5	0·110252 ± 0·000001	28·2245 ± 0·0003
6	0·0389 ± 0·0004	39·83 ± 0·41 (39·93)[b]
7	0·0137 ± 0·0006	56·1 ± 2·5 (53·5)[b]
8	0·0045[a]	74
9	0·0015[a]	98
10	0·0005[a]	131

[a] Probable value, [b] recommended value; see Eq. (*4.93*).

By inserting the volume element (*2.9*) into (*3.7*) and by taking into consideration that f_{12} outside the average volume $\mathscr{V}_{c_1+c_2}$ of the cores depends only on the distance l_c we get

$$B_2 = \tfrac{1}{2}\mathscr{V}_{c_1+c_2} - \frac{1}{2}\int f_{12}(l_c)\,\mathscr{S}_{c_1+l_c+c_2}\,dl_c\,. \qquad (3.26)$$

For hard convex bodies $f_{12} = -1$ for $l_c < \xi_1 + \xi_2 \equiv \sigma$ and $f_{12} = 0$ otherwise. Then

$$B_2 = \tfrac{1}{2}\mathscr{V}_{c_1+c_2} + \tfrac{1}{2}\mathscr{S}_{c_1+c_2}\sigma + 2\pi\mathscr{R}_{c_1+c_2}\sigma^2 + \tfrac{4}{3}\pi\sigma^3 = \tfrac{1}{2}\mathscr{V}_{c_1+\xi_1+c_2+\xi_2} = \tfrac{1}{2}\mathscr{V}_{1+2}\,, \qquad (3.27)$$

i.e. B_2 equals one half of the average excluded volume, defined by the average common volume of a pair of convex bodies in contact. This result is an extension of Eq. (*3.16*) for hard spheres. By using relation (*2.14*), the co-volume $\mathscr{V}_{1+2}$ in (*3.27*) can be expressed by means of the volume of the convex body,

$$B_2 = \mathscr{V} + \mathscr{R}\mathscr{S} = (1 + 3\alpha)\,\mathscr{V}\,, \qquad (3.28)$$

where α is a parameter of nonsphericity,

$$\alpha = \mathscr{R}\mathscr{S}/3\mathscr{V}\,. \qquad (3.29)$$

(As we deal in this section only with pure fluids, we have dropped the subscripts at the symbols for the geometric functionals.) For spheres $\alpha = 1$ while for all other convex bodies $\alpha > 1$. Eq. (*3.28*) expresses an important result, the so called conformity of convex bodies: Two convex body models with the same α have the same reduced second virial coefficient regardless of their actual shape.

General geometrical considerations have been extended also to the third virial coefficient, but in this case they yield only lower and upper bounds for B_3. Kihara and Miyoshi[47] considered the case of three particles with one being much larger than the other two, and the case of three spheres of different diameters. From examining the volume $\mathscr{V}_{1+2+3}$ they have come to a result

$$B_3 = \mathscr{V}^2 + 2\mathscr{R}\mathscr{S}\mathscr{V} + G/12\pi = (1 + 6\alpha)\,\mathscr{V}^2 + G/12\pi\,, \qquad (3.30)$$

where G must satisfy the following inequality:

$$\mathscr{S}^3 \leqq G \leqq (4\pi)^3\,\mathscr{R}^6\,. \qquad (3.31)$$

From the computational point of view, handling with the convex objects is in no way simple. The models most closely related to spheres are prolate and oblate ellipsoids[35,48] (called spheroids by some authors[49]), *i.e.* the bodies of revolution which have their origin in simple planar curves. For all other bodies all geometrical considerations reduce to finding the shortest distance between two cores of the bodies and this geometrical problem considerably limits our possibilities to consider various shapes. The simplest, and therefore most intensively studied, is the problem of two rods[32,50–53] (*i.e.* the hard cores of prolate spherocylinders). Next one is the problem of two infinitely thin platelets[33,34,54–56] (hard cores of oblate spherocylinders) and these are the only shapes, with exception of those in ref.[57], for which exact numerical computations have been performed so far. The last class of exactly tractable bodies is that of polyhedrons as *e.g.* tetrahedron, cube, *etc.* From all such shapes only the latter has been considered for evaluation of the virial coefficients[57]. Other convex bodies do not seem manageable in a rigorous way.

One can view a convex body as an envelope to an infinite number of hard spheres whose centres form the core of the body. For computational purposes one can therefore choose a finite number, N, of spheres and transform the original problem to a simple problem of N^2 spheres. To make this approximation accurate, N cannot be small which leads to slowing down significantly all computations. Nezbeda and Boublík[57] showed that at least nine spheres must be considered to accurately approximate the spherocylinder with $\gamma = 3$. They also computed in this way the virial coefficients of drop-like and diamond-like bodies[57].

The virial coefficients of all convex models considered so far are compiled in Tables III and IV. For some models the computations were performed by several authors and these are in most cases in mutual agreement. In these cases only the most reliable and accurate values are listed. An exception is the model of oblate spherocylinders, for which two new independent sets of results are available[33,34] but which disagree at high nonsphericities. Nezbeda[34] has recently analyzed in detail both sets by using various tests but has not been able to draw a definite conclusion about their accuracy and to explain the discrepancy.

The CB models listed in Tables III and IV may be roughly divided into two groups: *1*) realistic models (characterized by a low or moderate nonsphericity) which may mimic real molecules and *2*) purely academic models (usually with extreme nonsphericity) considered only for theoretical examination of certain trends and nonsphericity dependences.

From examining Table III it is immediately seen that the higher virial coefficients for different models with the same α disagree (compare *e.g.* prolate and oblate ellipsoids) and the difference becomes more pronounced with increasing α. It is not therefore possible to extend exactly the idea of conformity of the CB models (expressed by Eq. (*3.28*)) beyond the low density range. However, the assumption of the conformity may yet be a useful approximation for realistic models.

Due to the inequality $1 = \alpha_{\mathrm{HS}} < \alpha_{\mathrm{nonspherical}}$, the 2nd virial coefficient of the HS fluid provides a lower bound for $B_2/\mathscr{V}$ and the same seems to hold true also for higher virial coefficients of realistic models; due to the broken conformity nothing

TABLE III

Virial coefficients of convex body models

Parameter	$B_2/\mathscr{V}$	$B_3/\mathscr{V}^2$	$B_4/\mathscr{V}^3$	$B_5/\mathscr{V}^4$	Ref.
			Prolate spherocylinders		
γ					
1·2	4·046	10·21 ± 0·05	18·80 ± 0·30	–	57
1·4	4·150	10·64 ± 0·05	19·26 ± 0·30	–	32
1·6	4·284	11·18 ± 0·05	20·50 ± 0·35	–	57
1·8	4·436	11·84 ± 0·06	21·50 ± 0·30	–	32
2·0	4·600	12·34 ± 0·03	22·50 ± 0·23	31·9 ± 1·3	53
2·5	5·038	14·30 ± 0·07	26·06 ± 0·65	–	50, 52
3·0	5·500	16·20 ± 0·03	28·00 ± 0·28	36·8 ± 1·5	53
4·0	6·455	20·43 ± 0·04	31·90 ± 0·32	39·7 ± 1·6	53
5·0	7·429	24·92 ± 0·06	33·10 ± 0·33	39·9 ± 1·6	53
6·0	8·412	29·68 ± 0·06	31·60 ± 0·32	63·0 ± 2·5	53
11·0	13·375	–	−38·7 ± 1·6	–	53
			Prolate ellipsoids of revolution		
λ					
1·25	4·053	10·18 ± 0·05	–	–	35
1·50	4·178	10·69 ± 0·03	19·73 ± 0·20	29·88 ± 0·60	48
2·00	4·538	12·09 ± 0·03	21·56 ± 0·22	31·87 ± 0·62	48
2·75	5·211	14·81 ± 0·07	–	–	35
3·00	5·454	15·85 ± 0·08	–	–	35
5·00	7·552	25·23 ± 0·13	–	–	35
10·00	13·191	55·21 ± 0·28	–	–	35
			Diamond		
γ					
2·568	5·500	16·21 ± 0·05	28·00 ± 0·40	–	57
			Drop		
2·347	5·500	15·97 ± 0·05	26·00 ± 0·40	–	57
			Oblate spherocylinders		
$\varphi(= \gamma - 1)$					
1·0	4·387	11·65 ± 0·03	21·65 ± 0·13	32·38 ± 0·51	33
	–	11·66 ± 0·05	21·79 ± 0·05	–	34
1·5	4·702	13·08 ± 0·02	24·76 ± 0·13	35·79 ± 0·53	33
	–	13·09 ± 0·04	24·51 ± 0·30	–	34
2·0	5·044	14·79 ± 0·04	28·22 ± 0·24	39·02 ± 0·64	33
	–	14·73 ± 0·05	27·78 ± 0·40	–	34
2·636	5·500	17·07 ± 0·07	31·90 ± 0·60	–	57
3·0	5·767	18·65 ± 0·04	36·35 ± 0·25	43·90 ± 0·72	33
	–	18·29 ± 0·10	32·44 ± 0·65	–	34

TABLE III

(*Continued*)

Parameter	$B_2/\mathcal{V}$	$B_3/\mathcal{V}^2$	$B_4/\mathcal{V}^3$	$B_5/\mathcal{V}^4$	Ref.
		Oblate ellipsoids of revolution			
λ					
0·80	4·053	10·25 ± 0·03	—	—	35
0·6667	4·178	10·72 ± 0·03	19·62 ± 0·20	29·51 ± 0·60	48
0·50	4·538	12·30 ± 0·03	22·81 ± 0·23	33·18 ± 0·66	48
0·3636	5·211	15·49 ± 0·08	—	—	35
0·3333	5·454	16·74 ± 0·08	—	—	35
0·20	7·552	29·82 ± 0·15	—	—	35
0·10	13·191	84·15 ± 0·42	—	—	35
			Cube		
a	5·500	18·33 ± 0·15	42·00 ± 0·80	—	57

can be said about $B_i/\mathcal{V}^{i-1}$ for two models at the same α. If no upper bound is imposed on α, one can observe an interesting behaviour of higher virial coefficients with increasing nonsphericity. The 4th virial coefficient of prolate spherocylinders comes through a maximum beyond which it decreases with increasing γ. Monson and Rigby[53] analysed in detail contributions of individual graphs to B_4 and found that it becomes negative at $\gamma \approx 9$. Also the shape dependence of B_5 for the same system is rather surprising. If B_5 is reduced by $\mathcal{V}^4$, the changes are not very smooth. However, if B_5 is reduced by B_2^4 then B_5 is found to be a smoothly decreasing function of γ with fast decaying differences as γ increases. This behaviour is in contrast with the negative value of B_5 for infinitely thin discs (a system with infinite nonsphericity) found by Eppenga and Frenkel[55,56].

TABLE IV

Virial coefficients of infinitely thin platelets (discs) of diameter σ (ref.[56])

n	B_n/σ^3	B_n/B_2^{n-1}
2	$\pi^2/16$	1
3	0·1692 ± 0·0001	0·4447
4	0·00480 ± 0·00009	0·0205
5	−0·00867 ± 0·00016	−0·0599

3.2.4. Fused-Hard-Sphere Models

Unlike the convex body models, the FHS models do not possess such a generality and almost every model must be treated independently.

The second virial coefficient of homonuclear dumbells was first obtained analytically by Isihara[28] by a direct integration of Eq. (*3.9*). Quite recently Wertheim[58] has proposed a decomposition of the molecular Mayer function $f(1, 2)$ into certain site-site functions $F_{\alpha\beta}(1, 2)$ and managed[29] to evaluate analytically all graphs to get the average Boltzmann factor, $\langle e(1, 2)\rangle$, and consequently, also B_2 for general diatomics and linear symmetric triatomics with $\sigma_A \leqq \sigma_C$. These are the only exact analytical results for the FHS models. In the following the Wertheim's method is briefly outlined.

Starting from expression (*2.2*), placing the reference points within each molecule at the centers of spheres A, ($\sigma_A \geqq \sigma_B$), and performing a simple manipulation with site-site functions $f_{\alpha\beta}$ ($f_{\alpha\beta} = e_{\alpha\beta} - 1$) and $e_{\alpha\beta}$ we can write for the diatomics:

$$\begin{aligned} f(1, 2) &= f_{AA}(1, 2) + e_{AA}(1, 2) f_{AB}(1, 2) + e_{BA}(1, 2) f_{BA}(1, 2) + \\ &+ e_{AA}(1, 2) f_{AB}(1, 2) f_{BA}(1, 2) + e_{AA}(1, 2)\, e_{AB}(1, 2)\, e_{BA}(1, 2) f_{BB}(1, 2) \equiv \\ &\equiv F_{AA} + F_{AB} + F_{BA} + F_{BB,0} + F_{BB,1} \,. \end{aligned} \tag{3.32}$$

Let us denote by $F_{\alpha\beta}(z)$ an unweighted angle average of $F_{\alpha\beta}(1, 2)$,

$$F_{\alpha\beta}(z) = \int F_{\alpha\beta}(\mathbf{r}_{AA}, \omega_1, \omega_2)\, d\omega_1\, d\omega_2\,, \quad z = |\mathbf{r}_{AA}| \tag{3.33}$$

and

$$I_{\alpha\beta} = -\int F_{\alpha\beta}(z)\, z^2\, dz\,. \tag{3.34}$$

Then the average Mayer function and the second virial coefficients for the diatomics are given by

$$\langle f(1, 2)\rangle = F_{AA}(z) + F_{AB}(z) + F_{BA}(z) + F_{BB,0}(z) + F_{BB,1}(z) \tag{3.35}$$

$$B_2 = 2\pi(I_{AA} + 2I_{AB} + I_{BB,0} + I_{BB,1})\,. \tag{3.36}$$

By realizing that $e_{\alpha\beta} \equiv 0$ when spheres α and β overlap and $e_{\alpha\beta} \equiv 1$ when they do not, evaluation of all terms in (*3.35*) is straightforward (see Fig. 4) except for the last one which contains the f_{BB}-bond. It holds:

$$F_{AA}(z) = \begin{array}{ll} -1 & \text{for} \quad 0 < z < \sigma_A \\ 0 & \text{for} \quad z > \sigma_A \end{array} \tag{3.37}$$

$$I_{\mathrm{AA}} = \tfrac{1}{3}\sigma_{\mathrm{A}}^3 \tag{3.38}$$

$$F_{\mathrm{AB}}(z) = F_{\mathrm{BA}}(z) = \begin{array}{ll} -(G + L - z)(G - L + z)/4Lz\,, & \sigma_{\mathrm{A}} < z < G + L \\ 0 & \text{otherwise} \end{array} \tag{3.39}$$

$$I_{\mathrm{AB}} = I_{\mathrm{BA}} = \frac{U^2}{4L}\,[\sigma_{\mathrm{A}}G + (U - L)\,U/3 - U^2/12]\,, \tag{3.40}$$

where $U = L - (\sigma_{\mathrm{A}} - \sigma_{\mathrm{B}})/2$ and $G = (\sigma_{\mathrm{A}} + \sigma_{\mathrm{B}})/2$.

For $U = 0$ the B-sphere merges completely into the A-sphere and has no longer any effect. Further,

$$F_{\mathrm{BB},0}(z) = \begin{array}{ll} [(G + L - z)(G - L + z)/4Lz]^2\,, & \sigma_{\mathrm{A}} < z < G + L \\ 0 & \text{otherwise} \end{array} \tag{3.41}$$

$$I_{\mathrm{BB},0} = -U^3(4G^2/3 - GU + U^2/5)/16L^2\,. \tag{3.42}$$

A merit of decomposition (*3.32*) is in that it makes the most important contributions to $\langle f(1, 2)\rangle$ the most tractable: It has been shown that the easy terms I_{AA} and I_{AB} are dominant under all conditions. The most difficult term, F_{BB}, is only moderate for the largest values of U and declines rapidly with decreasing U so that it may be, eventually, neglected. Its exact analytical evaluation has been carried through by Wertheim[29] using tetrahedral geometry. The final result is (for details see ref.[29]):

$$\begin{aligned} I_{\mathrm{BB},1} &= U^3[\sigma_{\mathrm{A}}G/3 + UG/4 + U^2/20]/4L^2 + \\ &+ [-V(\sigma_{\mathrm{A}}^2 + \sigma_{\mathrm{B}}^2 + 2G^2 + 2L^2)/15 + Q_{\mathrm{A}}(\pi - \varphi_{\mathrm{A}}) + \\ &+ Q_{\mathrm{A}}(\pi - \varphi_{\mathrm{B}}) - 2Q_{\mathrm{G}}\varphi_{\mathrm{G}} - 2Q_{\mathrm{L}}\varphi_{\mathrm{L}}]/4\pi L^2\,. \end{aligned} \tag{3.43}$$

Here V and φ are certain geometric quantities which must be evaluated for the tetrahedron, where each sphere is tangent to both spheres of the other molecule. It means that the tetrahedron has sides σ_{A}, σ_{B}, G, and L. V is six times the volume of the tetrahedron and is given by

$$V = U(U + \sigma_{\mathrm{A}} - \sigma_{\mathrm{B}})\,[\sigma_{\mathrm{A}}\sigma_{\mathrm{B}} - U(\sigma_{\mathrm{A}} - \sigma_{\mathrm{B}})/2 - U^2/2]^{1/2}\,. \tag{3.44}$$

$\varphi_{\alpha\beta}$ is the internal angle between two face triangles $\alpha\beta\gamma$ and $\alpha\beta\delta$ (α, β, ... label the tetrahedron vertices),

$$\cos\varphi_{\alpha\beta} = -P_{\alpha\beta}/A_{\alpha\beta\gamma}A_{\alpha\beta\delta}\,, \tag{3.45}$$

$A_{\alpha\beta\gamma}$ is twice the area of the face triangle $\alpha\beta\gamma$ and $P_{\alpha\beta} = (\mathbf{r}_{\alpha\gamma} \times \mathbf{r}_{\alpha\beta})(\mathbf{r}_{\alpha\beta} \times \mathbf{r}_{\alpha\delta})$.

Q are auxilliary quantities given by

$$Q_{\mathrm{L}} = \frac{L^5}{60} - \frac{L^3}{12}\left[2G^2 - 2L^2 + \sigma_{\mathrm{A}}^2 + \sigma_{\mathrm{B}}^2\right] + \frac{L}{4}(G^2 - \sigma_{\mathrm{A}}^2)(G^2 - \sigma_{\mathrm{B}}^2)$$

$$Q_{\mathrm{G}} = \frac{G^5}{60} - \frac{G^3}{12}\left[2L^2 - 2G^2 + \sigma_{\mathrm{A}}^2 + \sigma_{\mathrm{B}}^2\right] + \frac{G}{4}(L^2 - \sigma_{\mathrm{A}}^2)(L^2 - \sigma_{\mathrm{B}}^2)$$

$$Q_{\sigma_\alpha} = \frac{\sigma_\alpha^5}{60} - \frac{\sigma_\alpha^3}{6}\left[L^2 + G^2 - \sigma_\beta^2\right] + \frac{\sigma_\alpha}{4}(L^2 - G^2)^2 . \qquad (3.46)$$

For a special model of linear triatomics with $\sigma_{\mathrm{C}} \geqq \sigma_{\mathrm{A}}$ (where C refers to the central sphere) and $A - C$ separation L, the second virial coefficient is given by a formula similar to *(3.36)*,

$$B_2 = 2\pi(I_{\mathrm{CC}} + 4I_{\mathrm{AC}} + 4I_{\mathrm{AA,0}} + 4I_{\mathrm{AA,1}}) \qquad (3.47)$$

with the same I coefficients as for diatomics.

The virial coefficient of homonuclear dumbells and linear polyatomics can be exactly calculated also by a method proposed by Boublík[59]. The method closely follows the approach for hard convex bodies and is outlined therefore in the next section.

The virial coefficients of the FHS models are compiled in Table V. Unlike the CB, discussion on these coefficients is more difficult because of nonexistence of a "parameter of nonsphericity".

Homonuclear diatomics closely resemble prolate spherocylinders and thus the same conclusions hold for them, too. All other models are defined by at least two parameters and are therefore incomparable. An interesting dependence of B_i on the valence angle ω is exhibited by nonlinear triatomics: the 2nd virial coefficient is independent of the valency angle for angles greater than a certain ω_c, $B_3\mathscr{V}^2$ *versus* ω dependence follows that of the volume of the molecule on ω, and $B_4\mathscr{V}^3$ has a pronounced maximum for a boomerang-like shape (for details see the original paper[60]). For other FHS models the body of data available does not allow us to discuss the parameter dependence of B_i and to draw general conclusions.

3.3. *Virial Coefficients: Approximate Results*

Any equation of state of fluids can be expanded in powers of density and the expansion coefficients provide then estimates of the virial coefficients. This type of approximation of the virial coefficients is considered in Section 4, where we deal with equations of state. In this section we consider real approximate integrations in Eqs *(3.7)*, *(3.11)*, ... and semi-empirical methods.

TABLE V

Virial coefficients of fused-hard-sphere models

Parameters		$B_2/\mathcal{V}$	$B_3/\mathcal{V}^2$	$B_4/\mathcal{V}^3$	$B_5/\mathcal{V}^4$	Ref.
			Homonuclear diatomics			
L						
0·05	—	4·004	10·01 ± 0·03	18·40 ± 0·08	—	70
0·10	—	4·014	10·13 ± 0·03	18·84 ± 0·30	—	70
0·20	—	4·055	10·23 ± 0·05	19·43 ± 0·35	—	51
0·30	—	4·132	10·58 ± 0·03	19·63 ± 0·20	—	34
0·40	—	4·212	10·94 ± 0·05	20·35 ± 0·30	—	32
0·60	—	4·474	12·13 ± 0·03	23·10 ± 0·07	35·58 ± 0·25	71
0·75	—	4·753	13·52 ± 0·05	26·26 ± 0·30	—	70
0·80	—	4·866	14·04 ± 0·08	27·61 ± 0·50	—	51
1·00	—	5·444	17·04 ± 0·06	34·52 ± 0·35	52·22 ± 1·05	34, 72
			Heteronuclear diatomics			
L	σ_B					
0·3333	0·6667	4·096	10·40 ± 0·10	19·31 ± 0·20	—	73
0·50	0·5555	4·252	11·12 ± 0·11	20·91 ± 0·21	—	73
0·50	0·6667	4·320	11·48 ± 0·12	21·61 ± 0·22	33·09 ± 0·33	73
0·50	0·8333	4·348	11·51 ± 0·12	21·70 ± 0·22	—	73
0·575	0·15	4·115	10·50 ± 0·15	19·70 ± 0·60	—	60
0·6250	0·50	4·506	12·34 ± 0·10	23·84 ± 0·25	—	34
0·6667	0·6667	4·648	12·92 ± 0·13	24·80 ± 0·25	—	73
0·80	0·60	5·079	15·20 ± 0·23	30·80 ± 0·92	—	60
			Linear symmetric triatomics			
L	σ_A					
0·575	0·15	4·227	11·10 ± 0·16	21·00 ± 0·63	—	60
0·80	0·60	6·093	20·50 ± 0·31	42·20 ± 1·27	—	60
0·80	1·00	5·812	18·50 ± 0·15	35·99 ± 0·50	—	34
1·00	1·00	6·853	24·50 ± 0·37	48·90 ± 1·47	—	60
1·0467	1·1669	4·8408	—	—	—	74
			Tetrahedral penta-atomics			
0·5206	1·0294	5·024 ± 0·005	15·26 ± 0·03	32·29 ± 0·16	—	63
			Non-linear symmetric triatomics $L = (\sigma_A + 1)/2$			
σ_A	ω, deg					
0·15	15	4·155 ± 0·002	—	—	—	60
	30	4·199 ± 0·002	11·00 ± 0·16	20·50 ± 0·61	—	60
	45	4·222 ± 0·002	—	—	—	60
	60	4·228 ± 0·002	11·10 ± 0·16	21·10 ± 0·63	—	60
	90	4·227 ± 0·002	11·10 ± 0·16	20·90 ± 0·63	—	60
	120	4·231 ± 0·002	11·10 ± 0·16	20·80 ± 0·63	—	60
	150	4·227 ± 0·002	11·00 ± 0·16	20·60 ± 0·62	—	60

TABLE V
(*Continued*)

		$B_2/\mathscr{V}$	$B_3/\mathscr{V}^2$	$B_4/\mathscr{V}^2$	Ref.
0·60	15	5·121 ± 0·008	—	—	60
	30	5·235 ± 0·008	16·20 ± 0·24	32·80 ± 0·98	60
	45	5·472 ± 0·008	17·60 ± 0·26	37·90 ± 1·14	60
	65	5·828 ± 0·009	19·80 ± 0·30	44·10 ± 1·32	60
	90	6·028 ± 0·009	20·90 ± 0·31	45·70 ± 1·37	60
	105	6·050 ± 0·009	20·80 ± 0·20	44·80 ± 0·90	69
	115	6·075 ± 0·009	—	—	60
	120	6·084 ± 0·009	20·90 ± 0·30	45·2 ± 1·35	60
	140	6·086 ± 0·009	—	—	60
	150	6·084 ± 0·009	20·50 ± 0·30	43·5 ± 1·30	60
	160	6·084 ± 0·009	—	—	60
1·0	30	5·320 ± 0·013	16·60 ± 0·25	34·50 ± 1·04	60
	60	5·859 ± 0·015	20·00 ± 0·30	45·20 ± 1·36	60
	90	6·519 ± 0·015	24·30 ± 0·35	57·50 ± 1·73	60
	120	6·782 ± 0·017	25·10 ± 0·38	53·60 ± 1·61	60
	150	6·824 ± 0·017	24·60 ± 0·37	50·70 ± 1·52	60
			$L = 0{\cdot}5$		
1·0	90	4·520 ± 0·010	12·38 ± 0·10	24·38 ± 0·35	34

Because of the complexity of the higher virial coefficients, attempts to perform integrations in Eqs (*3.7*)... have focused on the second virial coefficient mainly. This coefficient is known exactly for all convex body models and one evident possibility is therefore to extend this result to the FHS models. The other way is to decompose the integral into several terms and to neglect the most difficult ones, provided they do not contribute significantly to the total value.

For many FHS models the difference between them and the corresponding convex bodies is nearly negligible. Boublík[59] studied a general, homogeneous (*i.e.* $\sigma_\alpha = \sigma_\beta$ for all α, β) linear FHS molecule; its surface area, $\mathscr{S}$, is just equal to the surface area of the corresponding spherocylinder (with the rod-length, L, equal to the largest site-site span), whereas the volume of the FHS model is equal to that of the spherocylinder lessened by factor $\pi L^3\sigma/12$ in the case of diatomics and several such factors for polyatomics. Setting $\mathscr{R}$ equal to that of the corresponding spherocylinder, all the Steiner relations (for single bodies) are fulfilled also by the FHS models.

The average volume $\mathscr{V}_{1+2}$ of two FHS bodies, and thus twice the second virial coefficient, is

$$2B_2 = \mathscr{V}_{1+2} = 2(\mathscr{V} + \mathscr{R}\mathscr{S}) - \Delta v\,, \qquad (3.48)$$

where Δv is the volume of two "pyramids" formed by spheres of radii σ in the corners of the rhomboid with the base $L^2 \sin \tau$ (where τ determines the mutual orientation of the FHS body axes). For a given τ the volume of the pyramid can be expressed analytically and the Δv then follows by averaging over all τ.

Much simpler is the use of a semiempirical expression

$$\Delta v = \tfrac{1}{6}\pi L^2 h \sigma^3 \,, \qquad (3.49)$$

where

$$h = 1 - (1 - L^2/2)^{1/2} \,. \qquad (3.50)$$

This expression yields surprisingly good estimate of Δv. Owing to the fact that Δv itself is very small in comparison with $\mathscr{V}$ and $\mathscr{R}\mathscr{S}$, the prediction of B_2 by using Eq. (*3.49*) is very accurate (for details see ref.[59]).

Boublík and Nezbeda[61] used originally the above method for estimating the properties of the homonuclear dumbell fluid by neglecting completely the volume Δv. The result for homonuclear dumbells

$$B_2/\mathscr{V} = (8 + 12L + 3L^2 - L^3)/(2 + 3L - L^3) \qquad (3.51)$$

is quite accurate (see Table VI). Since for linear models the approximation $\Delta v \approx 0$ is well justified, similarly good results are obtained for heteronuclear dumbells[62],

$$B_2/\mathscr{V} = 1 + \frac{[\sigma_B + 1 + L + (1 - \sigma_B)^2/4L]\,[\frac{1}{2}(1 + \sigma_B^2) + (\sigma_B a_+ + a_-)]}{[(1 + \sigma_B^3) + 3(\sigma_B^2 a_+ + a_-) - 4(a_+^3 + a_-^3)]} \,, \qquad (3.52)$$

where

$$a_\pm = \tfrac{1}{2}L \pm (\sigma_B^2 - 1)/8L \qquad (3.53)$$

and for symmetric linear triatomics,

$$B_2/\mathscr{V} = (8 + 24L + 12L^2 - 2L^3)/(2 + 6L - 2L^3) \,. \qquad (3.54)$$

Neglecting Δv in Eq. (*3.48*) makes this equation identical to that for CB, *cf.* Eq. (*3.28*). It is possible therefore to evaluate (at least formally) B_2 of any FHS model similarly as for CB models, *i.e.* using a parameter of nonsphericity α_{FHS}, $\alpha_{FHS} = \mathscr{R}\mathscr{S}/3\mathscr{V}$, where $\mathscr{V}$ and $\mathscr{S}$ are the actual values of the FHS model and $\mathscr{R}$ is given by an appropriately defined associated CB. This approximation has been applied also to non-linear FHS models[60,63] and even in these cases the results are in a quite good agreement with the exact data (see Table VI).

Approximate integration for diatomics may start with factorization (*3.32*). The most difficult but at the same time the least important term is that containing the

TABLE VI

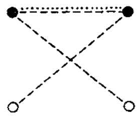
Comparison of the convex-body-like approximation for B_2 of FHS models (Eq. (*3.48*) with $\Delta v = 0$) with exact results

Parameters		$B_2/\mathscr{V}$	
		Eq. (*3.48*)	exact
L	Homonuclear diatomics		
0·2	—	4·056	4·055
0·4	—	4·214	4·212
0·6	—	4·482	4·474
0·8	—	4·889	4·866
1·0	—	5·500	5·444
	Heteronuclear diatomics		
L	σ_B		
0·50	0·5556	4·280	4·252
0·50	0·6667	4·333	4·320
0·625	0·50	4·505	4·506
0·6667	0·6667	4·694	4·648
0·80	0·60	5·110	5·079
	Linear symmetric triatomics		
L	σ_A		
0·575	0·15	4·236	4·227
0·8	0·6	6·225	6·093
	1·0	5·861	5·812
1·0	1·0	7·000	6·853
	Tetrahedral penta-atomics		
L_{AC}	σ_A		
0·5206	1·0294	5·152	5·024
	Nonlinear symmetric triatomics $L = (\sigma_A + 1)/2$		
σ_A	ω		
0·60	30	5·452	5·235
	45	5·787	5·472
	90	6·078	6·028
	140	6·222	6·086
1·00	30	5·546	5·320
	60	6·250	5·859
	90	6·561	6·519
	120	6·799	6·782

B—B bond. At any given separation r_{AA} the setting of $F_{BB,1}$ to 0 is a very good approximation. However, due to accumulation of errors during the integration over dr_{AA} the final result is rather inaccurate[64]. Better seems to start from the equation of state, *i.e.* to use the two-point representation, where the integrals are evaluated only at one value of r_{AA}. The second virial coefficient assumes then the form (for details see ref.[15])

$$B_2 = \tfrac{1}{2}\sum_{\alpha,\beta} \mathscr{V}_{\alpha+\beta}\,, \tag{3.55}$$

where $\mathscr{V}_{\alpha+\beta}$ is the average free volume associated with pair $\alpha-\beta$ and is given by the diagram

 .

Here $r_{AA} = \sigma_{AA}$ and ●······ ·····● denotes a certain function, different from both e- and f-bonds.

Nezbeda[15] evaluated this diagram by neglecting the e_{BB} bond and obtained for homonuclear dumbells the expression

$$B_2/\mathscr{V} = 8(1 + L/2)^2\,(1 + L/2 - L^2/4)/(2 + 3L - L^3)\,. \tag{3.56}$$

The same method has been also applied to heteronuclear dumbells[62] with the result slightly inferior to the CB approximation (*3.52*). On the other hand, an advantage of this approach is that it is quite general and may be used for estimating higher order graphs for both the virial coefficients and correlation functions[64].

Another approximate method related to the CB results is that which employs parameters of nonsphericity to estimate higher virial coefficients. As it has been shown above, the third virial coefficient of hard CB is given by expression (*3.30*), with known lower and upper bounds for G, Eq. (*3.31*).

Boublík[65] has shown that assuming

$$G = 4\pi\mathscr{R}^2\mathscr{S}^2 \tag{3.57}$$

the third virial coefficient can be also expressed in terms of the single parameter α, $\alpha = \mathscr{R}\mathscr{S}/3\mathscr{V}$, (*cf.* Eq. (*3.28*)). From Eq. (*3.30*) it follows

$$B_3/\mathscr{V}^2 = 1 + 6\alpha + 3\alpha^2\,. \tag{3.58}$$

This expression is identical to that of Gibbons[66], originally derived within the scaled particle theory, *cf.* Section 4.5., Eq. (*3.58*) reduces in the case of hard spheres (for which $\alpha = 1$) to the correct value $B_{3,HS}/\mathscr{V}^2 = 10$.

The only information available on the fourth virial coefficient of CB is the knowledge of B_4 for the special case of hard spheres. Considering a similar special case for four CB, as Kihara and Miyoshi considered for three particles, it can be concluded[65] that B_4 should include terms $\mathscr{V}^3$ and $\mathscr{V}^2\mathscr{S}\mathscr{R}$. A simple approximation for B_{CB}^4 in terms of powers of α only (consistent with an integer estimate of $B_{4,\mathrm{HS}}$ value, $B_{4,\mathrm{HS}} = 18$) has the form

$$B_4/\mathscr{V}^3 = 1 + 14\alpha + 3\alpha^2 \,. \tag{3.59}$$

Comparison of the third virial coefficient, calculated for a variety of CB from (*3.58*) is given in Table VII. In the same table the values obtained from the expression proposed for B_3 by Naumann and Leland[67] are also listed. They assumed the quantity G to be given by its lower bound, *i.e.*

$$G = \mathscr{S}^3 \,. \tag{3.60}$$

Then, after combining it with the HS value, they obtained

$$B_3/\mathscr{V}^2 = 1 + 6\alpha + \tfrac{3}{2}\alpha^2(1/\tau + 1) \,, \tag{3.61}$$

where τ is a second parameter (called "needleness") characterizing the shape of CB,

$$\tau = 4\pi\mathscr{R}^2/\mathscr{S} \,. \tag{3.62}$$

As $4\pi\mathscr{R}^2 \geqq \mathscr{S}$, $\tau \geqq 1$ (similarly as α) and Eq. (*3.61*) therefore yields – in contrast to (*3.58*) – always lower values of B_3 with increasing nonsphericity and thus better agreement for prolate spherocylinders at the highest values of α, but worse predictions for all the other CB, see Table V.

The idea that the higher CB virial coefficients depend on more than one parameter (α) is not new. Probably first was this idea formulated by Rigby[32] who, however, offered no quantitative relationship. Unfortunately, the expression of the virial coefficients in terms of α and τ does not bring any substantial improvement over the one-parameter relation.

Two last methods that we consider in this section make use of certain recursion formulas allowing us to estimate B_i by means of B_j, $j < i$.

Studying the asymptotic behaviour of the irreducible cluster integrals[20] β_k for $k \to \infty$, Tsykalo and Selevanyuk[68] found a recursion formula

$$[\beta_{\mathrm{k}+1}/\beta_{\mathrm{k}}^{(\mathrm{k}+1)/\mathrm{k}}]^{\mathrm{A}}\, \beta_{\mathrm{k}}^{(\mathrm{k}+2)\mathrm{k}} = \beta_{\mathrm{k}+2} \tag{3.63}$$

$$A = \frac{(k+2)^{2/3} - k^{-1/3}(k+2)}{(k+1)^{2/3} - k^{-1/3}(k+1)}$$

TABLE VII

Comparison of the third virial coefficient, $B_3/\mathscr{V}^2$, of convex bodies calculated from Eqs (*3.58*) and (*3.61*) with exact data

Parameter	α	τ	Eq. (*3.58*)	Eq. (*3.61*)	Exact
Prolate spherocylinders					
γ					
1·4	1·050	1·029	10·61	10·56	10·64
1·6	1·095	1·056	11·16	11·07	11·18
2·0	1·200	1·125	12·52	12·28	12·34
2·5	1·346	1·225	14·51	14·01	14·30
3·0	1·500	1·333	16·75	15·91	16·20
Prolate ellipsoids of revolution					
λ					
1·50	1·059	1·035	10·72	10·68	10·69
2·00	1·179	1·114	12·25	12·04	12·09
2·75	1·404	1·275	15·33	14·69	14·81
3·00	1·485	1·335	16·52	15·69	15·85
5·00	2·184	1·871	28·41	25·08	25·23
Diamond ($\sigma_B = 0{\cdot}2$)					
$\gamma = 2{\cdot}568$	1·500	1·422	16·75	15·75	16·21
Drop ($\sigma_B = 0{\cdot}2$)					
$\gamma = 2{\cdot}347$	1·500	1·422	16·75	15·75	15·97
Oblate spherocylinders					
φ					
1·0	1·129	1·038	11·60	11·53	11·65
1·5	1·234	1·059	12·97	12·85	13·08
2·0	1·348	1·076	14·54	14·35	14·79 14·73
2·636	1·500	1·094	16·75	16·46	17·07
3·0	1·589	1·103	18·11	17·76	18·65 18·29
Oblate ellipsoids of revolution					
λ					
0·6667	1·059	1·024	10·72	10·68	10·72
0·50	1·179	1·058	12·25	12·14	12·26
0·3636	1·404	1·101	15·33	15·06	15·49
0·3333	1·485	1·112	16·52	16·19	16·74
0·20	2·184	1·167	28·41	27·39	29·82

TABLE VII
(*Continued*)

Parameter	α	τ	Eq. (*3.58*)	Eq. (*3.61*)	Exact
			Cube		
a	1·500	1·178	16·75	16·24	18·33

which has two interesting features: (i) its accuracy should increase with increasing k, and (ii) it is independent of the potential model. For hard spheres Eq. (*3.63*) predicts B_5 with the accuracy of about 3 percent and B_6 of about 2·7 percent. Nezbeda[34] nvestigated in detail the applicability of Eq. (*3.63*) for B_5,

$$B_5 = \tfrac{4}{5}(\tfrac{4}{3}B_4)^{2{\cdot}17582}\,(\tfrac{3}{2}B_3)^{-1{\cdot}26373} \qquad (3.64)$$

and has come to the conclusion that this equation is a reliable tool for estimating the fifth virial coefficient of any hard body model of not too extreme nonsphericity (see Table VIII).

The other usuful result resembling recursion formulas are the relations of Malijevský and Labík[31] for the fourth and fifth virial coefficients:

$$B_4^* = B_{4,\mathrm{HS}}^* + 1{\cdot}514(B_3^* - B_{3,\mathrm{HS}}^*) + 1{\cdot}842(B_3^* - B_{3,\mathrm{HS}}^*)^2 \qquad (3.65)$$

$$B_5^* = B_{5,\mathrm{HS}}^* + 1{\cdot}013(B_3^* - B_{3,\mathrm{HS}}^*) + 2{\cdot}626(B_3^* - B_{3,\mathrm{HS}}^*)^2\,, \qquad (3.66)$$

where $B_i^* = B_i/B_2^{i-1}$. These relations were found by purely empirical means but work surprisingly well. It can be shown that (*3.65*) predicts accurately B_4 even in such cases where the derivative of B_4 with respect to the nonsphericity parameter changes its sign. Eq. (*3.66*) performs better than Eq. (*3.64*) but predictions must be made with caution because it is based on a relatively small body of data only. One feature is common to both (*3.65*) and (*3.66*): they are sensitive to the accuracy of the third virial coefficient. An error of 1 per cent in B_3 may give rise to errors up to 6 percent in B_4 and 7 percent in B_5.

Tables VI through VIII demonstrate potentialities of the approximate methods currently available for evaluating the virial coefficients of hard body fluids. We only remind that these are "direct" estimates of the coefficients without any relation to equations of state.

The convex-body-like approximation for B_2 of the FHS models is best suited for linear models for which it is also theoretically justified. (Unfortunately, the exact analytical expressions are available for these models.) It is quite accurate for diatomics and still good for triatomics with accuracy better than 3 per cent. Its formal extention to non-linear models makes it possible to obtain easily a reasonable estimate of B_2 for any FHS model. The worst results are obtained for strongly heteronuclear and non-linear models with discrepancy up to 6 per cent.

For B_3 of the CB models there seems to be no great difference between the results given by one- and two-parameter expressions (Eqs (*3.58*) and (*3.61*)) provided that α is not too large. Discrepancy starts appearing at greater nonsphericities with Eq. (*3.61*) being slightly better for prolate and Eq. (*3.58*) for oblate shapes. Eq. (*3.58*) may be also used for the FHS models with appropriately defined α_{FHS} but this

TABLE VIII

Comparison of B_5 given by recursion formula (*3.64*) with exact results

Body	Body parameter	$B_5/\mathcal{V}^4$	
		Eq. (*3.64*)	exact
Spheres		27·5	28·2
Prolate spherocylinders	$\gamma = 2$	32·8	31·9
	$\gamma = 3$	37·4	36·8
	$\gamma = 4$	37·0	39·7
	$\gamma = 5$	31·2	39·9
	$\gamma = 6$	22·6	63·0
Prolate ellipsoids	$\lambda = 1·5$	29·5	29·9
	$\lambda = 2·0$	30·6	31·9
Homonuclear diatomics	$L = 0·6$	35·5	35·6
	$L = 1·0$	55·3	52·2
Heteronuclear diatomics	$L = 0·5$ $\sigma_{\mathrm{B}} = 0·6667$	32·9	33·1
Oblate spherocylinders	$\varphi = 1·0$	32·4 32·8	32·4
	$\varphi = 1·5$	37·5 36·6	35·8
	$\varphi = 2·0$	42·7 41·4	39·0
	$\varphi = 3·0$	55·2 44·2	43·9
Oblate ellipsoids	$\lambda = 0·6667$	29·0	29·5
	$\lambda = 0·50$	33·9	33·2

way is closely linked to equations of state and is discussed therefore in the next section.

If the second and third virial coefficients are known, then the correlation formulas (*3.65*) and (*3.66*) make it possible to calculate quite accurately both B_4 and B_5 regardless of the model considered. The recursion formula (*3.63*) provides also a reasonable estimate of B_5 for realistic models.

4. EQUATIONS OF STATE OF PURE FLUIDS

Besides the virial expansion, Eq. (*3.1*), there are several other routes to obtain the equation of state. These methods can be divided, roughly, into two groups: Methods devised primarily for EOS and more general methods enabling one to calculate also the structure of the fluid. The former methods usually yield an EOS in a closed analytical form, which is undoubtedly their advantage. The latter methods are based on correlation functions and – with the only exception of the Percus–Yevick theory for the HS fluid – an EOS can be obtained only by numerical computations. Their merit is thus mainly methodological with little practical importance.

When discussing various methods and results we adopt a "mixed" approach focusing alternatively on methods and systems for the following reasons. First, lattice theories seem to have passed their momentum and despite a few new recent attempts their impact on nonspherical HB fluid theories is practically zero; they are therefore discussed separately. Secondly, the HS fluid has a prominent position among all HB fluids: nearly all methods available at present were devised originally for the HS fluid and only then extended to nonspherical body fluids. It seems therefore logical to talk first about the HS fluid and then about the nonspherical body ones.

4.1. *Basic Relations*

Within the canonical NVT ensemble it holds:

$$\beta P = (\partial \ln Z_N / \partial V)_{T,N} , \qquad (4.1)$$

where Z_N is the N-particle configuration integral (*3.3*). One possible way towards obtaining βP is to estimate directly the configuration integral and this is the way followed by lattice theories (see Section 4.3.). If the structure of the fluid is described by means of correlation functions and pairwise additivity of the potential is assumed (which is true for all HB fluids), then from Eq. (*4.1*) one can get[2]

$$\beta P/\varrho \equiv z = 1 - \frac{\beta\varrho}{6} \int \left[r_{12} \frac{\partial u(1,2)}{\partial r_{12}} \right] g(1,2)\, \mathrm{d}\mathbf{r}_{12}\, \mathrm{d}\omega_1 \mathrm{d}\omega_2 , \qquad (4.2)$$

where $\mathbf{r}_{12}$ is the vector formed by reference points, $\boldsymbol{\omega}$ denotes orientation, and $g(1, 2)$ is the pair correlation function (radial distribution function) defined generally by

$$g(1, 2) = \frac{N(N-1)}{Z_N \varrho^2} \int \dots \int \exp\left[-\beta U_N(1, \dots N)\right] d(3) \dots d(N) , \qquad (4.3)$$

Similarly, one can write in terms of $g(1, 2, \xi)$ also the chemical potential, μ. It holds[22]

$$\beta(\mu - \mu^*) \equiv \beta\mu_{\mathrm{res}} = \beta\varrho \int_{\mathrm{a}}^{\mathrm{b}} \mathrm{d}\xi \int \frac{\partial u}{\partial \xi} g(1, 2, \xi) \, \mathrm{d}\mathbf{r}_{12} \, \mathrm{d}\boldsymbol{\omega}_1 \, \mathrm{d}\boldsymbol{\omega}_2 , \qquad (4.4)$$

where μ^* is the chemical potential of the perfect gas and ξ is a coupling parameter characterizing a gradual inclusion of another particle to the given system: for $\xi = a$ we have the original system of N particles while for $\xi = b$ the additional particle is equivalent to all other particles.

For discontinuous potentials $g(1, 2)$ is also discontinuous. A correlation function continuous even for such potentials is the background correlation function, y, defined as

$$y(1, 2) = \exp\left[\beta u(1, 2)\right] g(1, 2) . \qquad (4.5)$$

For hard spheres $y(1, 2) = y(r)$, $g(1, 2) = g(r)$ and $g(r) \, \mathrm{d}u(r)/\mathrm{d}r = -\boldsymbol{k}T\delta(r - \sigma) . y(r)$. Eq. (*4.2*) assumes thus a very simple form,

$$\beta P/\varrho = 1 + \tfrac{2}{3}\pi\varrho\sigma^3 \, y(\sigma) = 1 + 4\eta g(\sigma+) \equiv 1 + 4\eta g_{\mathrm{c}} , \qquad (4.6)$$

where η is the packing fraction, $\eta = \varrho\mathscr{V}$. To calculate the equation of state (EOS) of the hard sphere fluid one thus needs only the contact value of the radial distribution function. The situation is not so simple for nonspherical bodies whose pair correlation function $g(1, 2)$ depends on both the separation and orientation of the particles. However, Eq. (*4.2*) can be considerably simplified by employing an appropirate coordinate system.

For convex bodies $u = u(s)$ and the appropriate Jacobian of transformation is given by (*2.9*). Further,

$$r_{12} \frac{\partial u(s)}{\partial r_{12}} = \frac{\partial u(s)}{\partial s} (\mathbf{r}_{12} \, . \, \mathbf{v}) . \qquad (4.7)$$

Performing coordinate transformation (*2.9*) and taking into account (*4.7*) one finds (for details see ref.[75])

$$\beta P/\varrho = 1 + \tfrac{1}{6}\varrho g_{\mathrm{c}}^{\mathrm{av}} \langle(\mathbf{r}_{12} \, . \, \mathbf{v})\rangle_{\mathrm{c}} \, \mathscr{S}_{1+1} . \qquad (4.8)$$

The average quantities $\langle A \rangle$ and g^{av} are defined by

$$\langle A \rangle \, g^{av}(s) = \frac{1}{\mathscr{S}_{1+s+1}} \int A g(s, \vartheta, \varphi, \boldsymbol{\omega}_{12}) \, \mathrm{d}\mathscr{S}_{1+s+2} \, \mathrm{d}\boldsymbol{\omega}_{12} \,, \tag{4.9}$$

subscript c denotes values at contact (*i.e.* for $s = \sigma$), and A is an arbitrary quantity. An alternative to (*4.8*) is an expression employing a function $\mathscr{G}^{av}(\xi)$,

$$\mathscr{G}^{av}(\xi) = \frac{1}{3\xi^2 \mathscr{V} + (2\xi + 1) \mathscr{R}\mathscr{S}} \int g_c(\xi) \, (\mathbf{r}_{12} \cdot \mathbf{v}) \, \mathrm{d}\mathscr{S}_{\xi 1+2} \, \mathrm{d}\omega_{12} \tag{4.10}$$

whose introduction is motivated by behaviour of μ for $\varrho \rightarrow 0$ (refs[14,76]). Since

$$\mathscr{G}^{av}(\xi = 1) = \frac{\mathscr{S}_{1+1}}{3\mathscr{V}_{1+1}} \, g_c^{av} \, \langle (\mathbf{r}_{12} \cdot \mathbf{v}) \rangle_c \tag{4.11}$$

we get

$$\beta P/\varrho = 1 + \frac{\varrho}{2} \, \mathscr{G}^{av}(1) \, \mathscr{V}_{1+1} \,. \tag{4.12}$$

For FHS models $u(1, 2) = \Sigma u_{\alpha\beta}(r_{\alpha\beta})$ and so the site-centred coordinate system is a natural choice. Similarly to (*4.7*) we have (for details see refs[15,69])

$$r_{12} \frac{\partial u(1, 2)}{\partial r_{12}} = \sum_{\alpha,\beta} \frac{\partial u(r_{\alpha\beta})}{\partial r_{\alpha\beta}} (\mathbf{r}_{12} \cdot \mathbf{v}_{\alpha\beta}) \,, \tag{4.13}$$

where $\mathbf{v}_{\alpha\beta} = \mathbf{r}_{\alpha\beta}/|\mathbf{r}_{\alpha\beta}|$ so that the EOS can be expressed as follows:

$$\beta P/\varrho = 1 + \tfrac{2}{3} \pi \varrho \sum_{\alpha,\beta} \sigma_{\alpha\beta}^2 G_{\alpha\beta}(r_{\alpha\beta} = \sigma_{\alpha\beta}) \, \langle (\mathbf{r}_{12} \cdot \mathbf{v}_{\alpha\beta}) \rangle_c \,. \tag{4.14}$$

Here $\sigma_{\alpha\beta} = (\sigma_\alpha + \sigma_\beta)/2$ and $G_{\alpha\beta}$ is the average site-site correlation function given by an unweighted angle-average of the full pair correlation function $g(1, 2)$ under the constraint $r_{\alpha\beta}$ = const,

$$G_{\alpha\beta}(r) = \int_{(r_{\alpha\beta} = \mathrm{const})} g(1, 2) \, d(1) \, d(2) \,. \tag{4.15}$$

Eq. (*4.14*) is completely general and holds for any FHS model. A FHS counterpart of Eq. (*4.12*) can also be derived but not in such a general form. For instance, for homonuclear dumbells we can write[15]

$$\beta P/\varrho = 1 + \tfrac{4}{3}\pi\varrho\,\Sigma\Phi_{\alpha\beta}(\xi = 1)\,\mathscr{G}^{\mathrm{av}}_{\alpha\beta}(\xi = 1)\,, \qquad (4.16)$$

where $\Phi_{\alpha\beta}$ is a certain function defined by dumbell's geometry (for details see ref.[15]).

Eqs (*4.12*) and (*4.16*) are relevant for the scaled particle theory (see Section 4.4.2.) which addresses $\mathscr{G}(\xi)$. On the other hand, Eqs (*4.8*) and (*4.14*) are well suited for evaluating $\beta P/\varrho$ from simulations but are not the only possible forms. Similar but rather cumbersome expressions for the FHS fluids have been also derived by Freasier and coworkers[72,77], Aviram and coworkers[78], and Bearman[79]. Another possibility (for convex bodies) is to employ a contact function[49,80–82]. A novel method to compute the pressure in an NVT ensemble has been proposed recently by Eppenga and Frenkel[56].

General theoretical approaches aim at evaluating the full pair correlation $g(1, 2)$ either *via* a perturbation method or by determining its spherical harmonic expansion coefficients[83] $g_{\mathrm{N(1),N(2)}}$,

$$g_{\mathrm{N(1),N(2)}} \equiv g_{\mathrm{ijk,lmn}}(r) = \frac{1}{8\pi^2}\int g(1, 2)\, D_{\mathrm{N(1)}} D^{*}_{\mathrm{N(2)}}\, \mathrm{d}\boldsymbol{\omega}_1\, \mathrm{d}\boldsymbol{\omega}_2\,. \qquad (4.17)$$

Then

$$g(1, 2) = 8\pi^2 \Sigma g_{\mathrm{N(1),N(2)}} D_{\mathrm{N(1)}}(\boldsymbol{\omega}_1)\, D^{*}_{\mathrm{N(2)}}(\boldsymbol{\omega}_2)\,. \qquad (4.18)$$

Here $D_{\mathrm{N}}(\boldsymbol{\omega})$ are orthogonal functions (Wiegner rotational matrices) spanning the orientational space and asterisk denotes complex conjugate. Due to a discontinuous nature of the HB potential the series in (*4.18*) is poorly convergent for these fluids which is a disadvantage of the expansion. Fortunately, one practically never needs the full pair correlation function since measurable quantities may be expressed by few harmonics only. The most important spherical harmonic expansion coefficient is the leading $(\mathbf{0}, \mathbf{0})$ term which is just an unweighted angle average of $g(1, 2)$. The scalar product $\langle(\mathbf{r}_{12} \,.\, \mathbf{v})\rangle$ is simply related to the $(\mathbf{1}, \mathbf{0}) \equiv (100{,}000)$ coefficient (in the site-centred coordinate system) and the EOS given by (*4.14*) may be rewritten into a form (for details see ref.[84])

$$\beta P/\varrho = 1 + \tfrac{2}{3}\pi\varrho\,\Sigma\sigma^2_{\alpha\beta}\,\{\sigma_{\alpha\beta}G_{\alpha\beta}(\sigma_{\alpha\beta}) - \frac{1}{\sqrt{3}}\,[L_\alpha g^{\alpha\beta}_{1,0}(\sigma_{\alpha\beta}) + L_\beta g^{\beta\alpha}_{1,0}(\sigma_{\alpha\beta})]\} =$$

$$= 1 + \tfrac{2}{3}\pi\varrho\,\Sigma\sigma^2_{\alpha\beta}G_{\alpha\beta}(\sigma_{\alpha\beta})\left\{\sigma_{\alpha\beta} - \frac{1}{\sqrt{3}}\,[L_\alpha g^{\alpha\beta *}_{1,0}(\sigma_{\alpha\beta}) + L_\beta g^{\beta\alpha *}_{1,0}(\sigma_{\alpha\beta})]\right\} \qquad (4.19)$$

especially well suited for a theoretical treatment. In (*4.19*) L_α denotes the intramolecular distance of site α from the reference point and superscripts on the harmonic expansion coefficients denote the reference points.

In the above expressions the correlation function has been used directly to calculate $\beta P/\varrho$. It is evident that the resulting compressibility factor is quite sensitive to the accuracy of the contact value of g_{av}. This sensitivity is, at least to a certain extent, suppressed in indirect methods, where another thermodynamic function (usually the Helmholtz free energy) is determined first. This route requires rather "accuracy-in-average" of $g(1, 2)$ than "point-wise" accuracy.

Besides the NVT ensemble discussed above two other ensembles have been used in simulations to evaluate EOS: the NPT ensemble and grand-canonical ensemble.

In the NPT ensemble the pressure is an independent variable and volume is calculated from the relation[85,86]

$$V = -kT(\partial \ln \Delta_c/\partial P)_{T,N}, \tag{4.20}$$

where Δ_c is an analogue of the common canonical configuration integral,

$$\Delta_c = \int_0^\infty Z_N(N, V, T) \exp\left[-\beta PV\right] dV. \tag{4.21}$$

The NPT ensemble does not seem to have any marked advantages when applied to pure fluids but it is a natural choice for studying liquid mixtures and particularly the thermodynamic excess properties.

In the grand-canonical ensemble, the number of particles fluctuates and the basic relation for evaluating EOS is

$$\frac{\langle N^2 \rangle - \langle N \rangle^2}{N} = \varrho kT\chi_T, \tag{4.22}$$

where χ_T is the isothermal compressibility,

$$\chi_T = \frac{1}{\varrho}\left(\frac{\partial \varrho}{\partial P}\right)_{V,T}. \tag{4.23}$$

The left-hand side of (*4.23*) can be expressed by means of the pair correlation function which yields[2]

$$kT\chi_T = 1 + \frac{\varrho^2}{N}\int[g(1, 2) - 1]\, d(1)\, d(2) =$$

$$= 1 + \varrho\int[g_{0,0}(r) - 1]\, d\mathbf{r}. \tag{4.24}$$

An alternative expression of χ_T is that by means of the direct correlation function, c, related to g through the Ornstein–Zernike equation,

$$h(1,2) = c(1,2) + \varrho \int c(1,3)\, h(2,3)\, d(3)\,, \tag{4.25}$$

where $h = g - 1$. Then, for hard spheres or, more generally, for a simple fluid, we can write

$$\beta \chi_T^{-1} = 1 - \varrho \int c(r)\, \mathrm{d}\mathbf{r}\,. \tag{4.26}$$

For molecular fluids the decoupling of c and h in (*4.25*) is not a trivial matter and an equation analogous to (*4.26*) can be derived only for specific models[2]. Eqs (*4.24*) and (*4.26*) are fundamental relations called the compressibility equations and unlike (*4.2*) their application is not limited to systems in which only the pair interactions exist.

4.2. *Computer Experiments*

4.2.1. Methods

Monte Carlo (MC) and molecular dynamics (MD) methods provide an experimental tool of the statistical physics, enabling one to study exactly model (often nonrealistic) systems. Since the first applications of the simulation methods they have grown into a large field called sometimes "computer theory" with a vast literature. Details about the basic principles of both simulation methods may be found *e.g.* in a monograph by Vesely[87] or in an article by Ree[88]. Very detailed description of the MC method including also various technical aspects and earlier results for hard spheres and other simple systems is given in a paper by Wood[85]. Methodology of the MC method has been reviewed in detail by Valleau and coworkers[89,90], while an extensive survey of applications with nearly exhausting list of references can be found in Chapters 2 of both volumes of the monograph on the Monte Carlo methods edited by Binder[91,92]. Modern methods aiming at direct evaluation of "entropical" functions (Helmholtz free energy, chemical potential) have been recently reviewed by Shing and Gubbins[93]. Concerning the MD methods, their methodological aspects have been recently reviewed by Hoover and coworkers[94], while their implementation for various systems may be found in a monograph edited by Lykos[95].

It is not the purpose of this article to review the above simulation methods and we will confine therefore our considerations only to the aspects relevant to HB fluids.

Monte Carlo method. In the overwhelming majority of simulations the quantities of primary interest are the correlation functions from which thermodynamic properties are evaluated. Practically all applications of the MC method to HB systems employ the original Metropolis and coworkers[96] algorithm and the NVT ensemble.

This method was apparently first extended to nonspherical bodies by Vieillard-Baron who investigated two-dimensional ellipses[80] and three-dimensional spherocylinders[81]. Despite the fact that more than a decade has elapsed since, number of qualitatively different HB fluids investigated so far is surprisingly very small. In fact, until recently only linear molecules were considered in the simulations and these were reviewed by Streett and Gubbins[5] who also discussed at length various technical aspects.

Although an extension of the Metropolis algorithm to nonspherical bodies is straightforward, a pitfall may be the way in which random walks in the rotational space are realized. For instance, direct changes of the Euler angles may lead to the so called "bottleneck effect" which means that the configurations become trapped in a small region of the configurational space[5]. As an attempt to link together translational and rotational moves, Streett and Tildesley[97] proposed a method which, however, does not overcome the above problem. In a subsequent paper[98] they proposed therefore another method but this is also ill-suited for the MC purposes. A simple scheme which does give a uniform distribution on the surface of a unit sphere was proposed by Nezbeda[99]. He also studied the effect of incorrect sampling of the rotational space but found no observable impact on the pressure. Another way of generating orientations was recently employed by Wojcik and Gubbins[33].

Convergence along the Markov chain of generated configurations is given, first of all, by the ratio of rejected and accepted configurations. This ratio is usually governed by two parameters, one for translational and one for rotational moves, and varies within the range $0{\cdot}3 \div 0{\cdot}8$ (for a discussion see *e.g.* ref.[5]). At present there seems to be a general consensus to set such values to these parameters so as to maintain the ratio approximatelly at the 0·5 level, although simulations with predominance of rejected configurations also appear.

Evaluation of the EOS from either (*4.8*) or (*4.14*) or (*4.19*) requires extrapolation of the involved functions to the contact which may be a source of additional errors. The scalar product $\langle \mathbf{r}_{12} \cdot \mathbf{v} \rangle$ is a linear function of s (or r) for both CB and FHS models and the same holds approximately true also for $g_{1,0}^{\alpha\beta*}$ close to contact. Main source of errors are therefore g^{av} and $G_{\alpha\beta}$. Being guided by an approximate result for hard spheres (see Section 4.4.3.), the function g^{av} may be fitted by a polynomial of the third degree. Better way seems to plot $\ln g^{av}$ *vs* s since this dependence has been found to be nearly linear[64]. For FHS models the r-dependence of $G_{\alpha\beta}$ may be very complex and the extrapolation must be made with caution (for one general possibility see ref.[71]).

A very important point is a reliable estimate of the experimental errors. Most commonly, the whole computer experiment is divided into shorter subruns which are assumed to be independent and the standard error of the mean is then evaluated accordingly. Besides the fact that the subruns themselves must be sufficiently long to produce reasonable results (which may lead to substantial increase in the computer time), the assumption of the lack of correlation among them is not soundly based. Smith and Wells[100] proposed recently a better way of evaluating the experimental error based on the assumption that the series of consecutive subruns is an autoregressive process of the first order. Advantages of this method are obvious. For instance, the number of configurations required to obtain a desired accuracy can be estimated, and reliable error estimates can be made for runs employing far fewer configurations.

The simulations are usually performed on big fast computers; however, for instance Labík and Malijevský[101], by employing integer algebra and the box edge equal to the largest integer number, have managed to perform effectively the MC simulations on a relatively slow minicomputer.

Besides the NVT ensemble, the NPT and grand-canonical ensembles are used in the simulations of more realistic systems, especially mixtures. For HB fluids the simulations in the NPT ensemble bring no particular advantage and we are only aware of old Wood's simulations[85] of hard discs and spheres and of very recent simulations on the fluids of infinitely thin platelets and ellipsoids by Frenkel and coworkers[35,56]

The methods mentioned above can yield directly internal energy and EOS with reasonable accuracy. The Helmholtz free energy can be also obtained by integrating an equation of state but this way is rather cumbersome. Methods have been therefore devised enabling one to calculate the Helmholtz free energy or the chemical potential, and hence phase equilibria, directly. In addition to the thermodynamic integration, the Helmholtz free energy can be obtained by means of methods due to McDonald and Singer[102] and Benett[103], or by using multistage[104] or umbrella [105] samplings. Concerning the chemical potential, methods for its direct calculation can be divided into those based on the Widom's test particle method[106] and its modifications (employing usually the umbrella sampling) and simulations employing the grand canonical ensemble. Some of the above methods (*e.g.* the test particle method) are quite general and can be used in combination with both the MC and MD methods without great additional programming effort. On the other hand, the umbrella sampling is ill-suited for quantities other than the chemical potential and is restricted to the MC method only. However, for pure hard body fluids all these methods have rather methodological than practical value.

Molecular dynamics. For purely repulsive nonspherical systems the molecular dynamics method has not played an important role and has been used quite rarely. One reason may be complexity in comparison with the MC method, which is due to the discontinuous nature of the potential. We may mention only simulations performed on the hard sphere and spherocylinder[107] fluids.

Quite recently Chapela and coworkers[108] extended Alder and Wainwright's method[109] to the case of potentials with any number of discontinuities. The method enabled them to study fluids of particles made up of complicated shape. The generalization is done by representing the interaction potential $u(1, 2)$ by a linear combination of products of the Heaviside functions. This seems a useful approximation; nevertheless, it makes their particles different from exact hard bodies and the results correspond only approximately to those obtained in a conventional way.

In a recent simulation study of the hard sphere fluid Erpenbeck and Wood[110] used a combination of the MD and MC methods. Instead of investigating only one trajectory (as is common in MD), a number of trajectories was generated with the initial configuration sampled *via* the ordinary Metropolis MC method. Advantage of this combination of MC and MD is that it makes possible to evaluate the pressure in a number of ways.

4.2.2. Results

Hard spheres (HS). Since the pioneering work of Metropolis and coworkers and Alder and Wainwright this system has been – because of its simplicity and importance – simulated very frequently. Review about these results may be found *e.g.* in refs[91,92]. The homogeneous fluid phase is stable up to the packing fraction $\eta_F = 0{\cdot}494 \pm 0{\cdot}002$ at which it is in thermodynamic equilibrium with the solid phase at the pressure[111,112] $\beta P\sigma^3 = 11{\cdot}69 \pm 0{\cdot}18$. Until recently the data for fluid phase most frequently referred to were those due to Barker and Henderson[113] obtained with 108 particles. Recently Labík and Malijevský[114] carried out MC simulations with 864 particles and Erpenbeck and Wood[110] did combined MC + MD simulations with as many as 4 000 particles; the latter authors investigated also the dependence of the pressure on system size. They fitted their data by a Padé approximant (*cf.* Section 4.4.1.) but this fitting cannot be, however, considered as a parametrization of the data because at higher densities it differs from them by more than the specified experimental errors. We have therefore performed our own simple parametrization,

$$\beta P/\varrho = (1 + \eta + \eta^2 - \alpha_1\eta^3 - \alpha_2\eta^4 - \alpha_3\eta^5)/(1 - \eta)^3 , \qquad (4.27)$$

where

$$\begin{aligned} \alpha_1 &= 0{\cdot}764314 \\ \alpha_2 &= 0{\cdot}151532 \\ \alpha_3 &= 0{\cdot}654551 \, . \end{aligned} \qquad (4.28)$$

The compressibility factor given by this equation also agrees with that at η_F: $(\beta P/\varrho)_F = 12{\cdot}39 \pm 0{\cdot}25$ and Eq. (*4.27*) gives 12·49. It also correlates the data of Labík and Malijevský within their error bars (see Fig. 10). It is worth mentioning that Erpenbeck and Wood claim extraordinarily high accuracy of their data (better than 0·01 per cent) despite the fact that their independent and comparable runs at the same density do not agree within these errors. In any case, Erpenbeck and Wood and Labík and Malijevský data are in mutual agreement; they are listed in Table IX.

Prolate spherocylinders (PSC). This system was the first nonspherical model to which the MC method was extended. It is primarily of interest in the study of nematic liquid crystals formed by elongated rod-like molecules. However, an attempt by Vieillard–Baron[81] to locate nematic-isotropic phase transition for a system of 616 PSC with $\gamma = 3$ failed. When evaluating the results of their MC simulations, Few and Rigby[115] used an incorrect pressure algorithm and their results must be therefore discarded. All other results due to Boublík and coworkers[75], Nezbeda[99,116], Monson and Rigby[117], and Rebertus and Sando[107] (MD simulations) are in mutual agreement and are listed in Table X.

Other convex body models. In addition to PSC, other CB systems simulated so far are prolate and oblate ellipsoids[82,118,119] and oblate spherocylinders[33] (OSC) and their extreme case: infinitely thin platelets[55,56], *i.e.* hard cores of OSC.

Systems of ellipsoids were studied by Frenkel and coworkers[118,119] using both NVT and NPT ensembles; two prolate ellipsoid systems were also studied by Perram and coworkers[82]. The former authors published extensive tables of their results

TABLE IX

Compressibility factors of the hard sphere fluid from computer simulations[a]

η	$\beta P/\varrho$
0·0296	1·12777 ± 0·00003[b]
0·0411	1·18282 ± 0·00005[b]
0·0740	1·35939 ± 0·00007[b]
0·1481	1·88839 ± 0·00022[b]
0·1572	1·964 ± 0·006[c]
0·2097	2·526 ± 0·008[c]
0·2468	3·03114 ± 0·00021[b]
0·2610	3·26 ± 0·01[c]
0·3149	4·30 ± 0·01[c]
0·3670	5·72 ± 0·02[c]
0·3702	5·85016 ± 0·00085[b]
0·3965	6·81 ± 0·02[c]
0·4114	7·43040 ± 0·00127[b]
0·4181	7·75 ± 0·03[c]
0·4356	8·60034 ± 0·00128[b]
0·4504	9·41 ± 0·04[c]
0·4628	10·19388 ± 0·00102[b]

[a] From ref.[110] only the results obtained with $N = 4\ 000$ are listed, [b] ref.[110], [c] ref.[114].

(about 260 state points in the isotropic phase) and these are shown in Tables XI and XII. Perram and coworkers' results, presented in a form of graphs, seem to be consistent with those of Mulder and Frenkel.

There is only one set[33] of results for OSC due to Wojcik and Gubbins and these are listed in Table XIII. However, Nezbeda[34] reported certain inconsistencies when the data were used in combination with virial coefficients and various analytical methods (see Subsection 4.5.4. for details).

TABLE X

Compressibility factors of the prolate spherocylinder fluids from computer simulations

γ	η	$\beta P/\varrho$
1·4	0·3142	4·42 ± 0·04[a]
1·6	0·2948	4·10 ± 0·06[a]
	0·3873	6·84 ± 0·10[a]
2·0	0·20	2·65 ± 0·02[b]
	—	2·69 ± 0·11[c,d]
	0·2454	3·23 ± 0·10[e]
	—	3·37 ± 0·04[b]
	0·30	4·48 ± 0·07[b]
	0·3351	5·53 ± 0·14[f]
	0·3879	7·44 ± 0·15[a]
	0·40	8·20 ± 0·20[b]
	—	8·18 ± 0·33[c,d]
	0·4460	10·74 ± 0·24[f]
	0·50	15·20 ± 0·20[b]
	0·5096	16·80 ± 0·90[f]
3·0	0·20	3·07 ± 0·03[b]
	0·2676	4·53 ± 0·23[e]
	0·30	5·40 ± 0·13[g]
	—	5·40 ± 0·10[b]
	0·3058	5·52 ± 0·28[e]
	0·3474	6·84 ± 0·34[e]
	0·35	7·17 ± 0·11[g]
	0·3927	8·99 ± 0·45[e]
	0·40	9·60 ± 0·10[g]
	0·45	13·00 ± 0·16[g]
	0·50	18·00 ± 0·40[g]
	0·54	23·33 ± 0·37[g,h]

[a] Re-calculated values from ref.[99], [b] ref.[117], [c] ref.[107], [d] our estimate of the experimental error, [e] ref.[75], [f] ref.[116], [g] ref.[81], [h] almost isotropic fluid phase.

TABLE XI

Compressibility factors of the isotropic prolate ellipsoid fluids taken from ref.[119]. The compressibility factors are claimed to be accurate, approximately, to within 1 per cent

$\lambda = 1{\cdot}25$		$\lambda = 2{\cdot}0$		$\lambda = 2{\cdot}75$		$\lambda = 3{\cdot}0$	
η	$\beta P/\varrho$	η	$\beta P/\varrho$	η	$\beta P/\varrho$	η	$\beta P/\varrho$
0·207	2·53	0·197	2·65	0·190	2·76	0·184	2·84
0·282	3·71	0·271	3·87	0·256	4·10	0·189	2·78
0·330	4·76	0·318	4·93	0·302	5·21	0·253	4·13
0·366	5·72	0·351	5·96	0·335	6·26	0·252	4·16
0·386	6·78	0·371	7·05	0·361	7·26	0·296	5·31
0·408	7·69	0·398	7·89	0·382	8·23	0·298	5·27
0·430	8·53	0·416	8·82	0·395	9·27	0·329	6·37
0·447	9·37	0·439	9·55	0·412	10·2	0·357	7·34
0·458	10·3	0·448	10·5	0·427	11·0	0·356	7·35
0·471	11·1	0·453	11·5	0·443	11·8	0·381	8·24
0·483	11·9	0·468	12·3	0·450	12·8	0·397	9·22
0·496	12·7	0·479	13·1	0·461	13·6	0·391	9·38
0·507	13·4	0·487	14·0	0·4712	14·2	0·407	10·3
0·510	14·4	0·496	14·8	0·473	14·4	0·422	11·2
0·520	15·1	0·504	15·6	0·479	15·3	0·422	11·2
0·528	15·9	0·510	16·4	0·4817	15·7	0·432	12·1
0·530	16·8	0·515	17·3	0·490	16·0	0·442	13·0
0·542	17·4	0·516	17·2	0·4922	16·8	0·443	13·0
0·5498	17·3	0·524	18·0	0·495	16·9	0·453	13·9
0·554	18·9	—	—	0·500	17·8	0·464	14·7
—	—	0·528	18·8	0·5027	18·2	0·462	14·7
—	—	0·530	18·8	0·509	18·5	0·4712	14·9
—	—	0·536	19·6	0·504	18·7	0·4712	15·0
—	—	0·534	19·6	0·513	18·8	0·4712	14·9
—	—	0·539	20·4	0·5131	19·1	0·4817	16·6
—	—	0·542	20·3	0·510	19·5	0·4817	16·5
—	—	0·545	21·2	0·517	19·2	0·4817	16·1
—	—	0·545	21·1	0·513	20·4	0·483	16·3
—	—	0·550	21·9	0·521	20·1	0·4922	17·7
—	—	0·551	21·9	0·5204	21·1	0·496	18·0
—	—	0·553	22·7	0·5236	20·3	0·5026	18·2
—	—	0·558	23·5	0·528	20·8	0·503	19·8
—	—	0·562	24·2	0·531	21·7	0·5131	19·6
—	—	0·5739	25·7	0·533	21·6	0·520	21·1
—	—	0·5760	26·2	0·534	22·4	0·5236	21·3
—	—	0·5849	27·8	0·5341	22·5	0·530	22·7
—	—	0·5891	29·7	0·539	23·3	0·5341	22·8
—	—	0·5959	31·5	0·5445	24·7	0·539	24·3

TABLE XI
(*Continued*)

$\lambda = 1{\cdot}25$		$\lambda = 2{\cdot}0$		$\lambda = 2{\cdot}75$		$\lambda = 3{\cdot}0$	
η	$\beta P/\varrho$	η	$\beta P/\varrho$	η	$\beta P/\varrho$	η	$\beta P/\varrho$
—	—	0·6063	34·5	0·548	24·9	0·5445	24·8
—	—	0·6021	33·2	0·5550	26·8	—	—
—	—	0·6199	40·3	0·5655	29·2	—	—
—	—	—	—	0·5760	32·5	—	—
—	—	—	—	0·5891	35·3	—	—

Concerning the system of infinitely thin platelets (an interesting system of particles with zero volume), Eppenga and Frenkel[56] focused in their simulations mainly on the nematic phase and nematic-isotropic phase transition. The equation of state (for both isotropic and nematic phases) was presented as a graph and is not therefore included in our tables.

Homonuclear diatomics (HOMO DB). This is the simplest FHS model and it has been therefore very intensively studied. In many cases, however, only structural properties have been evaluated. Older data on EOS are due to Freasier[77],Freasier and coworkers[72], and Streett and Tildesley[120]. Data of Aviram and coworkers[78] were shown[51] to be incorrect and must be therefore discarded. Newer data have been obtained by Freasier[71] and Tildesley and Streett[98] and are in mutual agreement. The latter authors performed extensive simulations at 45 state points covering elongations from 0·2 to 1·0 and packing fractions up to 0·47. These are the representative data of HOMO DB and are listed in Table XIV. Tildesley and Streett also parametrized these data by means of a Carnahan–Starling-type equation,

$$\beta P/\varrho = [1 + (1 + UL + VL^3)\eta + (1 + WL + XL^3)\eta^2 - - (1 + YL + ZL^3)\eta^3]/(1 - \eta)^3\,, \qquad (4.29)$$

where

$$U = 0{\cdot}37836 \quad V = 1{\cdot}07860 \quad W = 1{\cdot}30376$$
$$X = 1{\cdot}80010 \quad Y = 2{\cdot}39803 \quad Z = 0{\cdot}35700\,. \qquad (4.30)$$

The average difference between the simulation data and Eq. (*4.29*) is 0·4 per cent and the maximum difference is 1·1 per cent. Since the estimated accuracy of the MC data is 2·0 per cent, Eq. (*4.29*) enables one to determine accurately the compressibility

TABLE XII

Compressibility factors of the isotropic oblate ellipsoid fluids taken from ref.[119]. The compressibility factors are claimed to be accurate, approximately, to within 1 per cent

$\lambda = 0{\cdot}80$		$\lambda = 0{\cdot}50$		$\lambda = 0{\cdot}3636$		$\lambda = 0{\cdot}333$	
η	$\beta P/\varrho$	η	$\beta P/\varrho$	η	$\beta P/\varrho$	η	$\beta P/\varrho$
0·210	2·49	0·197	2·66	0·189	2·78	0·183	2·87
0·281	3·73	0·268	3·91	0·252	4·15	0·251	4·18
0·332	4·73	0·316	4·97	0·304	5·16	0·295	5·33
0·370	5·67	0·351	5·96	0·335	6·26	0·327	6·41
0·390	6·71	0·379	6·92	0·364	7·19	0·379	8·29
0·410	7·65	0·394	7·98	0·367	7·14	0·404	10·4
0·432	8·48	0·414	8·86	0·381	8·24	0·419	11·2
0·446	9·39	0·428	9·79	0·396	9·26	0·431	12·2
0·460	10·2	0·439	10·7	0·412	10·2	0·439	13·1
0·471	11·1	0·457	11·5	0·424	11·1	0·453	13·9
0·483	11·9	0·466	12·4	0·438	11·9	0·466	14·6
0·493	12·8	0·478	13·1	0·449	12·8	0·4712	15·6
0·500	13·6	0·481	14·1	0·458	13·7	0·4712	15·6
0·511	14·4	0·493	14·9	0·4650	14·6	0·481	16·3
0·521	15·1	0·502	15·6	0·4712	14·9	0·4817	16·5
0·526	15·9	0·507	16·5	0·471	14·9	—	—
0·537	16·6	0·515	17·3	0·4812	15·2	—	—
0·541	17·4	0·514	17·3	0·4817	15·9	—	—
0·544	18·3	0·518	18·2	0·482	15·8	—	—
0·547	19·1	0·522	18·1	0·485	16·2	—	—
—	—	0·526	18·9	0·4890	17·1	—	—
—	—	0·528	18·8	0·4922	17·0	—	—
—	—	0·530	19·8	0·492	16·9	—	—
—	—	0·533	19·7	0·502	17·7	—	—
—	—	0·543	20·3	0·495	18·0	—	—
—	—	0·534	20·6	0·5027	18·3	—	—
—	—	0·542	21·2	0·508	18·6	—	—
—	—	0·544	21·2	0·509	18·5	—	—
—	—	0·548	22·0	0·513	18·3	—	—
—	—	0·551	22·8	0·516	19·3	—	—
—	—	0·555	23·6	0·5236	21·5	—	—
—	—	0·563	24·2	0·5341	22·6	—	—
—	—	0·5624	25·0	0·5445	24·5	—	—
—	—	0·563	25·1	0·5550	27·1	—	—
—	—	0·5760	26·6	—	—	—	—
—	—	0·5849	27·9	—	—	—	—
—	—	0·5891	30·3	—	—	—	—
—	—	0·5927	31·0	—	—	—	—
—	—	0·6074	36·3	—	—	—	—
—	—	0·6168	40·6	—	—	—	—

factor of the fluid of HOMO DB with any elongation ($L \leqq 1$) and at any packing fraction.

TABLE XIII
Compressibility factors of the oblate spherocylinder fluids from computer simulations (ref.[33])

$\varphi(= \gamma - 1)$	η	$\beta P/\varrho$
0·5	0·35	5·41 ± 0·04
1·0	0·10	1·58 ± 0·01
	0·25	3·35 ± 0·07
	0·35	5·79 ± 0·07
	0·45	10·56 ± 0·09
		10·53 ± 0·07
1·5	0·35	6·23 ± 0·07
	0·45	11·35 ± 0·12
2·0	0·25	3·83 ± 0·05
	0·35	6·79 ± 0·05
		6·81 ± 0·08
	0·45	12·30 ± 0·10
		12·09 ± 0·16
2·5	0·35	7·37 ± 0·09
	0·45	13·00 ± 0·12

TABLE XIV
Compressibility factors of the homonuclear diatomic fluids from computer simulations (ref.[98])

η	$\beta P/\varrho$				
	$L = 0·2$	$L = 0·4$	$L = 0·6$	$L = 0·8$	$L = 1·0$
0·1047	1·56 ± 0·03	1·59 ± 0·03	1·63 ± 0·03	1·70 ± 0·03	1·79 ± 0·03
0·1571	2·01 ± 0·04	2·04 ± 0·04	2·13 ± 0·04	2·26 ± 0·05	2·46 ± 0·05
0·2094	2·59 ± 0·05	2·64 ± 0·05	2·78 ± 0·06	3·01 ± 0·06	3·36 ± 0·07
0·2618	3·36 ± 0·07	3·49 ± 0·07	3·67 ± 0·06	4·05 ± 0·08	4·62 ± 0·09
0·3142	4·45 ± 0·09	4·59 ± 0·09	4·95 ± 0·10	5·48 ± 0·11	6·40 ± 0·13
0·3665	5·95 ± 0·12	6·21 ± 0·12	6·69 ± 0·13	7·52 ± 0·15	8·95 ± 0·18
0·4189	8·02 ± 0·16	8·42 ± 0·17	9·23 ± 0·18	10·54 ± 0·21	12·64 ± 0·25
0·4451	9·44 ± 0·19	9·91 ± 0·20	10·89 ± 0·22	12·50 ± 0·25	15·12 ± 0·30
0·4712	11·17 ± 0·22	11·67 ± 0·23	12·87 ± 0·26	14·88 ± 0·30	18·06 ± 0·36

Heteronuclear diatomics. This system was studied long time ago by Jolly and coworkers[73] and by Streett and Tildesley[120]. The former authors considered five different models, each at two densities, while the latter authors considered several models but each at one density only. The latter results are also subject to relatively high uncertainty, about 7 per cent. Simulations of one model at several densities were carried out recently by Nezbeda and coworkers[121]. All the above mentioned data are listed in Table XV.

Other FHS *models.* Other FHS models for which simulation data are available are symmetric triatomics, both linear[74,121,122] and non-linear[69,122], and tetrahedral penta-atomics[63]. For each of these models only one set of data is available so that no comparisons and checks can be made. The results are shown in Tables XVI and XVII.

TABLE XV

Compressibility factors of the heteronuclear diatomic fluids from computer simulations

L	σ_B	η	$\beta P/\varrho$	Ref.
0·3333	0·6667	0·2094	2·660 ± 0·13	73
		0·3665	6·040 ± 0·30	73
0·375	0·5	0·4084	7·8 ± 0·55	120
0·50	0·8333	0·2094	2·780 ± 0·10	73
		0·3665	6·510 ± 0·33	73
	0·6667	0·2094	2·750 ± 0·14	73
			2·580 ± 0·13	73
		0·3665	6·450 ± 0·32	73
	0·5556	0·2094	2·680 ± 0·13	73
		0·3665	6·340 ± 0·32	73
	0·50	0·4084	8·3 ± 0·58	120
0·625	0·50	0·25	3·46 ± 0·12	121
		0·30	4·58 ± 0·15	121
		0·35	6·04 ± 0·25	121
		0·40	8·44 ± 0·32	121
		0·4084	8·90 ± 0·62	120
0·6667	0·6667	0·2094	2·93 ± 0·15	73
		0·3665	7·13 ± 0·36	73
0·75	0·84	0·4084	9.9 ± 0·69	120
	0·67	0·4084	10·1 ± 0·71	120
	0·50	0·4084	10·0 ± 0·70	120

4.3. *Lattice Theories*

The virial expansion, considered in the previous part, was originally formulated as a "gas-like" approach to the description of dense fluids. Lattice theories, intensively studied in 30–50ieths, represent an alternative "solid-like" approach. The main theoretical developments (including Kirkwood's work on communal entropy[123])

TABLE XVI

Compressibility factors of the symmetric triatomic fluids from computer simulations

L	$\sigma_{\rm A}$	ω, deg	η	$\beta P/\varrho$	Ref.
			Linear models		
0·3738	0·8333	—	0·4697	12·88 ± 0·64	74
0·4485	1·00	—	0·4697	12·84 ± 0·64	74
0·5233	1·1669	—	0·4697	14·84 ± 0·74	74
0·5	1·0	—	0·4533	12·88 ± 0·39	122
0·8	1·0	—	0·25	4·48 ± 0·18	121
			0·30	6·04 ± 0·24	121
			0·35	8·33 ± 0·30	121
			0·40	11·65 ± 0·45	121
			Non-linear models		
0·5	1·0	90	0·3988	8·34 ± 0·25	122
0·8	0·6	105	0·25	4·94 ± 0·12	69
			0·30	6·84 ± 0·17	69
			0·35	9·46 ± 0·24	69
			0·375	11·14 ± 0·33	69

TABLE XVII

Compressibility factors of the tetrahedral penta-atomic fluid from computer simulations. $\sigma_{\rm A}$ = 1·0294, L = 0·5206, $\mathscr{V}$ = 2·1474. Values are taken from ref.[63]

η	$\beta P/\varrho$
0·20	2·94 ± 0·09
0·30	5·39 ± 0·16
0·3555	7·70 ± 0·30
0·40	10·26 ± 0·30

and results are reviewed in monographs by Hill[22] and Barker[124]. At present, results of the classical lattice theories are only of limited value for describing the P–V–T behaviour of isotropic fluid phases but they have found applications in thermodynamics and chemical engineering of mixtures and polymers; some ideas of these theories formed also a basis for the development of methods discussed in Section 4.4.. Moreover, several theoretical works have appeared which have been devoted to the application of improved lattice theories to the problem of solid–fluid phase transition. Here we first sketch simple lattice theories and then outline recent improved versions.

In simple lattice theories a long-range order in liquids is assumed, with molecules moving for most of time in the vicinity of the lattice points – the centres of cages (cells) formed around molecules by their closest neighbours. The total potential energy is then a sum of the lattice energy (for all the molecules fixed in their lattice points), U_0, and contributions from single molecules given by their motion within the cell.

Assuming single occupancy and the independent motion of molecules in the cells, the configuration integral, Z, can be written as a product of two principal terms: the Boltzmann factor containing energy U_0, and the free volume, v_f, given by an integral over a volume accessible to a single molecule, *i.e.*

$$Z = \exp\left[-\beta U_0\right] v_f^N , \tag{4.31}$$

where

$$v_f = \int \exp\left\{-\beta[\varphi(r) - \varphi(0)]\right\} \mathrm{d}r , \tag{4.32}$$

φ denotes a sum of interactions of a chosen molecule with its closest neighbours; r is the distance from the cell centre. In the case of HS $U_0 = 0$ and the free volume can be easily evaluated from the cell geometry. Very often, however, v_f is related to the volume V of the system by means of a geometric factor, Ω, and the fact that in the case of the close-packed structure v_f equals zero is taken into account. Then

$$v_f = \frac{4}{3}\pi \frac{\Omega}{N}(V^{1/3} - V_c^{1/3})^3 \tag{4.33}$$

and

$$z = [1 - (V_c/V)^{1/3}]^{-1} , \tag{4.34}$$

where subscript c denotes a close-packed property; $V_c = N\sigma^3/\sqrt{2}$.

According to the cell theory, in which the number of cells, L, equals the number of molecules, N, each molecule is confined to only a very small fraction of the volume

V even at $\varrho \to 0$. As a consequence of this fact EOS (*4.34*) yields unsatisfactory description of fluids at low densities. This serious drawback of the cell theory is, at least in principle, removed in hole and tunnel theories of liquids. In the hole theory the number of cells is greater than N, so that there exist vacant and single-occupied cells in the system. Due to the lack of symmetry the determination of the free volume is not so simple. It is possible to relate it by a semiempirical rule (in six possible variants) to the volume of an empty cell and to the v_f from the cell theory. The tunnel theory makes use of the knowledge of the exact value of one-dimensional configuration integral; the remaining two-dimensional (2-D) integral is approximated by the 2-D cell model; for details see ref.[124]. Physically quite satisfying is the cell-cluster theory (see ref.[124]) in which multiple occupancy and correlation of molecular motions within clusters of one, two, ... cells is considered. Practical results, however, do not represent substantial improvement over the cell and hole theories. None of the variants of classical lattice theories yields satisfactory description of the P–V–T behaviour at very low densities. From comparison with pseudoexperimental data it appears that results of these theories for higher densities closely follow the properties of a solid.

Novel ideas have been brought to the formulation of lattice theories by Hoover and coworkers[125–126]. They considered cells of different sizes with the size distribution related to the path of a very light test molecule, quickly moving in comparison with others. For 1- to 3-D systems they get for the compressibility factor the expression

$$z = 1 + (\sigma/2D)\langle s_f/v_f\rangle\,, \tag{4.35}$$

where D stands for the dimensionality, σ is a characteristic parameter and s_f a bounary surface – *e.g.* surface area, line or point. The same relationship has been derived also by Speedy[127]. In the case of the 1-D system the mentioned approach yields the exact expression formerly derived by Tonks[128] for hard rods. This expression is related to the Γ distribution and this fact led Hoover and coworkers and later Vörtler and coworkers[129,130] to the assumption that also the cell size distributions in the 2-D and 3-D systems are governed by the same rule. Two parameters characterizing the Γ-distribution can be adjusted to the HS close-packed properties, or random close-packed ones. The equation of state of the latter authors possesses then the form

$$z = 1 + \tfrac{1}{2}m_{HS}/(m_{HS} - 1)\,[(\tfrac{1}{2}\pi\eta)^{-1/3} - 1]^{-1}\,, \tag{4.36}$$

where m_{HS} is a coefficient of dispersion, $m_{HS} \approx 2$ (*e.g.* $m_{HS} = 2{\cdot}12$ in ref.[130]).

As a unique attempt within the framework of lattice theories, Vörtler and Heybey[130] considered also nonspherical particles. For convex bodies they found

$$z_{CB} = 1 + \tfrac{1}{2}\alpha m_{HS}/(m_{HS} - 1)\,[(\tfrac{1}{2}\pi\eta)^{-1/3} - 1]^{-1}\,, \tag{4.37}$$

where α is the parameter of nonsphericity. Comparing the last two equations one can see, that the CB equation of state can be expressed in terms of z_{HS} at the same packing fraction,

$$z_{\text{nonsph}} = z_{HS} + (\alpha - 1)(z_{HS} - 1) . \qquad (4.38)$$

The same form of the equation of state was considered recently also by Chung and coworkers[131] as a simplified version of Boublík's semi-empirical equation of state (*4.118*). They showed that (*4.38*) is quite accurate for $\eta \geqq 0{\cdot}1$ and $\alpha \leqq 1{\cdot}5$. For $\alpha = 1{\cdot}5$, however, the second virial coefficient is approximately by about 10 per cent higher than the correct value.

Also a method recently proposed by Sugiyama[132] belongs to the group of the free volume theories. For HS he found exact expressions for the so-called vacancy volume, v_0, for the overlap volume, v_1, (volume available to the centre of molecule 1 when it overlaps with one neighbour) and for the fluctuation vacancy volume term, φ. For the second derivative of the configuration integral, Z'', which is in a simple relation to the isothermal compressibility, he obtained an exact expression

$$Z''(\eta) = \{F(\eta) - [\tilde{v}_0(\eta) + \tilde{v}_1(\eta)]\}/\eta\tilde{v}_0 , \qquad (4.39)$$

where tilde denotes quantities reduced by the HS volume. Also the volumes $\tilde{v}_0$ and $\tilde{v}_1$ are expressible in terms of the derivatives of Z with respect to η; after substituting into (*4.39*) a system of two differential equations for four variables results. At low densities, $\eta \leqq 0{\cdot}125$, the author employed the limiting values of Z and $\tilde{v}_1$ and found an expansion

$$z = 1 + 4\eta + (32/3)\,\eta^2 + 32\eta^3 + \ldots \qquad (4.40)$$

which, for the free volume theory, is in good agreement with the exact virial expansion.

The importance of the above approach is in its good description of the high density range. Introducing a quantity "vacancy number" defined as a number of HS that can be added to a given distribution of molecules in a given volume, and by finding its probability density, Sugiyama[132] managed to express quantities in expression (*4.39*) for Z'' for high densities. In this case two parameters of the solution were adjusted to computer data. There are two branches, (+) and (−), of the dependence of the isothermal compressibility on density. The positive branch is in close agreement with the Padé approximant for the compressibility of the low density fluid phase, whereas the (−) branch corresponds at high densities to the free volume curve. Most interesting is the fact that at $\eta \approx 0{\cdot}64$, corresponding practically to the random close-packing, the (+) branch tends to zero.

An attempt to describe the solid–fluid phase transition of hard spheres within the framework of the hole theory was made by Shinomoto[133]. For the free volume,

v_f, he proposed the relation

$$\ln v_f = \ln v_s + h_i \ln (v_0/v_s)\,, \qquad (4.41)$$

where $v_s = (v_0^{1/3} - v_c^{1/3})^3$ and $v_0 = V/L$. The dependence of the factor h_i on the number of neighbours, i, was determined numerically for given geometric structures. The theory yields only qualitative description of the phase transition.

In Fig. 6 the compressibility factors given by the cell theory, Eq. (*4.34*), and the Vörtler equation, Eq. (*4.36*), are compared with simulation data. It is seen that while the cell theory is uniformly poor, the latter theory provides substantial improvement but yet the overall agreement is only fair. Concerning Eq. (*4.37*), its only advantage is simplicity, otherwise it is inferior to most equations to be discussed in Section 4.5..

It can be concluded that the theories considered in this section remain, in spite of considerable effort, unsuitable for describing the *P–V–T* behaviour of fluids over the entire density range and their only merit lies in characterizing the phenomena at highest densities.

4.4. *Hard Sphere Fluid*

4.4.1. Expansions and Resummations

The virial expansion (*2.1*) provides the simplest and rigorous way to obtain the EOS. There are two problems associated with Eq. (*2.1*),namely (i) convergence of the expansion and (ii) limited knowledge of the virial coefficients.

Regarding the convergence, rigorously only lower bounds to the radius of convergence have been established: $\eta \sim 0{\cdot}018$ (ref.[134]) and then $\eta \sim 0{\cdot}019$ (ref.[135]).

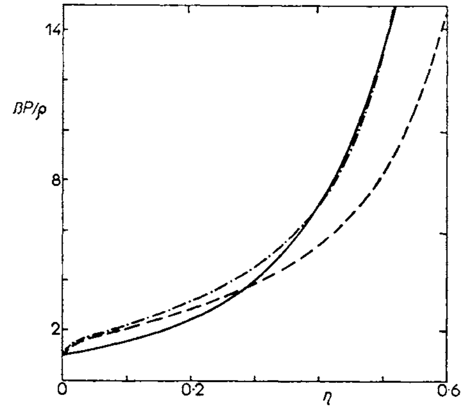


Fig. 6

Compressibility factors of the hard sphere fluid calculated from cell theories. —·—·— Eq. (*4.36*); — — — Eq. (*4.34*); ——— exact

However, these values are still too small compared with physically interesting and relevant values. There are, in general, two singular points that could be associated with possible singularities in the virial series: the regular close packing $\eta_0 = \pi\sqrt{2}/6$, corresponding to the maximum possible density for the crystalline branch of the hard sphere EOS and the random close-packing[136], $\eta_B \sim 0{\cdot}6535$, corresponding to the amorphous branch. At present there is no general consensus with which density to associate the singularity in the virial series. For details and references we refer a reader to a review article by Angell and coworkers[137].

The virial expansion is subconsciously linked with the low density region beyond which it becomes useless. This may be generally true but not in the case of hard spheres. In Fig. 7 we show the compressibility factor calculated from the virial expansion (*3.1*) with 3 through 10 terms (*i.e.* up to $B_{10}\varrho^9$). It is seen that the expansion is quite well converging and one may conjecture that adding few more terms would make the expansion coincide with the simulation data even at very high densities. There is however an important obstacle – evaluation of further virial coefficients is practically impossible. One may try to overcome this problem by proceeding along three possible paths: to estimate all remaining coefficients (*e.g.* by a recursion formula), or to apply some re-summation technique (as *e.g.* Padé approximants), or to accelerate convergence of the expansion by using another variable as an expansion parameter instead of the density.

Virial coefficients $B_4 \div B_6$ from Table II can be approximated by integers and the resulting progression can be then expressed by a formula[138]

$$B_i^* = i^2 + i - 2\,, \quad B_i^* = B_i/\mathscr{V}^{i-1}\,. \qquad (4.42)$$

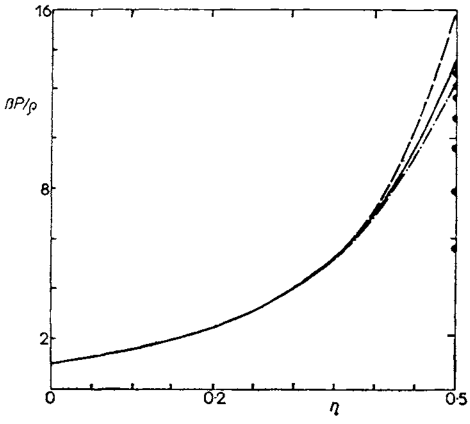


FIG. 7

Compressibility factors of the hard sphere fluid calculated from expansion and resummation methods. – – – P(3, 3), Eq. (*4.48*); –·–·– Eq. (*4.53*); ——— exact; ● correspond to the truncated virial expansions with 3 up to 10 terms. Results of Eqs (*4.44*), (*4.46*), (*4.49*), and (*4.52*) are indistinquishable from the exact data within the scale of the graph

Assuming that all virial coefficients can be approximated by Eq. (*4.42*), the virial expansion takes on a very simple form,

$$\beta P/\varrho = 1 + \sum_{i \geqq 0} (i^2 + 3i)\,\eta^i\,. \tag{4.43}$$

The infinite sum on the right-hand side of (*4.43*) can be simply evaluated which results in the Carnahan–Starling (C–S) equation of state:

$$\beta P/\varrho = (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3\,. \tag{4.44}$$

This simple equation performs surprisingly well: the maximum deviation from the parametrized equation (*4.27*) does not exceed 0·3 per cent. This result suggests that approximation (*4.42*) with a quadratic dependence of B_i^* on i is a very good approximation. This dependence gives rise to the $(1 - \eta)^3$ term in the denominator of an EOS and therefore such a functional form has been used to parametrize the simulation data (*cf*. Eq. (*4.27*)). The C–S equation can be further simply improved by improving prediction of the lower virial coefficients. The approximation[139]

$$B_i^* = \tfrac{5}{6}(i^2 + 3i - 6)\,, \quad i \geqq 3 \tag{4.45}$$

leads to the equation

$$\beta P/\varrho = (1 + \eta + \eta^2 - \tfrac{2}{3}\eta^3 - \tfrac{2}{3}\eta^4)/(1 - \eta)^3 \tag{4.46}$$

which is approximately by one order better than the C–S equation.

An infinite series, as *e.g.* (*3.1*), whose only M first coefficients are known, can be approximated in a number of ways. The usual way is to apply the Padé approximant[140] (PA),

$$\beta P/\varrho \approx P(m, n) = \frac{1 + a_1\eta + \ldots + a_m\eta^m}{1 + b_1\eta + \ldots + b_n\eta^n} \tag{4.47}$$

whose coefficients are defined so that the Taylor expansion of $P(m, n)$ reproduces exactly the first $M = n + m$ coefficients. In the case of the virial expansion (*3.1*), approximation (*4.47*) may be thus viewed as a sort of analytic continuation beyond the neighbourhood of $\eta \approx 0$. It is not necessary to estimate directly the given infinite series but another function related to it. This method may (but need not) lead to a better estimate of the original series.

Although PA provide a powerful tool for estimating infinite series and have been frequently used for evaluating EOS, general conclusions based on them must be made with caution.

Hard sphere EOS has been usually represented by the $P(3, 3)$ approximant based on the nominal values of B_5 and B_6 (together with the exact values of $B_2 \div B_4$).

Coefficients of this approximant are[141]:

$$\begin{array}{llll} a_1 = & 0{\cdot}836832 & b_1 = & -3{\cdot}16317 \\ a_2 = & 1{\cdot}14845 & b_2 = & 3{\cdot}80112 \\ a_3 = & -0{\cdot}098649 & b_3 = & -2{\cdot}03621\,. \end{array} \tag{4.48}$$

Other approximants, $P(m, n)$, along with their coefficients and discussion of occurring singularities (poles or a maximum in pressure) may be found in papers by Aguilera–Navarro and coworkers[142,143] or in a recent paper by Baker and coworkers[141].

In Fig. 7 the compressibility factors given by Eqs (*4.47*) and (*4.48*) are shown and, surprisingly, the result is in no way better than that from the truncated virial expansion with the same number of coefficients used.

Erpenbeck and Wood[110] used recently PA to fit their simulation data by allowing the coefficients B_6 and B_7 to vary about their nominal values so as to get the best fit: $B_6/B_2^5 = 0{\cdot}0389 + 0{\cdot}0004f_6$, $B_7/B_2^6 = 0{\cdot}0137 + 0{\cdot}0006f_7$, where f_6 and f_7 are adjustable parameters. They obtained the best result with PA in the form

$$\beta P/\varrho = P_{\mathrm{EW}} \equiv 1 + 4\eta\,\frac{1 + a_1\eta + a_2\eta^2 + a_3\eta^3}{1 + b_1\eta + b_2\eta^2} \tag{4.49}$$

with $f_6 = 0{\cdot}2394$ and $f_7 = -1{\cdot}0556$. The coefficients of P_{EW} are

$$\begin{array}{llll} a_1 = & 0{\cdot}2227128 & b_1 = & -2{\cdot}2772872 \\ a_2 = & 0{\cdot}22311216 & b_2 = & 1{\cdot}32624176 \\ a_3 = & -0{\cdot}08575744\,. & & \end{array} \tag{4.50}$$

(We remind that coefficient b_1 in Table III of ref.[110] is erroneous and should be $-0{\cdot}5693218$). Eq. (*4.49*) performs much better than $P(3, 3)$ with the coefficients given by (*4.48*), see Fig. 7, and with exception of the highest densities it agrees with the simulation data.

Comparison of the results based on the above two PA indicates their high sensitivity to the values of the virial coefficients and this is the main problem associated with their application. It can be easily shown that by varying the virial coefficients B_5 through B_7 within the limits of their expected values one can obtain even such an absurd result as $\beta P/\varrho = \pm\infty$ at about $\eta \sim 0{\cdot}38$ and this fact practically degrades higher order PA into a correlation scheme of data only. Or, equivalently, if PA are yet to be used to predict an EOS, then they must do with less virial coefficients.

Some years ago, Alder and Hoover[144] suggested to use approximants not directly for $\beta P/\varrho$ but for the function

$$(\beta P/\varrho)(1-\eta) \approx P(m,n)\,. \tag{4.51}$$

These approximants require virial coefficients up to $m+n+1$ and the coefficients for $P(3,2)$ and $P(2,3)$ approximants may be found in ref.[145]. Alder and Hoover's application of the PA may be viewed as a part of a general scheme in which the known (or expected) functional dependence of $\beta P/\varrho$ on η is explicitly considered[34]. The C–S equation (*4.44*) and integral equation results (see subsection 4.4.3.) indicate that the hard sphere EOS may be written in a form

$$\beta P/\varrho = \frac{1}{1-\eta} + \frac{\eta\varphi(\eta)}{(1-\eta)^2}\,, \tag{4.52}$$

where $\varphi(\eta)$ is an unknown function. If only this function is approximated by the PA, one may intuitively expect that fewer virial coefficients will be required to reach the same accuracy as with $\beta P/\varrho \approx P(m,n)$ or (*4.51*). Using only B_2 and B_3 (*i.e.* $P(1,1)$ approximant) in (*4.52*), the equation identical to the *P–Y* compressibility equation, Eq. (*4.89*), results. $P(2,1)$ approximant then yields an equation which is numerically equal to the C–S equation (for details see ref.[34]).

For completeness we may include into the application of the PA to the HS fluid older results aiming at developing a better EOS at that time. Let us name at least the equations due to Hall[146], Le Fevre[147], and Woodcock[148]. Another attempt was made recently by Hoste and van Dael[149] who fitted parameters of a general form of the EOS.

Other approximants that have been applied to the virial expansion are those of Levin and Tova. Levin[150] developed a scheme based, roughly, on fitting a series and its differences to an appropriate sequence, *e.g.* harmonic. For a power series the Levin approximants are represented by the ratio of two polynomials, similarly as the PA, but of higher degrees. The Tova approximant was considered by Baram and Luban[151]. However, the results based on both the Levin and Tova approximants are not much better than *e.g.* those based on the regular $P(3,3)$.

Independent theoretical approaches (see the next section) indicate that a hard sphere EOS may be written as a cubic polynomial in $\eta/(1-\eta)$. It is thus natural to consider the exact EOS as an infinite-order power series in this parameter[152]:

$$\beta P/\varrho = \frac{1}{\eta}\sum_{n\geq 1} C_n\left(\frac{\eta}{1-\eta}\right)^n\,, \tag{4.53}$$

where

$$C_{n+1} = \sum_{k=1}^{n+1} \binom{n}{k-1} (-1)^{n-k+1} B_k \mathscr{V}^{k-1} . \qquad (4.54)$$

Results of this approach are roughly similar to those obtained from (*4.52*) with $\varphi(\eta)$ being approximated by the PA: the three-term expansion (involving B_2 and B_3) is identical to Eq. (*4.89*) and the four-term expansion performs slightly worse than the C–S equation and comparably to the $P(3, 3)$ approximant (4·48). While the five-term expansion does not differ significantly from lower-order ones, the six-term expansion does and this indicates that, similarly to the PA method, higher-order expansions need not yield better results.

In Fig. 7 the results given by Eqs (*4.44*), (*4.46*), and (*4.49*) are, within the scale of the graph, indistinguishable from the simulation data over the entire fluid range. The truncated expansion (*4.53*), (B–G) does not seem to be a better alternative to the virial expansion which seems to converge very well. If an expected functional form of the EOS is made use of, then the PA with only a few virial coefficients can be used. Including the higher (and only approximately known) virial coefficients in PA makes the result unreliable. The best method seems to be a recursive estimation of all virial coefficients enabling one to sum up the infinite expansion. For further discussion see Subsection 4.4.4. and Fig. 10.

4.4.2. Theories for Fluids with Discontinuous Potentials

Majority of theories of fluids has been devised for systems with an arbitrary intermolecular potential function. There are, however, several theories especially developed for hard body systems or, more generally, for systems with pair potentials given by step functions. The scaled particle theory, theories of Andrews, Speedy, Meeron–Siegert, and a "simple kinetic theory" belong to this group of theories.

Scaled particle theory (SPT). The basic idea of the SPT[153–155] is the choice of the coupling parameter in Eq. (*4.4*). The authors found that a suitable choice of this parameter is the diameter of a test particle or a dimensionless dilatation parameter, ξ. For the interaction of the test particle with other particles $u = \infty$ for $r \leqq \sigma(1 + \xi)/2$ and $u = 0$ for $r > \sigma(1 + \xi)/2$. It is obvious that the change of ξ scales the size of the test particle: for $\xi = 1$ it is equal to that of other molecules of a system, for $\xi = 0$ we have a point-wise particle and the complete decoupling is reached at $\xi = -1$. With this choice of ξ the differentiation in (*4.4*) yields the Dirac function so that

$$\beta(\mu - \mu^*) = \beta W(1) = \tfrac{1}{2}\pi\varrho\sigma^3 \int_{-1}^{1} \mathscr{G}(\xi)\,(1 + \xi)^2\,\mathrm{d}\xi \qquad (4.55)$$

and the EOS is given by Eq. (*4.12*). This choice of the coupling parameter makes it possible to express both the compressibility factor and the chemical potential in terms of the function $\mathcal{G}(\xi)$ and the knowledge of $\mathcal{G}(\xi)$ for $\xi \in (-1, 1)$ is fully sufficient for determining all thermodynamic functions of hard spheres. Moreover, the form of $\mathcal{G}(\xi)$ is exactly known in the interval $\xi \in \langle -1, 0 \rangle$. Since the reversible work W to couple the ξ-particle to the system is the same as that for creating a cavity of the size $(1 + \xi)\,\sigma/2$,

$$W(\xi) = -\ln\left[1 - \pi\varrho\sigma^3(1 + \xi)^3/6\right] = -\ln\left[1 - \eta(1 + \xi)^3\right], \quad \xi \leqq 0\,, \qquad (4.56)$$

Eq. (*4.56*) enables one to determine $\mathcal{G}(\xi)$ and also the first and second derivatives, $\mathcal{G}'$ and $\mathcal{G}''$, at $\xi = 0$. Another relation holds for $\xi = \infty$, because in this case the surface of the scaled particle is planar and hence

$$\beta P = \varrho\mathcal{G}(\infty) = \varrho + \tfrac{2}{3}\pi\varrho^2\sigma^3\mathcal{G}(1)\,. \qquad (4.57)$$

Reiss and coworkers[153–155] employed the obtained values of $\mathcal{G}(0)$ and $\mathcal{G}'(0)$, *i.e.*

$$\mathcal{G}(0) = (1 - \eta)^{-1} \qquad (4.58)$$

$$\mathcal{G}'(0) = 3\eta/(1 - \eta)^2 \qquad (4.59)$$

and (*4.57*) for determining the three coefficients A, B, and C, in an approximate interpolation formula

$$\mathcal{G}(\xi) = A + B(1 + \xi)^{-1} + C(1 + \xi)^{-2}\,, \quad \xi \geqq 0\,. \qquad (4.60)$$

Then from (*4.11*) they obtained the equation of state

$$\beta P/\varrho = (1 + \eta + \eta^2)/(1 - \eta)^3\,. \qquad (4.61)$$

Eq. (*4.61*) is equivalent to the c-form of the Percus–Yevick EOS, derived four years later (see subsection 4.4.3.). It yields the correct 2nd and 3rd virial coefficients and predicts the P–V–T behaviour within 1 per cent for $\eta < 0{\cdot}25$.

In further studies Reiss and coworkers[156,157] tried to improve the accuracy of the SPT by considering higher-order interpolation formulas and further exact relationships, and also to extend the scheme to fluids with more realistic potentials but without any great success.

Theory of Andrews. Probability arguments employed recently in several successful approaches for one-, two-, and three-dimensional systems (1-D, ...) were introduced in a very simple way already by Andrews[158]. Because of this fact this theory is described here in a slightly more detailed way. The central function considered by

Andrews is the chemical potential, μ. From the well known relation (see *e.g.* refs[22,25]) between the residual chemical potential and the configuration integrals for N and $N + 1$ particles it follows that $\exp(-\beta\mu_{\text{res}})$ equals the probability that no centre of any HS lies in the domain of a diameter σ around a randomly chosen point in a volume V. This probability can be expressed as a product of the unconditional probability that a randomly chosen point (the centre of a test particle) lies outside all HS, and the conditional probability that, providing that the test particle's centre lies in a hole, no centre of the regular particle lies within the distance σ.

The determination of the probability is simple in the 1-D case: If L is the 1-D volume, the unconditional probability is $(L - N\sigma)/L = 1 - \eta_1$ (where $\eta_1 = N\sigma/L$ is the 1-D packing fraction and N/L the number density). For determining the conditional probability, the total empty space $(L - N\sigma)$ is divided into N particle separations. The probability that in the space $(L - N\sigma)$ a point lies outside a domain of length σ is $1 - \sigma/(L - N\sigma)$ and the sought conditional probability is just equal to the N-th power of the last expression. Thus

$$\begin{aligned}\exp(-\beta\mu_{\text{res}}) &= (1 - \eta_1)\left[1 - \sigma/(L - N\sigma)\right]^{\mathrm{N}} = \\ &= (1 - \eta_1)\exp\left[-\eta_1/(1 - \eta_1)\right]. \qquad (4.62)\end{aligned}$$

The corresponding equation of state which follows from the relation between the residual chemical potential and the compressibility factor possesses the exact form, first derived by Tonks[128].

In the 3-D HS system the unconditional probability is

$$(1 - \pi\varrho\sigma^3/6) = 1 - \eta. \qquad (4.63)$$

To insert the (whole) test particle into the system at a given point, an additional volume $\frac{4}{3}\pi\sigma^3 - \frac{1}{6}\pi\sigma^3 = \frac{7}{6}\pi\sigma^3$ is required. The conditional probability is again equal to the N-th power of the probability that one particle lies outside this additional volume. If $(V - Nw)$ is the free volume, then

$$\exp(-\beta\mu_{\text{res}}) = (1 - \eta)\left[1 - \frac{7\pi\sigma^3/6}{(V - Nw)}\right]^{\mathrm{N}} \qquad (4.64)$$

$$\begin{aligned}&= (1 - \eta)\exp\left[-\frac{7\pi\varrho\sigma^3/6}{1 - \varrho w}\right] \\ &= (1 - \eta)\exp\left[-7\eta/(1 - \varrho w)\right]. \qquad (4.65)\end{aligned}$$

In (*4.65*) w denotes an average volume per particle; Andrews relates it to the close-packed volume $v_c = \sigma^3/\sqrt{2}$. In the zeroth approximation $w = v_c$. A better approximation is the linear dependence of w on ϱ with the coefficients determined from the virial expansion. If d is the reduced density, $d = \varrho/\varrho_c = \eta/0{\cdot}74048$, then the resulting EOS is

$$\begin{aligned}\beta P/\varrho = {} & 5{\cdot}1834d/(1 - 1{\cdot}5340d + 0{\cdot}5340d^2) - (1{\cdot}3504/d)\ln(1 - 0{\cdot}7405d) - \\ & - (4{\cdot}8534/d)\ln(1 - 1{\cdot}5340d + 0{\cdot}5340d^2) - \\ & - (15{\cdot}977/d)\ln[(1 - 0{\cdot}5340d)/(1 - d)]\,. \end{aligned} \tag{4.66}$$

Speedy's method[159] copies in many respects the derivation of (*4.65*). The relation between the residual chemical potential and the probability Π that for a chosen point in V there is no HS within the distance σ is considered. Speedy introduces a modified volume w' in such a way that Π can be replaced by the probability that in an ensemble of points in the volume $(V - Nw')$ there lies no molecule within the distance σ around a randomly chosen point, *i.e.*

$$\exp(-\beta\mu_{\text{res}}) = [(V - Nw' - \tfrac{4}{3}\pi\sigma^3)/(V - Nw')]^N = \exp[-8\eta/(1 - \varrho w')]\,. \tag{4.67}$$

The linear dependence of w' on density is assumed; moreover, $w' \to v_c$ for $\varrho \to \varrho_c$. Thus

$$w' = \sigma^3[1 - (1 - 1/\sqrt{2})\,d] \tag{4.68}$$

and

$$\begin{aligned}\beta P/\varrho = 1 + \tfrac{4}{3}\pi\sqrt{2}d^{-1} & \left\{\frac{d^2}{(1 - d)[1 - (\sqrt{2} - 1)\,d]} + \frac{\ln(1 - d)}{2 - \sqrt{2}} - \right. \\ & \left. - \frac{\ln[1 - (\sqrt{2} - 1)\,d]}{3\sqrt{2} - 4}\right\}. \end{aligned} \tag{4.69}$$

In a subsequent work[160] Speedy considered a quadratic dependence of w' on ϱ and adjusted the coefficients to the 3rd through 5th virial coefficients. The resulting equation

$$\begin{aligned}\beta P/\varrho = 1 + \frac{4\pi\sqrt{2}}{3d} & \left\{\frac{d^2}{1 - C_0d - C_1d^2 - C_2d^3} - \frac{a}{a^3 - ab + c}\,\cdot\right. \\ & \left.\cdot\left[\ln\frac{\sqrt{(x/a)}}{1 + ad} + \frac{2a^2 - b}{\sqrt{q}}\left(\operatorname{arctg}\left(\frac{b + 2cd}{\sqrt{q}}\right) - \operatorname{arctg}\left(\frac{b}{q}\right)\right)\right]\right\} \end{aligned} \tag{4.70}$$

is very accurate up to very high densities and yields also accurate values of the virial coefficients B_6 through B_{10}. In (*4.70*) $q = 4ac - b^2$, $x = a + bd + cd^2$, $d = \eta/0{\cdot}74048$, and

$$\begin{array}{llll} C_0 = & 1{\cdot}38840 & a = & 0{\cdot}274141 \\ C_1 = & -0{\cdot}249386 & b = & -0{\cdot}455776 \\ C_2 = & -0{\cdot}19331 & c = & 0{\cdot}193316\,. \end{array}$$

Theory of Meeron and Siegert. In the SPT the idea of considering a cavity (of a radius σ) instead of the hard sphere of diameter σ appeared to be very fruitful. This concept was extended further by Meeron and Siegert[161] who considered two and more cavities, all of the same size corresponding to the given hard spheres. The concept is valid for 1-D, 2-D, and 3-D systems and is well-suited for introducing further approximations.

If μ_{res} is the residual chemical potential and a the activity at a given density, the probability Π_0 of finding a cavity (where subscript 0 denotes functions of cavities) is

$$\Pi_0(r) = \exp(-\beta\mu_{\text{res}}) = \varrho/a\,. \tag{4.71}$$

The probability $\Pi_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$ of finding two cavities at $\mathbf{r}_1$ and $\mathbf{r}_2$ depends only on r_{12}. For $r_{12} \geqq \sigma\, \Pi_0^{(2)}$ is equal to the probability of finding two HS at $\mathbf{r}_1$ and $\mathbf{r}_2$. For $r_{12} < \sigma$ the cavities overlap and for $r_{12} = 0$ one cavity merges into the other. Then

$$\Pi_0^{(2)}(0) = \Pi_0(0)\,. \tag{4.72}$$

For the distribution function of two cavities, $g_0^{(2)}(r)$, which is equal to the background correlation function $y(r)$, it holds

$$g_0^{(2)}(r_{12}) = y(r_{12}) = g(r_{12}) \quad \text{for} \quad r \geqq \sigma\,. \tag{4.73}$$

As $\Pi_0^{\text{n}}(\mathbf{r}_1 \ldots \mathbf{r}_{\text{n}}) = (\varrho/a)^{\text{n}}\, g_0^{\text{n}}(\mathbf{r}_1 \ldots \mathbf{r}_{\text{n}})$ and $g_0^{(1)}(\mathbf{r}) = 1$,

$$y(0) = g_0^{(2)}(0) = 1/\Pi_0 = a/\varrho\,. \tag{4.74}$$

This is the so-called zero-separation theorem (*cf.* Hoover and Poirier[162]). As $y(r)$ is related to the potential of the mean force its knowledge enables one to determine the EOS. By differentiating y one gets the mean force exerted on a cavity a distance r apart from another. In the case of HS it is given by a stress of purely kinetic character which depends only on the density of particles on the surface of the cavity. In the simplest case of the so-called pair stress approximation (PSA) this exact stress is substituted by a pair stress, assumingly constant for all angles (up to a maximum angle) measured with respect to the line connecting the pair of cavities.The equation of state in the PSA is

$$B_2\varrho = (z - 1)\, z^{-(2-a_1)}\,, \quad a_1 = 2 - B_3/B_2^2 \tag{4.75}$$

which is valid for 1-D to 3-D systems. The EOS is exact in the 1-D case and the accuracy decreases with dimensionality. The next higher approximation possesses the form

$$B_2\varrho = (z - 1)\exp\left[2a_2(z - 1)\right] z^{-(2-a_1+2a_2)}\,, \tag{4.76}$$

where

$$2a_2 = (B_3/B_2^2)(3B_3/B_2^2 - 1) - 2B_4/B_2^3 \, ; \tag{4.77}$$

(note that $B_2\varrho = 4\eta$ in the 3-D case). The accuracy of (*4.76*) is considerably better than that of (*4.75*) but slightly inferior to the SPT equation. An important feature is the fact that the maximum density on the ϱ *vs* z curve is close to the pseudoexperimental value of ϱ (in fluid) at fluid–solid phase transition. The Meeron–Siegert approach makes it possible to evaluate the background correlation function $y(r)$ in the interval $r \in (0, \sigma)$, see refs[163,164]. It also brings several important interrelations between a formalistic description connected with the BBGY equations (see next Subsection 4.4.3.) and the geometric view. Higher approximations can be also considered. One such attempt was made by Speedy[165], who generalized expressions for y. However, the equations of state corresponding to higher approximations in Speedy's expression yield neither improvement in accuracy of the P–V–T description nor better physical insight.

Simple kinetic theory. In the SPT, the limiting value of $\mathscr{G}(\xi)$ for $\xi \to \infty$ was obtained from the simple kinetic theory. In Shinomoto's work[166,167] the kinetic effect is considered in determining the potential of the mean force φ for a pair of HS in a manner similar to the Meeron–Siegert approach. For a given distance $x = r/\sigma$, φ is in the simplest approximation given by

$$\varphi = \tfrac{1}{2}(x - 2)^2 (x + 4) \, . \tag{4.78}$$

The knowledge of φ makes it possible to determine g. Considering results of collisions when a test particle is situated in the vicinity of a planar wall, the zeroth-order EOS results:

$$\beta P/\varrho = \exp(4\eta) \, . \tag{4.79}$$

Eq. (*4.79*) yields correctly only the second virial coefficient. The next approximation of φ gives the equation of state

$$\beta P/\varrho = \exp\left[4\eta(1 + \eta/2)\right] . \tag{4.80}$$

The corresponding expansion is

$$\beta P/\varrho = 1 + 4\eta + 10\eta^2 + 18{\cdot}67\eta^3 + 28{\cdot}67\eta^4 \, , \tag{4.81}$$

which compares well with values of B_i in Table II. The EOS possesses a simple form and is accurate at lower densities. There is, however, no value of η that gives a singularity.

The methods considered in this subsection (with an exception of Shinomoto's work) are applicable to 1-D through 3-D fluids and give the exact result in the 1-D case. In the 3-D case their accuracy is, however, usually only fair.

In Fig. 8 the theoretical curves are compared with the pseudoexperimental data. One can see that predictions of the zeroth-order approximations of Shinomoto and of Meeron and Siegert are in considerable disagreement with the exact data and that the first-order approximations are much better. Theories of Andrews and Speedy yield practically perfect prediction up to the packing fraction of $\eta < 0{\cdot}5$ with the latter equation being slightly better. However, Speedy's equation has not been extended to mixtures. A common week point of all theories of this subsection but the SPT is that their extensions to nonspherical HB fluids are not known. These facts make the SPT a very important and universal tool for deriving an EOS of hard body fluids.

4.4.3. Integro-Differential and Integral Equations

Integro-differential and integral equations serve to determining the dependence of correlation functions on density and particle separation. The equation of state follows from the knowledge of the pair correlation function at contact or from the course of the direct correlation function in the range of distances $r \in (0, \sigma)$ (*cf.* Eq. (*4.26*)).

Integro-differential equations. These equations were formulated by Kirkwood[168], who considered the change of the correlation function with gradual coupling of a test particle into the system, and by Bogolyubov[169], Yvon[170], and Born and Green[171], who took the gradient of the logarithm of the correlation function, dealing actually with the mean force in a way similar to the Meeron–Siegert theory. Performing

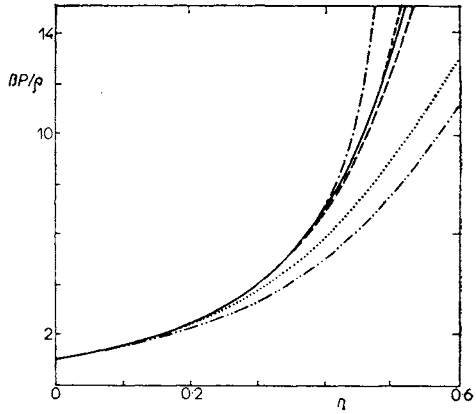


FIG. 8

Compressibility factors of the hard sphere fluid calculated from specific methods. ----- Eq. (*4.66*); ········ Eq. (*4.75*); —·—·— Eq. (*4.77*); —··— Eq. (*4.79*); ——— Eq. (*4.80*); ——— exact. Eqs (*4.69*) and (*4.70*) coincide with the exact data within the scale of the graph the differentiation (for details see *e.g.* ref.[22]) a hierarchy of expressions is obtained in which the required correlation function is given in terms of the correlation function of the higher order, *e.g.* the pair correlation function in terms of the third-order function. The superposition approximation (or an equivalent of it)

$$g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = g(\mathbf{r}_1, \mathbf{r}_2)\, g(\mathbf{r}_1, \mathbf{r}_3)\, g(\mathbf{r}_2, \mathbf{r}_3) \qquad (4.82)$$

must be therefore employed to break the infinite hierarchy. The following equation then results[22]:

$$kT \ln g(r, \xi) = -\xi u(r) + \frac{\pi \varrho}{r} \int_0^\infty [K(r - t, \xi) - K(r + t, \xi)]\,[g(t) - 1]\, \mathrm{d}t\,, \qquad (4.83)$$

where kernel K is either

$$K(t, \xi) = \xi \int_{|t|}^\infty (\partial u/\partial s)\, g(s, \xi)\,(s^2 - t^2)\, \mathrm{d}s \quad \text{(BBGY)} \qquad (4.84)$$

or

$$K(t, \xi) = -2 \int_0^\xi \int_{|t|}^\infty u(s)\, g(s, \tau)\, s\, \mathrm{d}s\, \mathrm{d}\tau \quad \text{(Kirkwood)}\,. \qquad (4.85)$$

In the case of hard spheres Eq. (*4.83*) can be simplified and easily solved numerically. The resulting dependence of the compressibility factor on the packing fraction for both versions is shown in Fig. 9. They both yield the correct second and third virial coefficients and thus the correct prediction of $\beta P/\varrho$ in the low density range. For higher values of η, however, the theoretical values are systematically lower. There

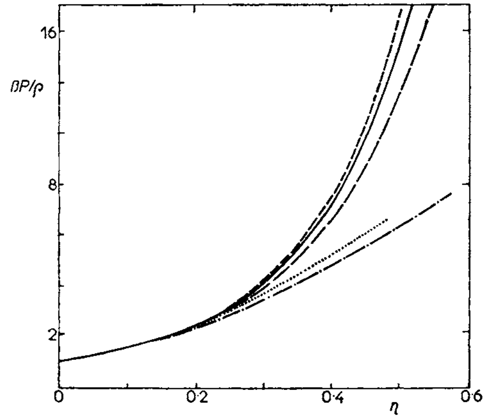


Fig. 9

Compressibility factors of the hard sphere fluid calculated from the radial distribution function. — · — · — Kirkwood equation; ········ BBGY equation; – – – – – P–Y c-form; — — — P–Y v-form; ——— exact is no solution of the Kirkwood equation for $\eta \gtrsim 0{\cdot}60$ and of the BBGY expression for $\eta \gtrsim 0{\cdot}50$. These values of η are usually interpreted as limits of stability of the HS fluid within these theories.

Better results obtained from the hierarchy of equations for g can be expected if higher order correlation functions are considered. Fisher and Kopeliovitsch[172] proposed a "superposition-like" closure for $g^{(4)} \equiv g(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \mathbf{r}_4)$ and Ree and coworkers[173] solved the resulting set of two integro-differential equations. The results at two relatively low densities considered ($\eta = 0{\cdot}22$ and $0{\cdot}275$) are in very good agreement with pseudoexperimental data.

Integral equations for g. The basis of integral equation methods is the Ornstein–Zernicke equation (*4.25*) which relates the total correlation function, $h(r)$, and the direct correlation function, $c(r)$. The merit of the introduction of the direct correlation function lies in the fact that the range where $c(r) \neq 0$ is approximately the same as that of the pair potential of the studied system. This makes it possible to introduce – in combination with the application of the theory of graphs – several useful approximations. The most common ones are the Percus–Yevick (P–Y) and hypernetted chain (HNC) approximations.

In the P–Y approximation[174] it is assumed that

$$c_{\mathrm{PY}}(r) = 0 \quad \text{for} \quad r > \sigma \tag{4.86}$$

whereas in the HNC (see refs in[175])

$$c_{\mathrm{HNC}}(r) = h(r) - \ln\left[h(r) + 1\right] \quad \text{for } r > \sigma\,. \tag{4.87}$$

For the HS fluid the HNC approximation is inferior to P–Y. Moreover, for the latter approximation an analytic solution for $g(r)$ and hence the equation of state have been found[177–179]. The result for the direct correlation function reads for $r < \sigma$ as

$$-c_{\mathrm{PY}}(r) = [(1 + 2\eta)^2 - 6\eta(1 + \eta/2)^2\, r + \tfrac{1}{2}\eta(1 + 2\eta)^2\, r^3]/(1 - \eta)^4 \tag{4.88}$$

which after substituting in Eq. (*4.26*) yields the compressibility (*c*) form of the P–Y EOS:

$$\beta P/\varrho = (1 + \eta + \eta^2)/(1 - \eta)^3 \qquad (\mathrm{c})\,. \tag{4.89}$$

For $r = 1$

$$-c(1) = g(1) = (1 + \eta/2)/(1 - \eta)^2\,, \tag{4.90}$$

so that from Eq. (*4.6*) the virial form of the EOS is obtained:

$$\beta P/\varrho = (1 + \eta + \eta^2 - 3\eta^3)/(1 - \eta)^3 \qquad (\mathrm{v})\,. \tag{4.91}$$

Results of the (c) and (v) EOS for the P–Y approximation are compared in Fig. 9 with the simulation data. It is seen that the (c)-form yields systematically higher and (v)-form systematically lower values of $\beta P/\varrho$. The results of the HNC equation exhibit the same bracketing property with (v)- and (c)-forms reversed. The difference between the (c) and (v) values measures the quality of the approximation – *e.g.* for the HNC the difference at given η is always larger then for the P–Y. Moreover, this bracketing offers a possibility to combine empirically (c)- and (v)-forms to obtain a more accurate equation of state. For instance, on taking $\frac{2}{3}$ of the (c)- and $\frac{1}{3}$ of the (v)-forms of the P–Y theory results, the Carnahan–Starling EOS (*4.44*) is recovered.

Similarly as for the integro-differential equations, the P–Y and HNC equations can be extended to the second order but this is not straightforward. Such extensions have been made by Verlet[180,181] and Wertheim[182] but both versions suffer from certain defects. Better way how to improve the performance of integral equations seems to make use of the inconsistency of the (v)- and (c)-forms of the EOS. "Self-consistent" theories, *i.e.* those giving identical results from the virial and compressibility equations, have been proposed *e.g.* by Rowlinson[183], Hutchinson and Conkie[184,185], and Verlet[186]. The common property of all these methods is that they are numerically very laborious which is not offset by the results.

Relatively simple and at the same time very accurate equations have been proposed recently by Martynov and Sarkisov[187] and by Verlet[188]. The direct correlation function in the former theory is given in terms of the background function y,

$$c_{\mathrm{MS}}(r) = fy + y - 1 - \ln\left[y(1 + \tfrac{1}{2}\ln y)\right]. \qquad (4.92)$$

Verlet's theory is a bit more complicated but both theories are identical up to the $\ln^2 y$ order and yield the best results of all integral equations. Results and comparison of all above mentioned integral equation theories can be found in a recent monograph by Malijevský and coworkers[189].

Integro-differential and integral equations are general theories serving first of all for determining the structure of fluid. The only analytical solution has been found for the P–Y theory and although the resulting EOS is not perfect it is of great practical importance: it tells about the functional form of the EOS upon which better equations may be built. Recent attempts directing to developing a better theory indicate that the integral equations possess capacity of providing very good results but yet these are rather of only theoretical than of practical value.

4.4.4. Discussion

In the preceeding subsections we have already assessed individual methods within each family of the approaches considered. In this subsection, which completes the part dealing with the pure HS fluid, we compare and assess in more detail the different approaches and discuss the best results at present available.

In the graph $\beta P/\varrho$ *vs* η the scale is usually so coarse that good methods yield results practically indistinguishable from simulation data. For this reason we show in Fig. 10 percentage deviations from the parametrized simulation data, Eq. (*4.27*). Erpenbeck and Wood's data[110] used for the parametrization are shown as black circles whose size roughly corresponds to the experimental errors. The other data shown with error bars are those of Labík and Malijevský[114].

Undoubtedly the most general approach is that *via* an integral equation for the radial distribution function. The best of these, the phenomenological closure of Verlet[188], exhibits deviations up to 2 per cent which is more than do the other methods. But in the light of the fact that the integral equations do not contain any adjustable parameters (although a certain sort of guessing for deriving a closure and its *a posteriori* verification are required) the accuracy is very good.

From the theories considered in Subsection 4.4.2., Eq. (*4.70*) of Speedy is the best. It is seen from Fig. 10 that it is very accurate and begins to deviate from the simulation data only at the highest density. However, it is fair to remind that in the process of deriving Eq. (*4.70*) the virial coefficients B_2 through B_5 and the condition of zero free volume at the close-packing density were used as input information.

In Fig. 7 we were not able to distinguish between the simulation data and Eqs (*4.44*), (*4.46*), and (*4.49*), and the truncated virial expansion with 10 terms. Eq. (*4.46*) remains to coincide with the parametrized simulation data even within the scale of the graph in Fig. 10 and the Carnahan–Starling equation (*4.44*) is seen also to retain its good accuracy. However, some doubts arise when examining the $P(3, 3)$ and P_{EW} approximants, and the virial expansion. First, one would expect the virial expansion to systematically underestimate the compressibility factor and this is not the case here. Further, one would also expect the $P(3, 3)$ approximant to peform much

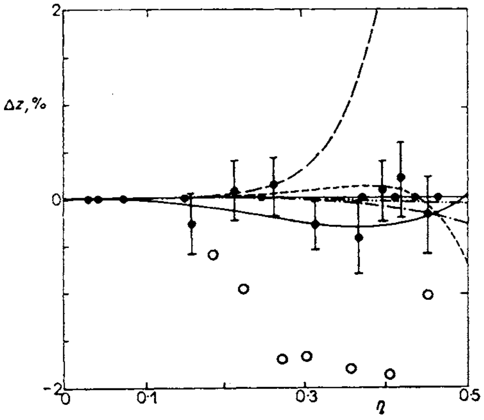


FIG. 10

Percentage deviations of the best hard sphere equations of state from the parametrized simulation data, Eq. (*4.27*). ——— Eq. (*4.44*); —·—·— Speedy's Eq. (*4.70*); —··— Erpenbeck and Wood P_{EW}, Eq. (*4.49*); — — — Padé approximant, P(3, 3), Eq. (*4.47*); ----- virial expansion; ○ Verlet's phenomenological theory. Eq. (*4.46*) coincides with the parametrized simulation data; ● Erpenbeck and Wood's data, ⫯ data of Labík and Malijevský better. Erpenbeck and Wood[110] fitted the virial coefficients B_6 and B_7 so as to get the best fit with their data. They obtained

$$B_6/\mathscr{V}^5 = 39.93 \quad B_7/\mathscr{V}^6 = 53.5 \tag{4.93}$$

and the resulting approximant P_{EW} only slightly deviates from Eq. (*4.27*) at the highest densities. They then argued that the "fitted" estimates of B_6 and B_7, Eq. (*4.93*), might be more accurate than Kratky's values listed in Table II. When the coefficients from Eq. (*4.93*) are used in place of those from Table II in the truncated virial expansion, the positive bump in Fig. 10 practically disappears and the virial expansion tends to underestimate the compressibility factor over the entire density range. Also the regular $P(3, 3)$ approximant based on the above values of B_6 and B_7 performs much better and we thus incline to support Erpenbeck and Wood's view and to recommend to use for B_6 and B_7 the values given by Eq. (*4.93*) instead of those of Kratky, see Table II. In any case, a new direct estimate of B_6 and B_7 would provide stronger arguments.

As regards the equations of state, the most frequently used Carnahan–Starling equation does seem to be quite good but equally simple and much better is the new equation (*4.46*). Advantage of these two equations is also their "definiteness": they have not been fitted to any simulation data and new simulation data thus cannot affect their parameters.

4.5. *Nonspherical Body Fluids*

Methods developed for the HS fluid discussed in the preceding section paved the way for studying more complicated nonspherical body fluids. With only one exception, all theories for nonspherical bodies represent extension of those developed for hard spheres or, generally, for simple fluids. Evidently, not all methods can be extended. Those which have been extended are the scaled particle theory, certain cell theories, methods based on the knowledge of virial coefficients, and integral equations. Some methods were extended first to convex bodies and only then, often empirically, to FHS models.

The most logical way of dealing with theories of nonspherical body systems would begin with virial expansions and their resummations. However, because of the limited knowledge of the virial coefficients even for the simplest members of the family of non-spherical bodies and also because of the fact that the nonsphericity parameter is introduced within the SPT in an essential way, we follow a different scheme. We begin with general formulation of the SPT and improved SPT which are followed by the SPT variants proposed for specific systems, namely for prolate spherocylinders and homonuclear diatomics. Then we consider virial expansions, their resummations, and equations of state which employ the SPT forms and generalized expressions for the virial coefficients.

In addition to the above methods there are perturbation theories discussed in Subsection 4.5.3., whose idea is to avoid the mathematical complexity by transforming the nonspherical bodies to suitable hard spheres or "soft" (*i.e.* with a repulsive tail) spheres. Since the hard body fluids are not the ultimate goal of our endeavour to develop a molecular theory of fluids, this may be viewed as a step back. However, the perturbation schemes are usually more general and their application to hard body fluids serves as one of simple tests.

4.5.1. Extended Scaled Particle Theory

The first attempt to extend the SPT to hard convex bodies was made by Ritchie[190] who, however, did not get a closed analytic expression. This was obtained by Gibbons[66,191], who expressed the CB geometric functionals $\mathcal{R}$, $\mathcal{S}$ and $\mathcal{V}$ in terms of a "characteristic radius", R,

$$\mathcal{R} = aR\,, \quad \mathcal{S} = dR^2\,, \quad \mathcal{V} = cR^3 \tag{4.94}$$

and assumed intuitively the validity of the polynomial

$$W(R) = W(0) + W'(0)\,R + \tfrac{1}{2}W''(0)\,R^2 + PV\,, \tag{4.95}$$

employed originally by Reiss and coworkers[153] for the reversible work, W, required for creating a cavity of diameter R in the HS fluid. Then, in an analogy with HS, Gibbons wrote down the expression for the chemical potential and from thermodynamic relationships he obtained the equation of state:

$$\beta P/\varrho = 1/(1-\eta) + 3\alpha\eta/(1-\eta)^2 + 3\alpha^2\eta^2/(1-\eta)^3\,, \tag{4.96}$$

where α is the usual parameter of nonsphericity, Eq. (*3.29*). This equation was later re-derived by Boublík[14] by means of microscopic arguments and using well-defined approximations. After introducing the average distribution function $\mathcal{G}^{\text{av}}(\xi)$, (Eq. (*4.10*)), the chemical potential can be written as (*cf.* Eq. (*4.55*))

$$\beta(\mu - \mu^*) = -\ln(1 - \varrho\mathcal{V}) + \varrho\int_0^1 \mathcal{G}^{\text{av}}(\xi)\,(3\xi^2\mathcal{V} + 2\xi\mathcal{R}\mathcal{S} + \mathcal{R}\mathcal{S})\,\mathrm{d}\xi\,. \tag{4.97}$$

For $\mathcal{G}(\vartheta, \varphi, \omega, \xi)$ Boublík used an extension of the interpolation formula for $\mathcal{G}_{\text{HS}}$, Eq. (*4.60*). Three coefficients of that formula were determined from the known values of $\mathcal{G}^{\text{av}}(0)$, $\partial\mathcal{G}^{\text{av}}(0)/\partial\xi$, and the relation between $\mathcal{G}^{\text{av}}(\infty)$ and $\mathcal{G}^{\text{av}}(1)$. Then for

$\mathscr{G}^{\mathrm{av}}(1)$ it follows

$$\mathscr{G}^{\mathrm{av}}(1) = \frac{1}{1-\eta} + \frac{3\alpha}{(1+3\alpha)}\frac{\eta}{(1-\eta)^2} + \frac{3\alpha^2}{(1+3\alpha)}\frac{\eta^2}{(1-\eta)^3}\,. \qquad (4.98)$$

After substituting (*4.98*) into (*4.12*), equation of state (*4.96*) is recovered.

Eq. (*4.96*) was originally derived for CB systems. Following the same approach as that for obtaining the second virial coefficient of FHS models (*cf.* Section 3.3.), Boublík[59] extended the above formulation also to linear homonuclear FHS models. He showed that if a "mean radius" of the FHS body is defined as

$$\mathscr{R} = \sigma(1 + L/2)/2\,, \qquad (4.99)$$

(where L is the separation between the outermost sites), the actual values of $\mathscr{V}_{\mathrm{FHS}}$ and $\mathscr{S}_{\mathrm{FHS}}$ are used, and if the small term Δv in the expression for $\mathscr{V}_{1+2}$ (see Eq. (*3.48*)) is neglected, Eq. (*4.96*) is obtained.

In the special case of homonuclear diatomics parameter α is explicitly given by

$$\alpha = \frac{(1+L)(2+L)}{2+3L-L^3}\,. \qquad (4.100)$$

To determine $\mathscr{G}^{\mathrm{av}}(1)$ and hence the EOS it was necessary to introduce an approximate expression for $\mathscr{G}(\xi, \vartheta, \varphi, \omega)$. This can be avoided by employing the thermodynamic expression for the reversible work[153],

$$\mathrm{d}W = P\,\mathrm{d}\mathscr{V} + \gamma\,\mathrm{d}\mathscr{S}\,, \qquad (4.101)$$

where γ is the surface tension and $\mathrm{d}\mathscr{V}$ and $\mathrm{d}\mathscr{S}$ are, respectively, changes in volume and surface area of a cavity. Kirkwood and Buff[192] showed that for a spherical cavity of not too small radius r it holds:

$$\gamma = \gamma_0(1 + \delta/r)\,. \qquad (4.102)$$

Specifying in a special way the dilatation of convex bodies and assuming that Eq. (*4.102*) holds for any molecular shape and size, Nezbeda[76] also re-derived the original Gibbons equation (*4.96*).

A consequence of employing the thermodynamic relation (*4.101*) in the process of deriving the EOS is the possibility to obtain, in addition to the EOS, also the surface tension of a fluid at a hard wall. It should be mentioned, however, that the application of the thermodynamic (*i.e.* macroscopic) relation (*4.102*) to a single particle is, rigorously speaking, not correct and so it is justified only *a posteriori.*

Eq. (*4.96*) and, consequently, the virial coefficients given by

$$B_{\mathrm{i}} = 1 + 3\alpha(i - 1) + \tfrac{3}{2}\alpha^2(i - 1)(i - 2)\,, \quad i \geqq 2 \tag{4.103}$$

exhibit the same features as Eq. (*4.61*) for hard spheres. The second virial coefficient is exact (for CB models) and the third one is in good agreement with numerical data at small α. Higher virial coefficients give systematically higher values in comparison with the computer data. Consequently, Eq. (*4.96*) overestimates the compressibility factor (see Figs 11 and 12). This property of the SPT has been generalized by Nezbeda and coworkers[51] into a conjecture

$$(\beta P/\varrho)_{\mathrm{SPT}} \geqq (\beta P/\varrho)_{\mathrm{exact}} \tag{4.104}$$

valid for all HB fluids at the same number density and used to test accuracy of some simulation data.

For $\alpha \to 1$ Eq. (*4.96*) reduces to Eq. (*4.61*) which is not very accurate and one would naturally wish a HB equation to reduce to the Carnahan–Starling or any other accurate HS equation for $\alpha \to 1$. An improved version of Eq. (*4.96*) satisfying this condition has been proposed by Boublík[193]. It was shown[194] that the C–S equation, Eq. (*4.44*), can also be obtained from the SPT by modifying the coefficient of the last term in the polynomial for $\mathscr{G}(\xi)$ at $\xi = 1$. Using the same approach for CB Boublík obtained the equation (improved SPT equation, ISPT)

$$\beta P/\varrho = 1/(1 - \eta) + 3\alpha\eta/(1 - \eta)^2 + \alpha^2\eta^2(3 - \eta)/(1 - \eta)^3\,. \tag{4.105}$$

The virial coefficients B_2 and B_3 given by this improved equation remain unchanged, see Eq. (*4.103*), while the higher coefficients are slightly reduced. It holds:

$$B_{\mathrm{i}} = 1 + 3\alpha(i - 1) + \alpha^2 i(i - 2)\,, \quad i \geqq 2\,. \tag{4.106}$$

For $i = 4$, this equation reproduces surprisingly well the data of oblate spherocylinders but for other models it seems good for low nonsphericities only (see Table XVIII). The compressibility factor given by (*4.105*) begins to deviate from the simulation data already at medium densities and $\alpha \gtrsim 1{\cdot}2$ (see Figs 11 and 12).

Equations derived within the SPT are usually associated with CB fluids. Eq. (*4.105*) can be evidently used also for the class of FHS models for which the parameter α can be defined. An extension of Eq. (*4.105*) to any FHS model is discussed in the next subsection.

Both the SPT and ISPT equations discussed above are quite general and can be applied to any CB fluid. A SPT equation, good only for the system of prolate spherocylinders, has been derived by Cotter and Martire[195] and Lasher[196] who followed an approach different from that described above. Cotter and Martire discretized

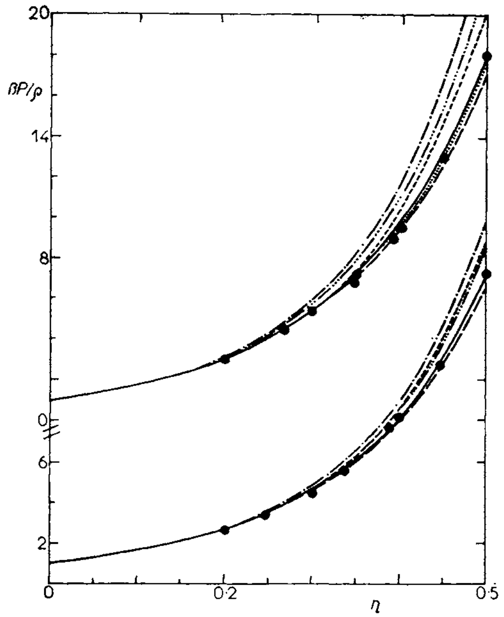


FIG. 11

Compressibility factors of prolate spherocylinders with the length-to-breadth ratio equal to 2 (lower set) and 3 (upper set). —·—·— Eq. (*4.96*); —···— Eq. (*4.105*); ----- Eq. (*4.107*); ——— Eqs (*4.117*) and (*4.118*); ·········· Eq. (*4.119*); — — — the virial expansion; ● pseudoexperimental data

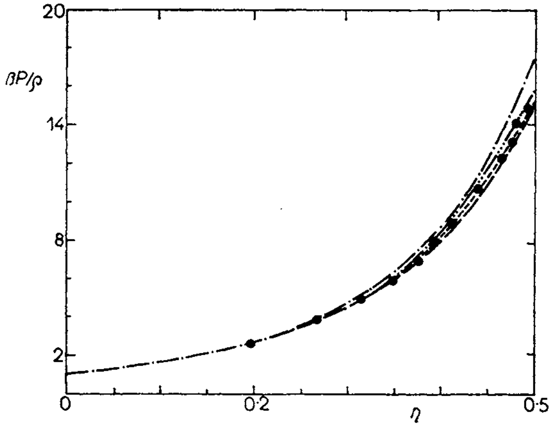


FIG. 12

Compressibility factors of oblate ellipsoids of the axis ratio $\lambda = 0{\cdot}5$. —·—·— Eq. (*4.96*); —···— Eq. (*4.105*); ----- Eq. (*4.117*); — — — Eq. (*4.118*); ● pseudoexperimental data orientations of spherocylinders and considered then only the orientations in directions of three axis of the solid coordinate system. They scaled independently the length and breadth of the core of the spherocylinder and arrived at the equation

$$\beta P/\varrho = [1 + \eta(3\gamma^2 - 3\gamma + 2)/(3\gamma - 1) + \\ + \eta^2(3\gamma^3 + 3\gamma^2 - 3\gamma + 1)/(3\gamma - 1)^2]/(1 - \eta)^3 \,. \tag{4.107}$$

TABLE XVIII

Comparison of the fourth virial coefficients, $B_4/\mathscr{V}^3$, of convex body models given by approximate equations of state with exact data

Parameter	α	τ	Eq. (*4.105*)	Eq. (*4.117*)	Eq. (*4.118*)	Eq. (*4.119*)	Eq. (*4.120*)	Exact
Prolate spherocylinders								
γ								
1·6	1·095	1·056	20·45	19·98	19·93	20·06	20·11	20·50
2·0	1·200	1·125	23·32	22·12	22·12	22·36	22·48	22·50
3·0	1·500	1·333	32·50	28·00	28·75	29·13	29·47	28·00
4·0	1·818	1·562	43·81	33·84	36·37	36·67	37·29	31·90
5·0	2·143	1·800	57·02	39·39	44·78	44·78	45·68	33·10
Oblate spherocylinders								
$\varphi(= \gamma - 1)$								
1·0	1·129	1·038	21·36	20·67	20·63	21·08	21·14	21·65 21·79
1·5	1·234	1·059	24·29	22·80	22·84	23·78	23·89	24·76 24·51
2·0	1·348	1·076	27·67	25·06	25·32	26·90	27·03	28·22 27·78
2·636	1·500	1·094	32·50	28·00	28·75	31·34	31·47	31·90
3·0	1·589	1·103	35·50	29·67	30·82	34·09	34·20	36·35
Diamond ($\sigma_B = 0{\cdot}02$)								
γ								
2·568	1·500	1·422	32·50	28·00	28·75	28·49	28·84	28·00
Drop ($\sigma_B = 0{\cdot}02$)								
2·347	1·500	1·422	32·50	28·00	28·75	28·49	28·84	26·00
Cube								
a	1·500	1·178	32·50	28·00	28·75	30·46	30·71	42·00

Eq. (*4.107*) yields the exact value of B_2, but values of B_3, given by

$$B_3 = (30\gamma^3 + 21\gamma^2 - 12\gamma + 1)/(3\gamma - 1)\,, \qquad (4.108)$$

are systematically lower[50]. On the other hand, the fourth virial coefficient produced by Eq. (*4.107*) overestimates the correct values[52], which leads to compensations in the EOS. As a result, Eq. (*4.107*) performs better than the original SPT equation (*4.96*) as it is seen from Fig. 11. In subsequent papers Cotter[197] and also Savithramma and Madhusudana[198] considered the continuous distribution of orientations; however, for the isotropic fluid the equation of state remained unchanged.

An obstacle for extending the SPT to FHS models without resorting to a "CB-like" approach is the lack of a general expression for the 2nd virial coefficient. Consequently, the SPT has been independently extended only to homonuclear diatomics[15]. To evaluate analytically certain integrals, Nezbeda[15] neglected $\bullet\cdots\bullet$ bonds (*cf.* Section 3.3.) in expressions for a pair of dumbells and obtained the following EOS:

$$\beta P/\varrho = \frac{1}{1-\eta} + \frac{\eta}{(1-\eta)^2}\,\frac{3 + \frac{9}{2}L + 2L^2 + \frac{1}{6}L^4}{1 + \frac{3}{2}L - \frac{1}{2}L^3} + \\ + \frac{\eta^2}{3(1-\eta)^3}\left[\frac{3 + \frac{9}{2}L + 2L^2 - \frac{1}{2}L^4}{1 + \frac{3}{2}L - \frac{1}{2}L^3}\right]^2 . \qquad (4.109)$$

Due to additional approximations involved, this equation does not give the exact 2nd virial coefficient but the approximate expression (*3.56*). Nevertheless, similarity between the CB equation of state, Eq. (*4.96*), and Eq. (*4.109*), and the fact that the coefficients at the second and third terms are almost identical and in a close relation to α defined by (*4.100*) are striking. On comparing Eqs (*4.96*) and (*4.109*) it is seen that they would possess exactly the same form if it were not for the different coefficients at L^4 and one may suspect the additional approximations used in deriving (*4.109*) of causing this difference. Since usually $L \leqq 1$, these terms can be completely neglected or, for instance, the term $L^4/6$ in the second fraction can be simply replaced by $-L^4/2$ which results[64] in both cases in the equation identical to the SPT equation (*4.96*) with the α-parameter defined by (for the latter choice)

$$\alpha = \frac{1 + \frac{3}{2}L + \frac{2}{3}L^2 - \frac{1}{6}L^4}{1 + \frac{3}{2}L - \frac{1}{2}L^3}\,. \qquad (4.110)$$

α given by this equation is identical to α given by (*4.100*) up to $\mathcal{O}(L^2)$. In Fig. 13 we show the SPT results for two HOMO DB with α given by Eq. (*4.100*). It is seen that the agreement is the same as that for convex bodies (*cf.* Figs 11 and 12).

4.5.2. Expansions, Resummations, and Semi-Empirical Methods

In comparison with the HS fluid, the potentialities of expansion and resummation methods for nonspherical HB fluids are rather limited because of limited knowledge of the virial coefficients. One can count at best with five coefficients only, with B_2 through B_4 computed directly and B_5 either computed or estimated from (*3.64*) or (*3.66*). This makes it possible to set up at maximum either a common $P(3, 2)$ approximant or Alder–Hoover's $P(2, 2)$ approximant, P_{AH} (*cf.* Eq. (*4.51*)). Additional drawback of these methods is that at least one more parameter describing the nonsphericity of the model is required. Consequently, the resulting EOS may be good for one specific model only, unless the virial coefficients are parametrized.

Nezbeda[34] applied both $P(3, 2)$ and P_{AH} to all HB fluids for which the simulation data were available and obtained the expected results: (i) the two approximants are always accurate up to medium density range; (ii) $P(3, 2)$ approximant tends to overestimate the correct values and P_{AH} usually tends to underestimate them; (iii) it cannot be said that they perform worse with increasing nonsphericity. For instance, for the fluid of PSC with $\gamma = 3$ the $P(3, 2)$ approximant matches the simulation data

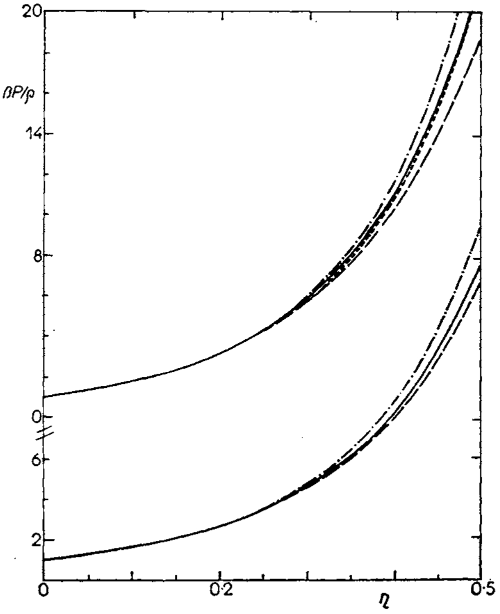


Fig. 13

Compressibility factors of homonuclear dumbells of $L = 0{\cdot}6$ (lower set) and 1 (upper set). —·—·— Eq. (*4.96*); ----- Eq. (*4.105*) with α from Rigby's rule; —·— — the virial expansion; · —— exact. Eq. (*4.105*) with α from the B–N method is indistinquishable from the exact data within the scale of the graph for all densities while for $\gamma = 2$ it does not; (iv) P_{AH} approximant is surprisingly good for the OSC and nonlinear triatomic fluids. In summary, performance of the two approximants is quite unpredictable which is in agreement with our conclusions for the HS fluid.

It is possible to view the functional form of the C–S equation or of the ISPT equation also as a PA. However, an attempt[70] to improve their performance by fitting their coefficients to B_2 through B_4 has failed as well. For hard spheres such an equation is inferior to the C–S equation (which yields the exact third but not fourth virial coefficient) and for nonspherical body fluids the results are comparable to the Barboy–Gelbart expansion (see below).

A chance to do better may have faster converging methods requiring first few virial coefficients only, such as, *e.g.*, approximant P_φ (*i.e.* a PA applied to function φ in (*4.52*)) or the Barboy–Gelbart method, Eq. (*4.53*). These two methods were also considered by Nezbeda[34] and while the Barboy–Gelbart method surprisingly fails, the P_φ approximant seems to be the best of all considered. It agrees with the simulation data over the entire density range for all linear models but fails for the OSC fluid of high nonsphericity and for the nonlinear triatomic fluid. Concerning the latter fluid, there may be a simple reason. The starting equation for the P_φ approximant, Eq. (*4.52*), has the form obtained from the SPT for convex bodies. It is known[60] that the nonlinear triatomic fluid exhibits certain properties not found in its CB counterpart and differs thus so much from it that Eq. (*4.52*) need not be appropriate for the fluid of triatomics. However, this cannot be the case of OSC for which (*4·52*) is undoubtedly correct. Detailed discussion on this and other peculiarities of the OSC fluid we postpone to the end of this section.

Virial expansion (*3.1*) represents a correction to the ideal gas which may be considered as a reference system. If another system is used as the reference, then the virial expansion assumes the form

$$\beta P/\varrho = (\beta P/\varrho)_{\text{ref}} + \sum_{i>1} (B_i - B_{i,\text{ref}})\, \varrho^{i-1}\,, \qquad (4.111)$$

where $B_{i,\text{ref}}$ are the virial coefficients of the reference system. For the HB fluids a natural choice for the reference is the HS fluid (at the same packing fraction) for it captures a good deal of the HB fluid behaviour. With this choice Eq. (*4.111*) may provide a lower bound of the compressibility factor. Nezbeda[34] has conjectured that for all realistic models it holds

$$\beta P/\varrho \geqq (\beta P/\varrho)_{\text{HS}} + \sum_{i>1}^{M} (B_i - B_{i,\text{HS}})\, \varrho^{i-1} \qquad (4.112)$$

and the validity of this inequality seems to be supported by all known computer data. Comparison with the simulation data shows that Eq. (*4.112*) performs surprisingly well[34]: In the low and medium density ranges the righ-hand side of (*4.112*) agrees with them within the experimental errors and only at high density it begins to underestimate $\beta P/\varrho$ in accordance with (*4.112*).

From the results discussed in Section 4.4. it seems that the best method for obtaining the EOS is that based on an estimation of all virial coefficients because it enables us to sum up the entire expansion. For this reason a certain parametrization of the virial coefficients is required which, consequently, leads to a more general EOS than that obtained by any of the above discussed methods.

The recursion formula (*4.42*) may be extended to convex bodies by writing

$$B_i = 1 + f_2(\alpha)(i-1) + f_3(\alpha)(i-1)(i-2) + f_4(\alpha)(i-2)(i-3)\,. \qquad (4.113)$$

If we require that

$$f_2(\alpha) \to 3\,, \quad f_3(\alpha) \to \tfrac{3}{2}\,, \quad f_4(\alpha) \to -\tfrac{1}{2} \quad \text{for} \quad \alpha \to 1 \qquad (4.114)$$

the C–S equation is recovered for $\alpha = 1$. The function $f_2(\alpha)$ follows exactly from the second virial coefficient,

$$f_2(\alpha) = 3\alpha\,, \qquad (4.115)$$

while f_3, f_4 require an empirical guess. Analyzing the virial coefficient data of prolate spherocylinders Nezbeda[52] showed that they are accurately fitted by

$$\begin{aligned} f_3(\alpha) &= \tfrac{1}{2}(\alpha^2 + 4\alpha - 2) \\ f_4(\alpha) &= -\tfrac{1}{2}\alpha(5\alpha - 4)\,. \end{aligned} \qquad (4.116)$$

Summing up the virial expansion with B_i given by (*4.113*), (*4.115*), and (*4.116*), the following equation is obtained:

$$\beta P/\varrho = \frac{1 + (3\alpha - 2)\eta + (\alpha^2 + \alpha - 1)\eta^2 - \alpha(5\alpha - 4)\eta^3}{(1-\eta)^3}\,. \qquad (4.117)$$

This equation agrees with the simulation data of the PSC fluid throughout the entire fluid density range and up to high elongation (see Fig. 11). Although Eq. (*4.117*) has a general form, it is worth reminding that it has been tailored for prolate spherocylinders and for other CB fluids it can be used only for not too large α, *i.e.*, in the case when the conformity of CB fluids approximately holds (see Fig. 12).

In order not to relate the EOS so tightly to one specific system only, Boublík[65] followed the same way as above but used general approximate expressions (*3.58*) and (*3.59*) for B_3 and B_4 to determine f_2, f_3, and f_4. The resulting equation has the appearance

$$\beta P/\varrho = \frac{1 + (3\alpha - 2)\eta + (3\alpha^2 - 3\alpha + 1)\eta^2 - \alpha(6\alpha - 5)\eta^3}{(1 - \eta)^3}. \qquad (4.118)$$

From the practical point of view there is no great difference between the results given by Eqs (*4.117*) and (*4.118*). Advantage of Eq. (*4.118*) may be that (i) it yields more realistic expressions for B_i and (ii) it can be quite simply extended to mixtures. However, since it describes the CB fluids again by only one parameter, its general applicability is also limited to small and medium α.

In Subsection 3.2.3. we have already discussed the necessity of introducing an additional parameter of nonsphericity to account for different shapes of CB of the same α. Naumann and Lelland[67] (N–L) introduced quite empirically a second parameter τ by Eq. (*3.62*) and their equation possesses the form

$$\beta P/\varrho = \{1 + (3\alpha - 2)\eta + [\tfrac{3}{2}\alpha^2(1 + \tau^{-1}) - 3\alpha + 1]\eta^2 - \\ - \tfrac{1}{2}\alpha^2[5 - 3\tau^{-1}]\eta^3 - 7\alpha^2(1 - \tau^{-1})\eta^4\}/(1 - \eta)^3. \qquad (4.119)$$

It contains one extra term over the C–S type equation but for spheres $\tau = 1$ and Eq. (*4.119*) reduces thus to the C–S equation. Another two-parameter equation of state has been derived by Boublík[199] within his attempt to approximate the CB average correlation function on the basis of that of HS. The equation has the form

$$\beta P/\varrho = 1 + \eta(1 + 3\alpha)[1 + \zeta(\tfrac{5}{2}\eta - 3\eta^2 + \eta^3)/(1 - \eta)^3], \qquad (4.120)$$

where ζ is the ratio of the surface areas of a given CB and of the equivalent HS (*i.e.* of the same volume); for example, for prolate spherocylinders it holds

$$\zeta = \gamma/[(3\gamma - 1)/2]^{2/3}. \qquad (4.121)$$

For systems characterized by a mild nonsphericity (small α) Eqs (*4.119*) and (*4.120*) yield results very similar to those obtained from the one-parameter equations (*4.117*) and (*4.118*). It is therefore interesting to compare the four equations in extreme cases, when the latter equations ((*4.117*) and (*4.118*)) are definitely outside the range of their guaranteed applicability.

In Table XVIII we compare the 4th virial coefficients given by the four above considered equations for PSC up to large elongations. It is seen that the Naumann–Leland results are practically identical to those of the Boublík B1 equation (*4.118*) and both are inferior to Nezbeda's results.

The other extreme system for which exact data are available is that of infinitely thin platelets. In this case $\alpha \rightarrow \infty$ and $\mathscr{V} \rightarrow 0$ with $3\alpha\eta = \mathscr{R}\mathscr{S}\varrho = B_2\varrho$, and the four equations assume the forms

$$\beta P/\varrho = 1 + B_2\varrho + \tfrac{1}{9}B_2^2\varrho^2 \qquad \text{(N)} \qquad (4.122)$$

$$\beta P/\varrho = 1 + B_2\varrho + \tfrac{1}{3}B_2^2\varrho^2 \qquad \text{(B1)} \qquad (4.123)$$

$$\beta P/\varrho = 1 + B_2\varrho + \tfrac{1}{6}B_2^2(1 + 8\pi^{-2})\,\varrho^2 \qquad \text{(N–L)} \qquad (4.124)$$

$$\beta P/\varrho = 1 + B_2\varrho\,. \qquad \text{(B2)} \qquad (4.125)$$

The third virial coefficients thus are

0·1692	exact
0·0423	(N)
0·1268	(B1)
0·1148	(N–L)
0·0	(B2),

while all higher virial coefficients are zero from all equations. It is seen the B1 and N–L are again quite similar and not too bad while the B2 equation completely fails. If we compare the compressibility factors, then Boublík's B1 and Naumann–Leland's equations agree well with the virial expansion of the fifth order (based on MC data) but overestimate the pressure at high densities where, on the other hand, the Nezbeda equation performs well.

The above discussed results produced by both two-parameter EOS are in no way encouraging. Although originally introduced as tools to distinguish between different shapes, the parameter τ as well as the parameter ζ fail to do so for diamonds and drops, see Table XVIII. As a result, the application of these parameters and consequently of equations (*4.119*) and (*4.120*) does not seem well justified.

In the preceding subsection it has been shown that certain FHS models can also be characterized by means of the parameter α. For these models the ISPT equation can be evidently used as well. It seems thus natural to assume that the ISPT equation can be applied to any FHS fluid provided that the parameter of nonsphericity is suitably defined. (An exception may be quite artificial model considered recently by Malijevský and Labík[31]). This was made first quite empirically by Rigby[200] and by Boublík and Nezbeda[61]. The former author evaluates α from the correct value of B_2 using Eq. (*3.28*). The latter authors make use of the similarity between the CB and FHS models and determine α from Eq. (*3.29*) using for the volume and surface area the actual values of the FHS body considered and for $\mathscr{R}$ the value given by an enveloping convex body. Later on, Boublík[59] showed that this method has a sound theoretical basis (see Subsection 4.5.1.). For most systems considered the Rigby (R) and Boublík–Nezbeda (B–N) methods yield similar results with the latter being better. The difference becomes more pronounced for tetrahedral pentaatomics[63]. Surprisingly, agreement with exact data is usually better for the compressibility factor than for virial coefficients (see Table XIX). This is especially remarkable for nonlinear triatomics and indicates that fortituous cancellations take place. Accuracy of the B–N method is very good for homonuclear linear models (see Fig. 13) and deteriorates, in general, with increasing heterogeneousness of bodies.

The CB fluid equations of state (*4.117*) and (*4.118*) are definitely better than the SPT and ISPT equations and one would naturally assume that they should be also used for FHS models instead of the latter equations. However, when this is done the results are rather bad due to the fact that for FHS models the geometric functionals employed for determining the parameter α are only approximate. In an atempt to use the accurate CB fluid equations also for diatomics, Abascal and Lago[201] employed another definition of α. They argue that the diatomic molecules (and, similarly, any other FHS bodies) do not experience the actual volume $\mathscr{V}$ but a slightly larger one (see also a Discussion in ref.[31]). Writing for the "corrected" volume $\mathscr{V}_{\text{cor}}$ of HOMO DB

$$\mathscr{V}_{\text{cor}} = (3L - \tfrac{1}{2}L^3 - 3h\vartheta)\,\sigma^3/6 \qquad (4.126)$$

with

$$h = (1 - L^2/4)^{1/2}\,, \quad \vartheta = \arcsin\,(L/2) \qquad (4.127)$$

they define α by

$$\alpha = \frac{1}{3\pi\mathscr{V}_{\text{cor}}}\,\frac{\partial\mathscr{V}_{\text{cor}}}{\partial\sigma}\,\frac{\partial^2\mathscr{V}_{\text{cor}}}{\partial\sigma^2}\,. \qquad (4.128)$$

Although this definition is correct for some CB, for FHS and many CB models the derivatives of the volume with respect to σ are not related to $\mathscr{S}$ and $\mathscr{R}$, and so the α's calculated from (*3.29*) and (*4.128*) are different. Other two points which hinder further applications of the Abascal–Lago method are: (i) the good agreement of B_2 given by $\alpha_{\text{B—N}}$ and exact $\mathscr{V}_{\text{FHS}}$ deteriorates when using (*4.126*) and (*4.128*); (ii) the determination of $\mathscr{V}_{\text{cor}}$ is theoretically difficult for heteronuclear FHS and mixtures. (For an analytical evaluation of $\mathscr{V}_{\text{FHS}}$ of a few special models see ref.[202]).

4.5.3. Perturbation Theories and Integral Equations

The basic idea of perturbation theories is to estimate properties of the considered system by means of a simpler reference system whose properties are known. For hard nonspherical bodies such reference systems are either bare hard spheres or hard spheres with a soft repulsive tail. Besides the methods originally proposed for simple fluids and then extended to molecular fluids (Barker–Henderson theory, the blip-function approximation; for details and references see ref.[203]), there are theories devised solely for molecular fluids. The most important of these are the Gubbins–Gray theory[3,4], RAM theory[9], median potential[204], and the conformal theory[205]. The first one is, however, inapplicable to HB fluids.

The simplest approach is to evaluate the pressure of a HB fluid from the EOS of hard spheres of a certain effective volume $\mathcal{V}_{\mathrm{HS,eff}}$. For this purpose the Carnahan–Starling equation is usually used because of its simplicity. In the present review we

TABLE XIX

Comparison of the third and fourth virial coefficients of the FHS models given by approximate equations of state with exact data. The improved SPT equation, Eq. (*4.105*), has been used. B–N and R denote the Boublík–Nezbeda and Rigby methods, respectively, of determining the parameter α

		$B_3/\mathcal{V}^2$			$B_4/\mathcal{V}^3$		
		B–N	R	exact	B–N	R	exact
				Homonuclear diatomics			
L							
0·2	—	10·22	10·21	10·23	18·46	18·46	19·43
0·4	—	10·87	10·86	10·94	19·83	19·81	20·35
0·6	—	12·01	11·97	12·13	22·22	22·15	23·10
0·8	—	13·82	13·71	14·04	26·11	25·88	27·61
1·0	—	16·75	16·47	17·04	32·50	31·89	34·52
				Heteronuclear diatomics			
L	σ_{B}						
0·50	0·5556	11·14	11·03	11·12	20·40	20·16	20·91
0·50	0·6667	11·37	11·31	11·48	20·88	20·76	21·61
0·50	0·8333	11·50	11·43	11·51	21·16	21·01	21·70
0·80	0·60	14·85	14·70	15·20	28·35	28·03	30·80
				Linear symmetric triatomics			
L	σ_{A}						
0·575	0·15	10·96	10·92	11·10	20·02	19·94	21·00
0·80	0·60	20·55	19·83	20·50	40·94	39·33	42·20
1·0	1·0	25·00	24·12	24·50	51·00	49·01	48·90
				Tetrahedral penta-atomics			
L_{AC}	σ_{A}						
0·5206	1·0294	15·05	14·44	15·26	28·78	27·46	32·29

use the new better Eq. (*4.46*):

$$\beta P/\varrho \approx (\beta P/\varrho)_{\mathrm{HS}} = \frac{1 + \eta_{\mathrm{eff}} + \eta_{\mathrm{eff}}^2 - \frac{2}{3}\eta_{\mathrm{eff}}^3 - \frac{2}{3}\eta_{\mathrm{eff}}^4}{(1 - \eta_{\mathrm{eff}})^3}\,;$$

$$\eta_{\mathrm{eff}} = \varrho \mathscr{V}_{\mathrm{HS,eff}}\,. \qquad (4.129)$$

If the simulation data for $\beta P/\varrho$ are used in this equation, then $\mathscr{V}_{\mathrm{HS,eff}}$ can be evaluated and its density dependence provides an indication to what extent the HS fluid can approximate the nonspherical body fluid in question. In Fig. 14 we plot $\mathscr{V}_{\mathrm{HS,eff}}/\mathscr{V}$ *versus* η for three different systems: PSC of $\gamma = 3$, HOMO DB of $L = 0{\cdot}6$, and tetrahedral penta-atomics. It is seen that the ratio $\mathscr{V}_{\mathrm{HS,eff}}/\mathscr{V}$ is a monotonicaly decreasing function with the upper bound given by the low density limit and the lower bound by the volume of the original molecule. Further, the difference between the upper and lower bounds increases with increasing nonsphericity. Consequently, *no* density-independent HS fluid can fit correctly the P–V–T behaviour of a nonspherical HB fluid over a wide density range.

The problem of approximating nonspherical HB fluids by bare hard spheres was investigated intensively quite recently by Williams and coworkers[206,207] who considered the median potential and the Barker–Henderson theory. A third possibility to determine an equivalent HS is the conformal theory of Nezbeda and Leland proposed several years ago[208].

The median potential $u_{\mathrm{med}}(r)$ is defined by the relation[204]

$$\int \mathrm{sgn}\left[u(r, \omega_1, \omega_2) - u_{\mathrm{med}}(r)\right] \mathrm{d}\omega_1\, \mathrm{d}\omega_2 = 0\,. \qquad (4.130)$$

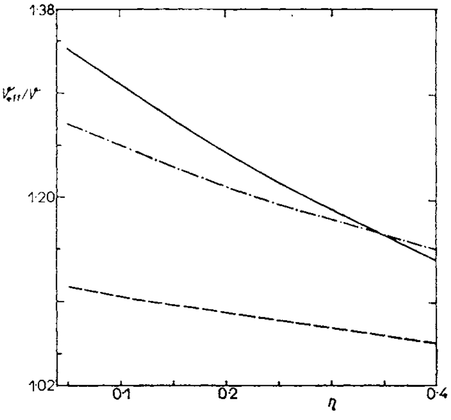


FIG. 14

The dependence of the effective volume of hard spheres on density calculated from Eq. (*4.117*) for prolate spherocylinders of $\gamma = 3$ (———) and from Eq. (*4.105*) for homonuclear dumbells of $L = 0{\cdot}6$ (— — —) and tetrahedron penta-atomics (—·—·—)

For HB interactions it is more convenient to make use of the fact that (i) the median minimizes the sum of absolute deviations and (ii) if $u_0 = \text{med}\,(u)$ then also $\varphi(u_0) = \text{med}\,[\varphi(u)]$ for arbitrary φ. Eq. (*4.130*) is thus equivalent to the condition that functional (*4.131*),

$$\int \{\exp[-\beta u(r, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)] - \exp[-\beta u_{\text{med}}(r)]\}\,\mathrm{d}\boldsymbol{\omega}_1\,\mathrm{d}\boldsymbol{\omega}_2\,, \tag{4.131}$$

is minimized by u_{med}. From here it immediately follows that if u is a HB potential then u_{med} is the HS potential with the diameter σ_{eff} defined by

$$e_{\text{av}}(\sigma_{\text{eff}}) \equiv \int \exp[-\beta u(r = \sigma_{\text{eff}}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)]\,\mathrm{d}\boldsymbol{\omega}_1\,\mathrm{d}\boldsymbol{\omega}_2 = \tfrac{1}{2}\,. \tag{4.132}$$

Results obtained from the median potential are nearly identical to those obtained from the Barker–Henderson theory[206] which defines σ_{eff}, in general, by

$$\sigma_{\text{eff}}^{\text{B-H}} = \int \{1 - \exp[-\beta u(r, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)]\}\,\mathrm{d}r\,\mathrm{d}\boldsymbol{\omega}_1\,\mathrm{d}\boldsymbol{\omega}_2\,. \tag{4.133}$$

For hard bodies this equation reads as

$$\sigma_{\text{eff}}^{\text{B-H}} = \int R(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2)\,\mathrm{d}\boldsymbol{\omega}_1\,\mathrm{d}\boldsymbol{\omega}_2 \tag{4.134}$$

which is identical to the expression proposed many years ago by Bellemans[209]. In (*4.134*) $R(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$ is the closest approach distance for two molecules at angular configurations $\boldsymbol{\omega}_i$.

In Tables XX and XXI we compare the results based on the median potential with simulation data. The median EOS yields the results which at low densities are lower and at high densities higher than the experimental data. It is thus evident that somewhere in between there must be a region where the agreement is perfect. With increasing nonsphericity the region of such good agreement however shrinks to a very narrow one.

In the conformal theory (considered for CB only) the configurational partition function is expanded in powers of an appropriate functional and the effective volume is obtained by annulling the first order term. The result is[208]

$$\mathscr{V}_{\text{HS,eff}}/\mathscr{V} = \frac{1 + 6\alpha x}{1 + 6x}\,, \tag{4.135}$$

where x is an adjustable parameter. There is no exact mathematical route enabling

TABLE XX

Compressibility factors of prolate spherocylinders calculated from perturbation and conformal theories

γ	η	$\beta P/\varrho$			
		exact	RAM[b]	median[c]	conformal[d]
2	0·15	2·07[a]	2·04	1·99	2·04
	0·20	2·65	2·63	2·56	2·65
		2·69			
	0·30	4·48	4·43	4·40	4·68
	0·40	8·18	7·19	8·05	8·84
		8·20			
	0·45	11·02[a]	9·34	11·24	12·57
	0·50	15·20		16·09	18·44
3	0·20	3·07		2·68	3·08
	0·30	5·40		4·75	6·01
	0·40	9·60		9·06	13·00
	0·45	13·00		12·95	20·22
	0·50	18·00		19·13	33·21
	0·54	23·33		26·90	52·06

[a] Calculated from the Nezbeda equation of state, Eq. (*4.117*). [b] First order RAM theory result (taken from ref.[222]). [c] Calculated from Eq. (*4.46*) with σ_{HS} given by Eq. (*4.132*). [d] Calculated from Eq. (*4.46*) with $\sigma_{HS}^3 = 3(1 + \alpha)\mathcal{V}_{SC}/\pi$.

TABLE XXI

Compressibility factors of homonuclear diatomics of $L = 0{\cdot}6$ calculated from perturbation and integral equation theories

η	$\beta P/\varrho$			
	exact	RAM[a]	median[b]	RHNC[c]
0·2094	2·78	2·82	2·71	2·82
0·3142	4·95	5·01	4·86	5·18
0·4189	9·23	9·49	9·36	10·67
0·4712	12·87	13·21	13·49	

[a] Zeroth order RAM theory, Eq. (*4.138*); taken from ref.[223]. [b] Calculated from Eq. (*4.46*) with σ_{HS} given by Eq. (*4.132*). [c] "Reference" HNC theory; taken from ref.[227].

one to choose x unambiguously and it is therefore necessary to argue on the basis of either physical requirements or some analogies. For $x = 0$ the lower bound is recovered, $\mathscr{V}_{\mathrm{HS,eff}} = \mathscr{V}$, while for $x \to \infty$ we get $\mathscr{V}_{\mathrm{HS,eff}}/\mathscr{V} = \alpha$. The exact upper bound (*i.e.* low density value) corresponds to $x = 1/2$. Nezbeda and Leland took the mean value $(1 + \alpha)/2$ corresponding to $x = 1/6$ and reported very good results for the PSC of $\gamma = 2$ up to $\eta \lesssim 0{\cdot}35$. In general, the conformal theory produces good results at low and medium densities while rapid deterioration of the results with increasing nonsphericity is observed, see Tables XX and XXI.

The other group of theories either introduces a density-dependent reference HS (blip-function theory) or hard spheres with a soft repulsive tail (RAM theory). It might be anticipated that these methods would do better than the conformal or median theories but they suffer from one important disadvantage: they require much more computer calculations and do not provide the EOS in a closed form unless a certain parametrization is made. Also the IMIS (independent-molecular-interaction-sites) theory, proposed independently by Naumann and Lippert[210] and Nezbeda and Smith[211], belongs into this family of theories. This theory is identical to the RAM theory for homonuclear models. For heteronuclear models it transforms the original fluid to a simple fluid mixture which, however, was shown[212] to be a very poor approximation.

The blip-function theory, originally proposed for simple fluids[213] with short--ranged repulsions, was shown to converge slowly for molecular fluids[214]. It defines the reference hard sphere fluid from the requirement that the free energy of both fluids be identical to first order, which leads to the equation

$$\int \{e_{\mathrm{av}}(r) - \exp\left[-\beta u_{\mathrm{HS,eff}}(r)\right]\}\, y_{\mathrm{HS}}(r)\, \mathrm{d}\mathbf{r} = 0\,. \tag{4.136}$$

Nezbeda[215] considered the fluid of PSC and obtained good results only for small elongations. Further, for $\gamma = 2$ the results were reasonable only at very low densities which is in full agreement with Sung and Chandler's qualitative estimation of the blip-function usefulness[214].

The RAM theory defines[218,219] the reference potential *via* the average Boltzmann factor,

$$\beta u_{\mathrm{RAM}}(r) = -\ln e_{\mathrm{av}}(r)\,. \tag{4.137}$$

The potential contains a hard core corresponding to the closest separation distance and a soft repulsive tail accounting for a gradual increase of rotational freedom of a pair of particles with increasing their separation. To determine properties of the simple fluid reference the blip function could be used, at least in principle, but due to a slowly decaying repulsions spread over a wide range the results would be definitely rather bad. Labík and coworkers[220] extended therefore the EXP approximation to this type of potentials, which makes the evaluation of the pressure even more complicated. Another possibility is to use the "corrected" HNC equation which was shown to be the most accurate of all integral equations[221]. Comparison of the final results with simulation data shows that the reference fluid approximates the EOS of the HB fluids very poorly (see *e.g.* Table III in ref.[222]). It is therefore necessary to evaluate the first order corrections to the Helmholtz free energy. Very good results are then obtained for low and medium nonsphericities, see Table XX.

Instead of evaluating the pressure of a molecular fluid directly from the expressions given by the RAM theory, this theory can be also used in another way. From Eq. (*4.19*) it follows that for FHS fluids we need two pieces of information: contact values of the site–site correlation functions $G_{\alpha\beta}$ and their (100)-spherical harmonic expansion coefficients. For the reduced coefficients (of linear models) the zeroth-order RAM theory gives[9]

$$G^{\alpha\beta*}_{\mathrm{klm}} = e^{\alpha\beta}_{\mathrm{klm}}(r)/e_{\mathrm{av}}(r)\,, \qquad (4.138)$$

where e_{klm} is the spherical harmonic expansion coefficient of the Boltzmann factor $\exp\left[-\beta u(1,2)\right]$. Eq (*4.138*) is exact for $r \to r_{\mathrm{contact}}$ for certain FHS models and very accurate for others. If $G_{\alpha\beta}(r)$ is available from some source, it can be then combined with Eq. (*4.138*) to calculate pressure from (*4.19*). Nezbeda and Smith[223] tested this way using the simulation data for $G_{\alpha\beta}$ and obtained very good results for all HB fluids considered. In Table XXI the results are displayed for HOMO DB of $L = 0{\cdot}6$. The RAM theory results obtained *via* the above discussed route are in no way worse than those from the median EOS.

The last group of theories we may mention here are integral equations. The output of these equations are correlation functions and so they are better suited for describing the structure than for the P–V–T behaviour of fluids. None of them yields the EOS in a closed analytical form. All integral equations represent extensions of equations and relations proposed originally for simple fluids. With the only exception, the RISM theory of Andersen and Chandler[224], until recently only a low density solution of the P–Y equation for PSC was known[225]. Lado[226] recently proposed a method of solving numerically integral equations and did calculations for the RHNC (reference HNC) equation for HOMO DB fluids[227]. At low densities the computed values are uniformly good. With increasing density a dependence on elongation becomes more pronounced and the computed pressure quickly deteriorates. The RISM theory provides us with the set of the site–site correlation functions $G_{\alpha\beta}$ for FHS models. Besides certain defects of the theory itself (*e.g.* incorrect low density limit), the complicated routes *via* the Helmholtz free energy or *via* the compressibility equation must be used if unreliable contact values of $G_{\alpha\beta}$ for obtaining the EOS are to be avoided[120,228]. This is another deterrence to use this theory to calculate the thermodynamic properties.

4.5.4. Discussion

Similarly to the HS fluid, a number of EOS has been proposed also for nonspherical body fluids. Some of them are quite general, other are good for specific systems only. General equations employ the parameter of nonsphericity introduced by the SPT of convex bodies. The concept of describing the shape of particles by this parameter has been then extended also to FHS models but yet it seems worthwhile (and often necessary) to differentiate between the convex and nonconvex models.

The SPT and its various implementations play a key role in theories of nonspherical body fluids. It is the only theory available at present which defines rigorously the parameter of nonsphericity and although the resulting equations are not very accurate they provide a basis upon which better equations are built. The value of rigour is best esteemed by reminding the failure of empirically introduced parameters τ and ζ when they are applied to cubes or infinitely thin platelets.

The method which seems to yield the most accurate equations is the same as that for HS: to estimate all the virial coefficients which allows to sum up the entire virial expansion (*cf.* Eqs (*4.42*) and (*4.45*)). For accomplishing this scheme the coefficients must be parametrized, usually by means of the parameter α, so that the resulting equation is at least formally general – see Eqs (*4.117*) and (*4.118*). This generality enables us to apply these equations to any CB model at low densities.

There is now no doubt about insufficiency of one parameter to describe properties of higher-order clusters of nonspherical particles beyond the two-particle ones. At medium and high densities the application of Eqs (*4.117*) and (*4.118*) is therefore limited, in general, to small values of α only. Although for linear models Eq. (*4.117*) remains accurate up to $\alpha \sim 1{\cdot}5$ and Eq. (*4.118*) seems good for oblate shapes, any general conclusion on performance of Eqs (*4.117*) and (*4.118*) for $\alpha \gtrsim 1{\cdot}2$ is hard to make. As an attempt to remedy this situation, two equations employing an additional parameter have been proposed, Eqs (*4.119*) and (*4.120*). However, presumably due to the purely empirical nature of their derivation, they do not do better than Eqs (*4.117*) and (*4.118*) and may hardly be recommended.

Results based on Padé approximants are usually only fair and unpredictable. This is a consequence of the high sensitivity of PA to the values of the virial coefficients and, presumably, not necessarily "regular" behaviour of higher virial coefficients. On the other hand, the truncated virial expansion with the HS reference performs very well. The five term expansion yields results within experimental errors up to medium densities regardless of the model considered. At high densities it begins to underestimate the compressibility factor in accordance with the inequality $B_i/\mathscr{V}^{i-1} - B_{HS,i}/\mathscr{V}_{HS}^{i-1} > 0$ valid for all known coefficients of realistic models. The truncated perturbed virial expansion is believed to provide, in general, a lower bound for the compressibility factor.

In Subsection 3.2.3. we mentioned a discrepancy between two existing sets of data of the virial coefficients of oblate spherocylinders. At larger values of $\varphi(=\gamma-1)$ the fourth virial coefficients due to Wojcik and Gubbins[33] seem too large and do not satisfy Eq. (*3.65*). The values due to Nezbeda[34] seem too low and B_4 for $\varphi = 3$ also fails to satisfy Eq. (*3.65*). When either set of the data is used to calculate the approximant $\varphi(\eta)$ in Eq. (*4.52*), the resulting compressibility factor is not as good as that for other models. Since Eq. (*4.52*) is correct for CB this may only reflect uncertainty in the virial coefficients used. But there comes an additional problem when the high density simulation data are compared with the truncated perturbed virial expansion. At $\eta = 0{\cdot}45$ and for $\varphi = 1{\cdot}5$ and $2{\cdot}0$ the results look as follows:

$$\begin{array}{llll} \varphi = 1{\cdot}5 & 11{\cdot}35 \pm 0{\cdot}12 & \textit{versus} & 11{\cdot}22\,(11{\cdot}23) \\ \varphi = 2{\cdot}0 & 12{\cdot}30 \pm 0{\cdot}10 & \textit{versus} & 12{\cdot}16\,(12{\cdot}21) \\ & 12{\cdot}09 \pm 0{\cdot}16 & & \end{array}$$

where the values in parantheses correspond to Nezbeda's set of the virial coefficients. Agreement between the simulated and calculated results is, at such a high density, astonishing: One would intuitively, and in accordance with the discussion in the preceding paragraph, expect the calculated values to fall well below the simulated ones. An explanation might be that the higher virial coefficients are negative and large in the absolute value but this seems very unlikely. Since there is no other reliable theoretical method at present available to test the simulation results we must conclude that either our contemporary understanding of HB behaviour is still unsatisfactory or that the existing numerical data on the oblate spherocylinder fluid must be questionned.

The perturbation and integral equation methods yield results which are uniformly inferior to those obtained from either Eq. (*4.117*) or (*4.118*). With the exception of the simplest methods, the EOS is not given in a closed analytic form and the main merit of these methods lies thus in their ability to describe the structure of fluids.

Concerning the FHS models, the best method at present available for describing their P–*V*–*T* behaviour is that due to Boublík and Nezbeda[61]: the ISPT equation with appropriately defined parameter α. It estimates properties of all so far considered models quite well but yet it should be used with caution. Although it is theoretically justified for ceratin models, its success stems largely from fortuituous cancellations. The method fails for models not much different from convex models (due to the failure of the ISPT equation to produce accurate results for CB) and deteriorates with increasing heterogeneousness.

5. HARD BODY MIXTURES

Phase diagram of fluid mixtures is much richer than that of pure fluids making thus mixtures very interesting and challenging, especially for theorists. Besides that, practically all real fluid systems chemical engineers have to deal with are mixtures and proper understanding of their properties along with developing an accurate theory are of high importance. Despite these facts very little has been done for mixtures, especially concerning computer simulations. Existing computer data (not only for HB fluids) up to 1984 together with theoretical methods explaining them have been reviewed recently by Gubbins and coworkers[229] who have also discussed general future needs.

In this section we discuss together both the virial coefficients and compressibility factors. Practically all methods considered are simple extensions of those discussed in Chapters 3 and 4 for pure fluids. However, not all pure fluid theories could be or have been extended. For instance, from all specific methods devised for discontinuous potentials (Subsection 4.4.2.) only the SPT and Andrew's methods have been extended. Further, we do not consider lattice theories for their negligible role in HB fluid mixtures, resummation techniques because of the lack of data on virial cofficients, and integral and integro-differential equations with the exception of the P–Y theory.

5.1. *Basic Relations*

Basic expressions and relations given in the previous Chapter for pure fluids can be readily extended to mixtures. For simplicity we shall confine our considerations to binary mixtures only, extension to an arbitrary m-component mixture is straightforward.

Let N_α denote the number of molecules of species α, $\alpha = 1, 2$. Number density and concentrations, respectively, are then $\varrho_\alpha = N_\alpha/V$ and $x_\alpha = N_\alpha/N$, $N = N_1 + N_2$. Throughout this chapter we shall use the packing fraction $\eta = \Sigma\eta_\alpha$ for the dimensionless density of a mixture, $\eta_\alpha = \varrho_\alpha \mathscr{V}_\alpha$. The pair potential function u depends now also on the assignement of species to space variables, $u(1, 2) \rightarrow u(1_\alpha, 2_\beta) \equiv u_{\alpha\beta}(1, 2)$, and hence also all functions related to u. Consequently, the total potential energy is no longer invariant under permutations of all the molecules but only under permutations involving molecules of the same species. The configuration partition function, $Q_{N_1N_2}$, of a binary mixture is thus given by

$$Q_{N_1N_2} = \frac{1}{N_1!N_2!} Z_N(N_1, N_2)\,, \tag{5.1}$$

where Z_N is the configuration integral given formally by the same expression as that of pure fluids, *cf.* Eq. (*3.3*). From Eq. (*5.1*) and a similar extension of Eq. (*3.4*) we can get all required expressions for the mixture.

In Chapters 3 and 4 dealing with pure fluids we have always assumed that the characteristic measure of the size of hard bodies is unity. In this chapter this convention must be dropped so that the characteristics (diameters, *etc.*) will explicitly appear in expressions.

In the case of hard body interactions the cross interaction, u_{12}, is usually defined on the geometrical basis, it means $u_{12} = \infty$ when the two particles overlap and $u_{12} = 0$ otherwise. However, it is also possible to define the so-called non-additive interaction. For instance, for a HS mixture the cross diameter of a pair of unlike spheres of diameters σ_α may be defined in general by

$$\sigma_{12} = (\sigma_1 + \sigma_2)(1 + \delta)/2\,, \tag{5.2}$$

where δ can be both positive and negative or zero. For $\delta = 0$ we have a pair of real hard spheres (additive HS) whereas for $\delta \neq 0$ we have a non-additive HS mixture. Nonadditivity can be evidently extended also to nonspherical bodies but such an extension has not been considered so far.

The virial expansion for the mixture has the same form as (*3.1*),

$$\beta P/\varrho = 1 + B\varrho + C\varrho^2 + \ldots\,, \tag{5.3}$$

where now

$$\begin{aligned} B &= \Sigma x_\alpha x_\beta B_{\alpha\beta} \\ C &= \Sigma x_\alpha x_\beta x_\gamma C_{\alpha\beta\gamma} \\ &\vdots \end{aligned} \tag{5.4}$$

$B_{\alpha\beta}$ denotes the 2nd virial coefficient with bond $f_{\alpha\beta} = \exp\left[-\beta u_{\alpha\beta}\right] - 1$, *etc.* To simplify notation we have used in (*5.3*) capital letters for the virial coefficients in place of B with an additional subscript,

$$B \to B_2\,, \quad C \to B_3\,, \ldots\,. \tag{5.5}$$

With the exception of the additional summation over species, *i.e.* pairs $1-1$, $1-2$, and $2-2$, the virial form of equation of state of a mixture is given formally by the same expressions as the EOS of the pure fluid. For instance, for a mixture of CB it holds[14,230] (*cf.* Eqs (*4.8*) and (*4.12*)):

$$\beta P/\varrho = 1 + \tfrac{1}{6}\varrho \sum_{\alpha,\beta} x_\alpha x_\beta g^{\mathrm{av}}_{\mathrm{c},\alpha\beta} \langle(\mathbf{r}_{12} \cdot \mathbf{v}_{\alpha\beta})\rangle_{\mathrm{c}}\, \mathcal{S}_{\alpha+\beta} \tag{5.6}$$

$$\begin{aligned} &= 1 + \tfrac{1}{6}\varrho \sum_{\alpha,\beta} x_\alpha x_\beta \big[\mathcal{G}^{\mathrm{av}}_{\alpha\beta,\mathrm{c}}(3\mathcal{V}_\alpha + 2\mathcal{S}_\alpha \mathcal{R}_\beta + \mathcal{R}_\alpha \mathcal{S}_\beta) + \\ &\quad + \mathcal{G}^{\mathrm{av}}_{\beta\alpha,\mathrm{c}}(3\mathcal{V}_\beta + 2\mathcal{S}_\beta \mathcal{R}_\alpha + \mathcal{R}_\beta \mathcal{S}_\alpha)\big] \end{aligned} \tag{5.7}$$

and similarly for FHS models.

The Ornstein–Zernike relation for a mixture reads as

$$h_{\alpha\beta}(1,2) = c_{\alpha\beta}(1,2) + \varrho \sum_{\gamma} x_{\gamma} \int c_{\alpha\gamma}(1,3)\, h_{\beta\gamma}(2,3)\, d(3)\,; \quad \alpha, \beta = 1, 2 \qquad (5.8)$$

from which the mixture counterparts of the compressibility EOS, Eqs (*4.24*) and (*4.26*), are simply derived.

There is one exact analytic result if we consider the extreme case where bodies of one species, let us say 1, shrink to the point body. All the volume unoccupied by the bodies of species 2 is then available to the point particles and we get

$$\beta P/\varrho = x_1/(1 - \eta_2) + x_2(\beta P/\varrho)_2\,, \qquad (5.9)$$

where η_2 is the fraction of the volume occupied by bodies 2 and the compressibility factor $(\beta P/\varrho)_2$ is evaluated at density ϱ_2.

In addition to common functions encountred in theories of pure fluids there are functions relevant only to mixtures. For example, when dealing with mixtures at low pressures then excess thermodynamic functions, defined as the difference between the thermodynamic function of mixing and the value corresponding to an ideal mixture at the same temperature, pressure, and composition, are of interest rather then the thermodynamic functions themselves. For hard body fluids the excess functions are simply attainable from EOS using the standard thermodynamic relations[231]. Further, since there is no energy change on mixing, the excess Gibbs free energy of mixing, G^{E}, can be calculated from

$$G^{\mathrm{E}} = \int_0^{\mathrm{P}} V^{\mathrm{E}}\, \mathrm{d}P'\,, \qquad (5.10)$$

where V^{E} is the excess volume of mixing. At zero pressure it holds:

$$V^{\mathrm{E}} = x_1 x_2 (2B_{12} - B_{11} - B_{22})\,. \qquad (5.11)$$

Quantity G^{E} is useful for studying phase transitions. For example, the inequality

$$G^{\mathrm{E}} < 0 \qquad (5.12)$$

is a sufficient condition for complete miscibility.

Other functions relevant to mixtures are the partial molar quantities $\bar{A}_{\alpha}$ defined for any extensive property A by[231]

$$\bar{A}_{\alpha} = \left(\frac{\partial A}{\partial N_{\alpha}}\right)_{N_{\beta},P,T}\,. \qquad (5.13)$$

Functions $\bar{A}_\alpha$ cannot be simultaneously changed arbitrarily but are subject to a constraint (at constant T and P)

$$0 = \sum_\alpha N_\alpha \, \mathrm{d}\bar{A}_\alpha \tag{5.14}$$

called the Gibbs–Duhem equation. In the special case of taking the Gibbs energy, G, for A we get

$$\sum N_\alpha \, \mathrm{d}\mu_\alpha = 0 \tag{5.15}$$

and, consequently,

$$\sum_\alpha \varrho_\alpha (\partial \mu_\alpha / \partial \varrho_\beta)_{\mathrm{T,P},\rho_\alpha} = 0 \, . \tag{5.16}$$

This relation must be satisfied by any correct EOS of mixtures.

5.2. *Virial Expansion*

5.2.1. Exact Results

For HB mixtures the situation is a bit worse than for pure fluids. For a mixture of additive HS the exact analytical results are known for B and C and for most diagrams contributing to D. For one specific model of nonadditive HS with positive departure from additivity quite a large number of coefficients have been calculated both analytically and numerically.

For nonspherical HB mixtures only the second virial coefficient is known for convex bodies. In all other cases the virial coefficients are determined numerically but only few such computations have been actually performed.

Hard sphere mixtures. For a mixture of additive HS the cross diameter σ_{12} is given by Eq. (*5.2*) with $\delta = 0$ and it thus holds

$$B_{12} = \tfrac{2}{3}\pi\sigma_{12}^3 \, . \tag{5.17}$$

For the third virial coefficient Kihara[47] derived the result

$$\begin{aligned} C_{\alpha\beta\gamma} = {} & (4\pi/3)^2 \, \{(R_\alpha^3 R_\beta^3 + R_\alpha^3 R_\gamma^3 + R_\beta^3 R_\gamma^3)/3 + 3R_\alpha^2 R_\beta^2 R_\gamma^2 + \\ & + R_\alpha^3(R_\beta^2 R_\gamma + R_\beta R_\gamma^2) + R_\beta^3(R_\alpha^2 R_\gamma + R_\alpha R_\gamma^2) + R_\gamma^3(R_\alpha^2 R_\beta + R_\alpha R_\beta^2)\} \, , \end{aligned} \tag{5.18}$$

where $R_\alpha = \sigma_\alpha/2$, *etc.*

The fourth virial coefficient is given by terms D4, D5, D6 and these are given by subterms which differ in assignment of spheres in the diagrams. Rigby and Smith[232], following the former study of McLelan and Alder[233] (and references quoted there), calculated the fourth virial coefficients in the mixtures of HS of the diameter ratios 0·6 : 1 and 1/3 : 1. With the exception of the three most complicated clusters they succeeded in expressing analytically all the others. The values of the three remaining clusters the authors evaluated numerically. Their final results are listed in Table XXII.

Calculations of the virial coefficients have been also performed[234] for a nonadditive HS mixture defined by the potential

$$\begin{aligned} u_{11} &= u_{22} = 0 \\ u_{12} &= \infty \quad \text{for} \quad r_{12} < \sigma \\ &\ 0 \quad \text{for} \quad r_{12} > \sigma\,. \end{aligned} \tag{5.19}$$

In this case the only nonvanishing graphs are the so-called bicoloured graphs, *i.e.* the graphs where there are no bonds between pairs of the same species (for details see refs[235,236]). The virial expansion can be then cast into the form

$$\beta P/\varrho = 1 + \sum_{i,j} (i + j - 1)\, x_1^i x_2^j \eta^{i+j-1} C_{ij}\,, \tag{5.20}$$

where $\eta = \frac{4}{3}\pi\varrho\sigma^3$ and C_{ij} are coefficients corresponding to all irreducible graphs with i molecules of species 1 and j molecules of species 2; they are listed in Table XXIII.

Convex body mixtures. The second cross virial coefficient follows immediately from the basic relations of the CB geometry, *cf.* Eq. (*2.14*). It holds:

$$\begin{aligned} B_{12} &= \tfrac{1}{2}(\mathcal{V}_1 + \mathcal{V}_2 + \mathcal{R}_1\mathcal{S}_2 + \mathcal{R}_2\mathcal{S}_1) = \\ &= \tfrac{1}{2}(1 + 3\alpha_1)\,\mathcal{V}_1 + \tfrac{1}{2}(1 + 3\alpha_2)\,\mathcal{V}_2 + \Delta B\,, \end{aligned} \tag{5.21}$$

TABLE XXII

Fourth virial coefficients of mixtures of hard spheres taken from ref.[232]. The virial coefficients are reduced by σ_{12}^9 and their accuracy is about 0·01 per cent

$D_{\alpha\beta\gamma\delta}$	$\sigma_1/\sigma_2 = 0{\cdot}6$	$\sigma_1/\sigma_2 = 0{\cdot}3333$
D_{1111}	0·19789	0·00515
D_{1112}	0·66367	0·07938
D_{1122}	2·0900	1·0464
D_{1222}	6·7957	12·275
D_{2222}	19·637	101·32

where

$$\Delta B = \tfrac{3}{2}\alpha_1\left(\frac{\mathcal{S}_2}{\mathcal{S}_1} - 1\right)\mathcal{V}_1 + \tfrac{3}{2}\alpha_2\left(\frac{\mathcal{S}_1}{\mathcal{S}_2} - 1\right)\mathcal{V}_2 =$$

$$= \tfrac{3}{2}\alpha_1\left(\frac{\mathcal{R}_2}{\mathcal{R}_1} - 1\right)\mathcal{V}_1 + \tfrac{3}{2}\alpha_2\left(\frac{\mathcal{R}_1}{\mathcal{R}_2} - 1\right)\mathcal{V}_2 . \qquad (5.22)$$

It is thus seen that the parameters of nonsphericity of individual components, so useful in describing properties of pure fluids, lose this ability for mixtures: with the exception of one specific case where either $\mathcal{S}_1 = \mathcal{S}_2$ or $\mathcal{R}_1 = \mathcal{R}_2$ it is not possible to express even B_{12} by means of α_i only.

The third virial coefficient is given[47] by a similar extension of Eq. (*3.30*):

$$C_{\alpha\beta\gamma} = \tfrac{1}{3}\left[\mathcal{V}_\alpha\mathcal{V}_\beta + \mathcal{V}_\alpha\mathcal{V}_\gamma + \mathcal{V}_\beta\mathcal{V}_\gamma + \mathcal{V}_\alpha(\mathcal{R}_\beta\mathcal{S}_\gamma + \mathcal{R}_\gamma\mathcal{S}_\beta) + \right.$$

$$\left. + \mathcal{V}_\beta(\mathcal{R}_\gamma\mathcal{S}_\alpha + \mathcal{R}_\alpha\mathcal{S}_\gamma) + \mathcal{V}_\gamma(\mathcal{R}_\alpha\mathcal{S}_\beta + \mathcal{R}_\beta\mathcal{S}_\alpha) + (1/4\pi)\, G_{\alpha\beta\gamma}\right], \qquad (5.23)$$

where

$$\mathcal{S}_\alpha\mathcal{S}_\beta\mathcal{S}_\gamma \leqq G_{\alpha\beta\gamma} \leqq (4\pi)^3\, \mathcal{R}_\alpha^2\mathcal{R}_\beta^2\mathcal{R}_\gamma^2 . \qquad (5.24)$$

This inequality forms a basis for the formulation of approximate expressions analogous to Eqs (*3.58*) and (*3.59*) for the third and fourth virial coefficients. Values determined in this way represent the only source of $C_{\alpha\beta\gamma}$ and $D_{\alpha\beta\gamma\delta}$ since no computer data have been published so far.

Fused hard body mixtures. In this case an exact general expression is unknown even for $B_{\alpha\beta}$. In the special case of mixtures of homonuclear dumbells of the same

TABLE XXIII

Coefficients C_{ij} ($C_{ij} = C_{ji}$) of the virial expansion of the mixture of nonadditive hard spheres defined by Eqs (*5.19*) and (*5.20*) (ref.[234])

i	j	$10^2 C_{ij}$
1	1	−100·0
1	2	0
2	2	8·095
2	3	1·220
3	3	−0·8824
2	4	0·1646
2	5	0·01985
3	4	−0·3687

site–site separation and differing only in diameters, the earlier mentioned expressions due to Ishihara or Wertheim (see Subsection 3.2.4.) can be used with $\sigma = (\sigma_1 + \sigma_2)/2$.

On the other hand, for two mixtures of HOMO DB Aviram and Tildesley[237] calculated B_{12} from the simulation results of $\beta P/\varrho$ and for several mixtures of HOMO DB all the coefficients B_{12}, $C_{\alpha\beta\gamma}$, and $D_{\alpha\beta\gamma\delta}$ were evaluated numerically by Wojcik and Gubbins[238]. These data are listed in Tables XXIV and XXV.

5.2.2. Approximate Results

The third virial coefficient of a CB mixture can be calculated from (*5.23*) provided that the factor G is known. Boublík[65] has proposed to use for G an approximation (*cf.* Eq. (*3.57*))

$$G_{\alpha\beta\gamma} = (4\pi/3)\left(\mathscr{R}_\alpha^2 \mathscr{S}_\beta \mathscr{S}_\gamma + \mathscr{R}_\beta^2 \mathscr{S}_\alpha \mathscr{S}_\gamma + \mathscr{R}_\gamma^2 \mathscr{S}_\alpha \mathscr{S}_\beta\right). \tag{5.25}$$

This approximation yields $C_{\alpha\beta\gamma}$ which is identical to the result produced by the ISPT equation of state of mixtures (see Eq. (*5.76*)).

In the absence of any detailed information on the 4th virial coefficient, Boublík[65] has proposed also an expression for D by analogy with B and C:

$$\begin{aligned} D_{\alpha\beta\gamma\delta} = {} & \tfrac{1}{4}\{\mathscr{V}_\alpha \mathscr{V}_\beta \mathscr{V}_\gamma + \mathscr{V}_\alpha \mathscr{V}_\beta \mathscr{V}_\delta + \mathscr{V}_\alpha \mathscr{V}_\gamma \mathscr{V}_\delta + \mathscr{V}_\beta \mathscr{V}_\gamma \mathscr{V}_\delta + \\ & + \tfrac{14}{9}[\mathscr{V}_\alpha \mathscr{V}_\beta(\mathscr{R}_\gamma \mathscr{S}_\delta + \mathscr{S}_\gamma \mathscr{R}_\delta) + \mathscr{V}_\alpha \mathscr{V}_\gamma(\mathscr{R}_\beta \mathscr{S}_\delta + \mathscr{S}_\beta \mathscr{R}_\delta) + \\ & + \mathscr{V}_\alpha \mathscr{V}_\delta(\mathscr{R}_\beta \mathscr{S}_\gamma + \mathscr{S}_\beta \mathscr{R}_\gamma) + \mathscr{V}_\beta \mathscr{V}_\gamma(\mathscr{R}_\alpha \mathscr{S}_\delta + \mathscr{S}_\alpha \mathscr{R}_\delta) + \\ & + \mathscr{V}_\beta \mathscr{V}_\delta(\mathscr{R}_\alpha \mathscr{S}_\gamma + \mathscr{S}_\alpha \mathscr{R}_\gamma) + \mathscr{V}_\gamma \mathscr{V}_\delta(\mathscr{R}_\alpha \mathscr{S}_\beta + \mathscr{S}_\alpha \mathscr{R}_\beta)] + \\ & + (1/12\pi)(\mathscr{V}_\alpha G_{\beta\gamma\delta} + \mathscr{V}_\beta G_{\alpha\gamma\delta} + \mathscr{V}_\gamma G_{\alpha\beta\delta} + \mathscr{V}_\delta G_{\alpha\beta\gamma})\}. \end{aligned} \tag{5.26}$$

The factor 14/9 in this relationship has been introduced quite empirically in order to retain the approximate value of $B_4 = 18{\cdot}0$ in the case of pure HS. Introduction of this factor reflects oversimplifications used in the derivation of (*5.26*) where, for example, only those combinations of the geometric quantities of the order $\mathcal{O}(\mathscr{V}^3)$ are considered which already appeared in the relationships for the lower-order coefficients.

Due to the lack of exact data on C and D of CB models, nothing can be said about accuracy of Eqs (*5.23*), (*5.25*), and (*5.26*) in addition to the quality of their predictions in the case of one-component fluids.

The situation is much better for FHS mixtures since for a number of these mixtures values of $C_{\alpha\beta\gamma}$ and $D_{\alpha\beta\gamma\delta}$, in addition to $B_{\alpha\beta}$, are available.

To determine B_{12} of a mixture of HOMO DB Boublík[59] has followed the same route as for pure fluids and proposed an expression (*cf.* Eqs (*3.48*)–(*3.50*))

$$2B_{12} = \mathscr{V}_1 + \mathscr{V}_2 + \mathscr{R}_1 \mathscr{S}_2 + \mathscr{R}_2 \mathscr{S}_1 - \Delta v_{12}, \tag{5.27}$$

where for the volume difference Δv_{12} it holds

$$\Delta v_{12} = \frac{\pi}{6} L_1 L_2 h \sigma_1 \sigma_2 \qquad (5.28)$$

and

$$h = \sigma_{12} - (\sigma_{12}^2 - \tfrac{1}{4}L_1^2\sigma_1^2 - \tfrac{1}{4}L_2^2\sigma_2^2)^{1/2} \,. \qquad (5.29)$$

Comparison of the cross virial coefficients given by Eq. (*5.27*) with the numerical data of Wojcik and Gubbins is shown in Table XXVI. It can be seen that Eqs (*5.27*)–(*5.29*) yield very accurate results with errors not exceeding the double error of the numerical data. Further, it is seen that the approximation $\Delta v_{12} = 0$ practically does not bring about additional errors and it is therefore possible to use Eqs (*5.23*) and (*5.26*) also for HOMO DB mixtures.

In Table XXVII we compare the third and fourth virial coefficients of two types of mixtures: one is that of HS and the other is made up of HS and HOMO DB. In the case of HS mixtures Eq. (*5.23*) is exact and for the mixtures of HS + HOMO DB it seems also quite accurate: the maximum difference is about 1·7 per cent in comparison with the error estimate of 0·5 per cent. Surprisingly good results are also obtained for D. For HS mixtures the maximum deviation is about 2 per cent and only slightly worse accuracy is achieved for a realistic mixture of HS and HOMO DB of $L^* = 0{\cdot}6$. In the extreme case of the mixture containing HOMO DB of $L^* = 1{\cdot}0$ the accuracy evidently deteriorates but yet it remains quite good with the exception of the D_{1111} term. This is a consequence of the fact that Eq. (*5.26*) con-

TABLE XXIV

Second cross virial coefficients of mixtures of homonuclear diatomics ($L^* = L/\sigma$)

L_1^*/L_2^*	Conditions	B_{12}/σ_{12}^3	Ref.
0·6/0·3	$\sigma_1 = \sigma_2$	3·616 ± 0·003	238
	$\mathscr{V}_1 = \mathscr{V}_2$	3·603 ± 0·003	238
	$\mathscr{V}_1 = (\sigma_1/\sigma_2)^2\, \mathscr{V}_2$	3·573 ± 0·002	238
1·0/0·6	$\sigma_1 = \sigma_2$	4·897 ± 0·003	238
	$\mathscr{V}_1 = \mathscr{V}_2$	4·890 ± 0·007	238
	$\mathscr{V}_1 = \tfrac{2}{3}\mathscr{V}_2$	4·856 ± 0·006	238
0·2/0·4	$\sigma_1 = \sigma_2$	3·08 ± 0·15	237
0·2/0·6	$\sigma_1 = \sigma_2$	3·32 ± 0·16	237

TABLE XXV

Third and fourth virial coefficients of mixtures of homonuclear diatomics taken from ref.[238]. The virial coefficients are reduced by appropriate powers of σ_{12}; $L_i^* = L_i/\sigma_i$

Component		L_1^*/L_2^*		
	0·6/0·0	0·6/0·0	0·6/0·0	0·6/0·3
	$\sigma_1 = \sigma_2$	$\mathscr{V}_1 = \mathscr{V}_2$	$\mathscr{V}_1 = \frac{2}{3}\mathscr{V}_2$	$\sigma_1 = \sigma_2$
C_{111}	10·64 ± 0·05	5·77 ± 0·03	3·65 ± 0·02	10·64 ± 0·05
C_{112}	6·82 ± 0·03	5·43 ± 0·03	4·54 ± 0·02	8·78 ± 0·04
C_{122}	4·34 ± 0·02	5·08 ± 0·03	5·57 ± 0·03	7·22 ± 0·04
C_{222}	2·74 ± 0·01	4·78 ± 0·02	6·79 ± 0·03	5·93 ± 0·03
		L_1^*/L_2^*		
	1·0/0·0	1·0/0·0	1·0/0·0	1·0/0·6
	$\sigma_1 = \sigma_2$	$\mathscr{V}_1 = \mathscr{V}_2$	$\mathscr{V}_1 = \frac{2}{3}\mathscr{V}_2$	$\sigma_1 = \sigma_2$
C_{111}	18·68 ± 0·09	8·98 ± 0·04	5·64 ± 0·03	18·68 ± 0·09
C_{112}	9·88 ± 0·05	7·50 ± 0·04	6·24 ± 0·03	15·47 ± 0·08
C_{122}	5·22 ± 0·03	6·29 ± 0·03	6·85 ± 0·03	12·85 ± 0·06
C_{222}	2·74 ± 0·01	5·27 ± 0·02	7·44 ± 0·04	10·64 ± 0·05
		L_2^*/L_2^*		
	0·6/0·0	0·6/0·0	0·6/0·0	0·6/0·3
	$\sigma_1 = \sigma_2$	$\mathscr{V}_1 = \mathscr{V}_2$	$\mathscr{V}_1 = \frac{2}{3}\mathscr{V}_2$	$\sigma_1 = \sigma_2$
D_{1111}	18·98 ± 0·19	7·58 ± 0·08	3·81 ± 0·04	18·98 ± 0·19
D_{1112}	11·59 ± 0·12	7·18 ± 0·07	4·94 ± 0·05	15·48 ± 0·15
D_{1122}	7·12 ± 0·07	6·79 ± 0·07	6·35 ± 0·06	12·54 ± 0·13
D_{1222}	4·34 ± 0·04	6·41 ± 0·06	8·12 ± 0·08	10·17 ± 0·10
D_{2222}	2·64 ± 0·03	6·06 ± 0·06	10·29 ± 0·10	8·31 ± 0·08
		L_1^*/L_2^*		
	1·0/0·0	1·0/0·0	1·0/0·0	1·0/0·6
	$\sigma_1 = \sigma_2$	$\mathscr{V}_1 = \mathscr{V}_2$	$\mathscr{V}_1 = \frac{2}{3}\mathscr{V}_2$	$\sigma_1 = \sigma_2$
D_{1111}	40·03 ± 0·40	13·33 ± 0·13	6·63 ± 0·07	40·03 ± 0·40
D_{1112}	20·16 ± 0·20	11·33 ± 0·11	7·80 ± 0·08	33·17 ± 0·33
D_{1122}	10·21 ± 0·10	9·68 ± 0·10	9·07 ± 0·09	27·53 ± 0·28
D_{1222}	5·14 ± 0·05	8·29 ± 0·08	10·32 ± 0·10	22·98 ± 0·23
D_{2222}	2·64 ± 0·03	7·02 ± 0·07	11·79 ± 0·12	18·98 ± 0·19

siderably underestimates B_4 of pure nonspherical components. This is presumably due to the approximation $\Delta v_{12} = 0$ and better results may be therefore anticipated for CB mixtures.

5.3. *Simulation Results for the Compressibility Factor*

5.3.1. Hard Sphere Mixtures

Additive HS. There are several sets of data covering the range of diameter ratios σ_1/σ_2 from 0·3333 up to 0·9091. Besides the most frequently simulated equimolar mixtures, concentration ends have been studied as well. The data are listed in Table XXVIII. Unlike other systems, for some sets of data we have not been able to specify estimates of the simulation uncertainties. The list of data contains also the results due to Smith and Lea[239] which were obtained with very small samples only – in most cases with 32 particles.

Non-additive HS. There are two sets of data: one for $\delta > 0$ due to Melnyk and Sawford[240] and one for $\delta < 0$ due to Adams and McDonald[241].

For $\delta > 0$ the system is expected to exhibit a fluid–fluid transition: if the density increases the components should separate in order to minimize the volume (and thus G) excluded by hard spheres. In a special case of $\sigma_1 = \sigma_2 = 0$, $\delta \neq 0$, (*cf.* Eq. (*5.18*)) the model is isomorphic to the Widom–Rowlinson[242] model of pene-

TABLE XXVI

Comparison of the second cross virial coefficients of mixtures of homonuclear diatomics ($L^* = L/\sigma$) given by Eq. (*5.27*) with exact data

L_1^*/L^*	Conditions	B_{12}/σ_{12}^3		
		Eq. (*5.27*)	Eq. (*5.27*) with $\Delta v_{12} = 0$	exact
0·6/0·3	$\sigma_1 = \sigma_2$	3·615	3·618	3·616
	$\mathcal{V}_1 = \mathcal{V}_2$	3·600	3·603	3·603
	$\mathcal{V}_1 = (\sigma_1/\sigma_2)^2\, \mathcal{V}_2$	3·568	3·571	3·573
1·0/0·6	$\sigma_1 = \sigma_2$	4·890	4·920	4·897
	$\mathcal{V}_1 = \mathcal{V}_2$	4·883	4·914	4·890
	$\mathcal{V}_1 = \frac{2}{3}\mathcal{V}_2$	4·848	4·885	4·856
0·2/0·4	$\sigma_1 = \sigma_2$	3·09	3·09	3·07
0·2/0·6	$\sigma_1 = \sigma_2$	3·41	3·42	3·32

trable spheres. Melnyk and Sawford considered the case $\sigma_1 = \sigma_2 = \sigma$ and $\delta = 0{\cdot}2$. They simulated equimolar mixtures within the range of the packing fraction $\eta \in (0{\cdot}15, 0{\cdot}35)$ and diluted mixtures with concentrations up to 0·1 at $\delta = 0{\cdot}3$. For the equimolar mixture they deduced an estimate of the critical point associated with demixing to be

$$\eta_c = 0{\cdot}22 \pm 0{\cdot}02$$
$$(\beta P/\varrho)_c = 0{\cdot}85 \pm 0{\cdot}10\,. \tag{5.30}$$

TABLE XXVII

Comparison of the approximate and exact results of the 3rd and 4th virial coefficients of hard sphere and homonuclear diatomic mixtures. $L_i^* = L_i/\sigma_i$ and $\sigma_{HS} = \sigma_{diatomic}$. The virial coefficients are reduced by the appropriate power of σ_{12}

Component	$\sigma_1/\sigma_2 = 0{\cdot}60$		$\sigma_1/\sigma_2 = 0{\cdot}333$	
	Eq. (*5.26*)	exact	Eq. (*5.26*)	exact
D_{1111}	0·1940	0·19789	0·00505	0·00515
D_{1112}	0·6619	0·66367	0·0819	0·07938
D_{1122}	2·163	2·0900	1·161	1·0464
D_{1222}	6·691	6·7957	13·08	12·275
D_{2222}	19·25	19·637	99·33	101·32

Component	$L_1^*/L_2^* : 0{\cdot}6/0{\cdot}0$		$L_1^*/L_2^* : 1{\cdot}0/0{\cdot}0$	
	Eq. (*5.23*)	exact	Eq. (*5.23*)	exact
C_{111}	10·57	10·64	18·37	18·68
C_{112}	6·80	6·82	9·78	9·88
C_{122}	4·33	4·34	5·19	5·22
C_{222}	2·74	2·74	2·74	2·74
	Eq. (*5.26*)	exact	Eq. (*5.26*)	exact
D_{1111}	17·59	18·98	33·01	40·03
D_{1112}	10·98	11·59	17·55	20·16
D_{1122}	6·81	7·12	9·29	10·21
D_{1222}	4·21	4·34	4·91	5·14
D_{2222}	2·58	2·64	2·58	2·64

TABLE XXVIII

Compressibility factors of mixtures of additive hard spheres

σ_1/σ_2	x_1	η	$\beta P/\varrho$
0·9091[a]	0·5	0·1168	1·63
		0·1296	1·71
		0·1620	2·02
		0·1969	2·37
		0·2334	2·83
		0·2544	3·13
		0·2716	3·41
		0·3107	4·19
		0·3503	5·23
		0·3902	6·45
		0·3928	6·57
		0·4073	7·06
		0·4212	7·75
		0·4301	8·36
		0·4344	8·51
		0·4470	8·99
		0·4589	9·83
0·90[b]	0·5	0·49	12·3
	0·75	0·47	10·6
0·60[c]	0·125	0·2618	3·09
	0·25	0·2618	3·02
		0·3665	4·95
	0·5	0·1571	1·85
		0·2094	2·30
		0·2618	2·97
			2·96
			2·92
			3·01
		0·3142	4·02
			4·16
		0·3665	5·22
			4·93
			5·02
			5·15
		0·3864	5·86
		0·4189	7·11
		0·4451	8·19
	0·75	0·2618	3·13
		0·3665	5·43

At $\eta = 0{\cdot}3$ they obtained

$$x_1' = 0{\cdot}029 \pm 0{\cdot}006\,. \quad x_2'' = x_1'$$
$$\beta P/\varrho = 4{\cdot}22 \pm 0{\cdot}05 \tag{5.31}$$

for the concentration and compressibility factor, respectively, at the coexistence curve. The results are shown in Table XXIX.

For $\delta < 0$ no phase transition exists and equimolar mixtures with $\sigma_1 = \sigma_2 = \sigma$ and $-\delta = 0{\cdot}1$, $0{\cdot}2$, $0{\cdot}3$, $0{\cdot}4$, and $0{\cdot}5$ were simulated. The results are shown in Table XXX.

TABLE XXVIII
(*Continued*)

σ_1/σ_2	x_1	η	$\beta P/\varrho$
0·5[d]	0·80078	0·45	7·55
		0·50	10·1
		0·55	14·3
	0·89844	0·45	7·82
		0·50	10·7
		0·55	14·8
		0·59	22·5[e]
	0·95	0·45	8·17
		0·50	11·5
		0·55	16·4
0·33	0·50	0·233	2·37 ± 0·02[f]
		0·269	2·78 ± 0·03[f]
		0·311	3·36 ± 0·03[f]
		0·358	4·24 ± 0·04[f]
		0·381	4·76 ± 0·05[f]
		0·439	6·57 ± 0·07[f]
		0·507	9·77 ± 0·10[f]
	0·938	0·45	6·27[d]
		0·50	8·47[d]
		0·55	11·3[d]
	0·98	0·45	8·42[d]
0·30	0·5	0·49	8·81[b]

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[a] Taken from ref.[247]. The compressibility factors have been calculated from the data on $g_{\alpha\beta}$ at contact; no error specification of the original data was given. [b] Taken from ref.[248]. No error estimate specified. [c] Taken from ref.[239]. Most of date were obtained with 32 particles only. [d] Taken from ref.[249]. Accuracy of the data is about 3 per cent. [e] Metastable fluid range. [f] Taken from ref.[246].

TABLE XXIX

Compressibility factors of mixtures of nonadditive hard spheres with $\sigma_1 = \sigma_2$ and $\delta = 0{\cdot}2$ (ref.[240])

Concentration	η	$\beta P/\varrho$
$x_1 = x_2 = 0{\cdot}5$	0·15	2·36 ± 0·01
	0·20	3·12 ± 0·02
	0·22	3·47 ± 0·02
	0·25	3·90 ± 0·03
	0·30	5·01 ± 0·04
	0·35	6·70 ± 0·07

Density	x_1	$\beta P/\varrho$
$\eta = 0{\cdot}30$	0·0234	4·20 ± 0·02
	0·0352	4·25 ± 0·02
	0·0469	4·32 ± 0·03
	0·0625	4·44 ± 0·02
	0·1016	4·69 ± 0·03

TABLE XXX

Compressibility factors of equimolar mixtures of nonadditive hard spheres with $\sigma_1 = \sigma_2$ (ref.[241]). The compressibility factors are accurate to within 5 per cent

η	$-\delta$				
	0·1	0·2	0·3	0·4	0·5
0·1047	1·46	—	1·31	—	1·26
0·1571	1·80	—	—	—	—
0·2094	2·17	—	1·80	—	1·61
0·3142	3·39	—	2·43	—	2·06
0·4189	5·22	3·95	3·12	—	2·65
0·5236	8·63	5·60	4·25	3·69	3·40
0·6283	12·23	8·07	5·73	4·99	4·61
0·7330	—	—	7·89	6·53	5·92
0·8376	—	—	—	—	8·10

5.3.2. Other Mixtures

The list of simulated mixtures, especially of those with both nonspherical components, is quite scanty.

Concerning the CB fluids, mixtures of spheres and prolate spherocylinders were studied by Boublík and Nezbeda[230,243] and Monson and Rigby[244]. The former authors considered both equimolar and non-equimolar mixtures with components of the same diameter. The latter authors considered two equimolar mixtures, one with components of the same volume and the other with the same diameters. The results are listed in Table XXXI.

For the FHS models there are four sets of data. Aviram and Tildesley[237] and Wojcik and Gubbins[238] studied mixtures of homonuclear diatomics and of these with spheres. In order to extend the list of data by other, qualitatively different models, Nezbeda and coworkers[121,245] simulated quite recently binary mixtures (both equi-

TABLE XXXI

Compressibility factors of mixtures of hard spheres (1) and prolate spherocylinders (2) of $\gamma = 2$

Conditions		$\beta P/\varrho$		
	η	$x_1 = 0·20$	$x_1 = 0·50$	$x_1 = 0·7143$
$\sigma_{HS} = \sigma_{PSC}$	0·20		$2·50 \pm 0·06^a$	
	0·2979			$4·03 \pm 0·07^c$
	0·30		$4·10 \pm 0·05^a$	
	0·3128		$4·52 \pm 0·08^b$	
	0·3277	$5·17 \pm 0·10^c$		
	0·3965			$7·02 \pm 0·12^c$
	0·40		$7·31 \pm 0·07^a$	
	0·4163		$8·07 \pm 0·15^b$	
	0·4361	$9·89 \pm 0·20^c$		
	0·45		$9·87 \pm 0·10^a$	
	0·4530			$9·70 \pm 0·21^c$
	0·4757		$11·59 \pm 0·23^b$	
	0·4983	$14·34 \pm 0·40^c$		
$\mathcal{V}_{HS} = \mathcal{V}_{PSC}$	0·20		$2·52 \pm 0·04^a$	
	0·30		$4·20 \pm 0·05^a$	
	0·40		$7·39 \pm 0·06^a$	
	0·45		$10·22 \pm 0·10^a$	

[a] Ref.[244]. [b] Ref.[230]. [c] Ref.[243].

molar and non-equimolar) composed of spheres, heteronuclear diatomics, and linear symmetric triatomics. All these data are listed in Tables XXXII–XXXVI.

The main conclusions of all the simulations (for additive mixtures) may be summarized as follows:

(i) The excess volume is very small and usually within uncertainties of simulations, $V^E \approx 0$.

(ii) The effect of molecular shape on the compressibility factor of the mixture is quite strong. This often leads to a large difference between the mixture compressibility factor and that of the HS mixture whose components have the same volume as those of the molecular fluid mixture.

(iii) The effects of mixing are, at least for the properties considered, not very pronounced. This is reflected in the fact that the pair correlation functions of the mixtures differ only slightly from those in the corresponding pure fluids at the same overall density.

TABLE XXXII

Compressibility factors of mixtures of homonuclear diatomics with $\sigma_1 = \sigma_2$ ($L^* = L/\sigma$)

Conditions	η	$\beta P/\varrho$		
		$x_1 = 0{\cdot}25$	$x_1 = 0{\cdot}50$	$x_1 = 0{\cdot}75$
$L_1^* = 0{\cdot}6$; $L_2 = 0{\cdot}0$[a]	0·30		4·20	
	0·45	9·78	10·15	10·76
$L_1^* = 1{\cdot}0$; $L_2 = 0{\cdot}0$[a]	0·30		4·88	
	0·35	5·95		7·26
	0·43	9·74	11·06	12·31
$L_1^* = 0{\cdot}4$; $L_2^* = 0{\cdot}2$[b]	0·0750		1·41	
	0·1500		2·02	
	0·2249		2·94	
	0·2999		4·58	
	0·3749		7·54	
	0·4499		12·78	
$L_1^* = 0{\cdot}6$; $L_2^* = 0{\cdot}2$[b]	0·0808		1·47	
	0·1617		2·22	
	0·2425		3·39	
	0·3234		5·50	
	0·4042		9·34	

[a] Ref.[238]. Error in $\beta P/\varrho$ is about 3 per cent. [b] Ref.[237]. Error in $\beta P/\varrho$ is about 3·5 per cent.

5.4. *Theories of Mixtures of Hard Spheres*

5.4.1. Additive Hard Spheres

Scaled particle theory. Derivation of the SPT equation of state for mixtures follows the same route as that for pure fluids[155].

Let R_α be the radius of spheres α and R_t the radius of a test particle which is gradually coupled into the system considered. Then the interaction potential $u_{\alpha t}(r)$ of a pair α–t equals zero for $r > R_\alpha + R_t$ and infinity otherwise. If $R_t = 0$ we have a point-wise particle and the total decoupling is reached for $R_t = -R_m$ where R_m is the radius of the largest HS. For $R_t < 0$ the excluded volume $V_{t+\alpha}$ is smaller than volume $\mathcal{V}_\alpha$ of a given particle. This fact makes it possible to write an exact expression for $\mathcal{G}$ at $r = R_t + R_\alpha$ (for definition of $\mathcal{G}$ and other details see Section 4.1. and Subsection 4.4.2.):

$$\mathcal{G}(R_t + R_\alpha) = 1/(1 - \Sigma \varrho_\beta \mathcal{V}_{t+\beta}) , \quad R_t < 0 . \tag{5.32}$$

TABLE XXXIII

Compressibility factors of mixtures of homonuclear diatomics (ref.[238]). Error in $\beta P/\varrho$ is about 4 per cent; $L^* = L/\sigma$

Conditions	Length of dumbells	$\beta P/\varrho$			
		η	$x_1 = 0{\cdot}25$	$x_1 = 0{\cdot}50$	$x_1 = 0{\cdot}75$
$\mathcal{V}_1 = \mathcal{V}_2$	$L_1^* = 0{\cdot}6, L_2 = 0{\cdot}0$	0·30		4·25	
		0·45	9·76	10·27	10·82
	$L_1^* = 1{\cdot}0, L_2 = 0{\cdot}0$	0·30		4·83	
		0·43		10·71	
	$L_1^* = 0{\cdot}6, L_2^* = 0{\cdot}3$	0·30		4·30	
		0·45		10·52	
	$L_1^* = 1{\cdot}0, L_2^* = 0{\cdot}6$	0·45	12·14	13·27	14·37
$\mathcal{V}_1 = \frac{2}{3}\mathcal{V}_2$	$L_1^* = 0{\cdot}6, L_2 = 0{\cdot}0$	0·30		4·19	
		0·45	9·63	10·06	10·60
	$L_1^* = 1{\cdot}0, L_2 = 0{\cdot}0$	0·30		4·63	
		0·43		10·24	
	$L_1^* = 1{\cdot}0, L_2^* = 0{\cdot}6$	0·45	11·86	12·92	13·94
$\mathcal{V}_1 = (\sigma_1/\sigma_2)^2 \mathcal{V}_2$	$L_1^* = 0{\cdot}6, L_2^* = 0{\cdot}3$	0·30		4·27	
		0·45		10·25	
				10·29	

TABLE XXXIV

Compressibility factors of mixtures of hard spheres (1) and heteronucelar dumbells (2). $L/\sigma_A = 0·625$, $\sigma_B/\sigma_A = 0·5$. Values for the equimolar mixtures are taken from ref.[121], for the non-equimolar mixtures from ref.[245]. The compressibility factors are accurate to within 4 per cent

Conditions	η	$\beta P/\varrho$		
		$x_1 = 0·25$	$x_1 = 0·50$	$x_1 = 0·75$
$\sigma_{HS} = \sigma_A$	0·25	3·40	3·26	3·19
	0·30	4·45	4·26	4·17
	0·35	5·88	5·66	5·50
	0·40	7·96	7·73	7·35
$\sigma_{HS} = \sigma_B$	0·25	3·21	2·94	2·77
	0·30	4·22	3·84	3·58
	0·35	4·61	5·04	4·64
	0·40	7·61	6·63	6·09
$\mathcal{V}_{HS} = \mathcal{V}_{DB}$	0·25	3·37	3·26	3·21
	0·30	4·48	4·33	4·14
	0·35	5·88	5·57	5·46
	0·40	7·91	7·54	7·30

TABLE XXXV

Compressibility factors of mixtures of hard spheres (1) and linear symmetric triatomics (2). $L/\sigma_C = 1·6$, $\sigma_A/\sigma_C = 1·0$. Values for the equimolar mixtures are taken from ref.[121], for the non-equimolar mixtures from ref.[245]. The compressibility factors are accurate to within 4 per cent

Conditions	η	$\beta P/\varrho$		
		$x_1 = 0·25$	$x_1 = 0·50$	$x_1 = 0·75$
$\sigma_{HS} = \sigma_C$	0·25	4·11	3·69	3·36
	0·30	5·56		4·50
	0·35	7·68	6·68	5·98
	0·40	10·44		8·01
$\mathcal{V}_1 = \mathcal{V}_2$	0·25	4·03		3·35
	0·30	5·46		4·40
	0·35	7·52		5·92
	0·40	10·36		7·95

Another exact relation holds for $R_t \to \infty$, *i.e.* when the surface of the test particle is planar and the stress is purely kinetic:

$$\lim_{R_t \to \infty} \Sigma \varrho_\alpha \mathscr{G}(R_t + R_\alpha) = \beta P = \Sigma \beta P_\alpha \,. \qquad (5.33)$$

Similarly to pure fluids, for $R_t \geqq 0$ the function $\mathscr{G}$ can be estimated by a polynomial whose coefficients are determined from (*5.33*) and from the known values of $\mathscr{G}$ and its first derivative at $R_t = 0$:

$$\mathscr{G}(R_\alpha) = 1/(1 - \eta) \qquad (5.34)$$

$$\mathscr{G}'(R_\alpha) = 4\pi \Sigma R_\beta^2 \varrho_\beta/(1 - \eta)^2 \,. \qquad (5.35$$

The contact value of the radial distribution function $g_{\alpha\beta}$, required for determining EOS, equals $\mathscr{G}(R_t + R_\alpha)$ in the case of $R_t = R_\beta$. It holds:

$$g_{\alpha\beta}(\sigma_{\alpha\beta}) = \mathscr{G}(R_\beta + R_\alpha) \equiv \mathscr{G}_{\beta\alpha} =$$

$$= \frac{1}{1 - \eta} + \frac{6\zeta_2}{(1 - \eta)^2} \frac{R_\alpha R_\beta}{R_\alpha + R_\beta} + \frac{12\zeta_2^2}{(1 - \eta)^3} \left(\frac{R_\alpha R_\beta}{R_\alpha + R_\beta}\right)^2 , \qquad (5.36)$$

where quantities ζ_i are defined by

$$\zeta_i = \frac{\pi}{6} \Sigma \varrho_\alpha (2R_\alpha)^i \,, \quad 0 \leqq i \leqq 3 \,, \quad (\zeta_3 \equiv \eta) \,. \qquad (5.37)$$

TABLE XXXVI

Compressibility factors of an equimolar mixture (ref.[121]) of heteronuclear dumbells ($\sigma_B/\sigma_A = 0{\cdot}5$, $L/\sigma_A = 0{\cdot}625$) and linear symmetric triatomics ($L/\sigma_C = 1{\cdot}6$, $\sigma_A/\sigma_C = 1{\cdot}0$) with $\sigma_{A,\text{dumbell}} = \sigma_{C,\text{triatomic}}$. The compressibility factors are accurate to within 4 per cent

η	$\beta P/\varrho$
0·25	3·69
0·30	4·92
0·35	6·70
0·40	9·20

The EOS corresponding to Eq. (*5.36*) is

$$\beta P/\varrho = \frac{1}{1-\eta} + \frac{3\zeta_1\zeta_2}{\zeta_0(1-\eta)^2} + \frac{3\zeta_2^3}{\zeta_0(1-\eta)^3} \tag{5.38}$$

which is, similarly to the case of pure hard spheres, identical to the c-form of the P–Y EOS (see below).

For pure hard spheres Eq. (*5.38*) works only fair and it is not therefore possible to assume this equation to do better for mixtures. A modification of Eq. (*5.38*) has been proposed independently by Boublík[193] and Mansoori and coworkers[250] with the same final results. Following the same way as that leading from the SPT equation (*4.61*) to the C–S equation (*4.44*) (*cf.* derivation of Eq. (*4.105*)), it is easy to obtain for a mixture the equation (BMCSL equation)

$$\beta P/\varrho = \frac{1}{1-\eta} + \frac{3\zeta_1\zeta_2}{\zeta_0(1-\eta)^2} + \frac{\zeta_2^3(3-\eta)}{\zeta_0(1-\eta)^3} \tag{5.39}$$

which reduces to the C–S equation for pure fluids.

The same trick as that used for the above extension of the C–S equation to mixtures can be also applied to Eq. (*4.46*). Because of the additional term over the C–S equation, Boublík[251] made further use of the fact that for $\eta = 0{\cdot}5$ Eqs (*4.44*) and (*4.46*) coincide and obtained

$$\beta P/\varrho = \frac{1}{(1-\eta)} + \frac{3\zeta_1\zeta_2}{\zeta_0(1-\eta)^2} + \frac{\zeta_2^3(9-2\eta-2\eta^2)}{3\zeta_0(1-\eta)^3}\,. \tag{5.40}$$

In Table XXXVII the results given by Eqs (*5.39*) and (*5.40*) are compared with simulation data. It is seen that the BMCSL equation performs very well throughout the entire density range. Eq. (*5.40*) yields practically identical results. It should be reminded that in the limiting case when the ratio of diameters of components tends to zero, both the above discussed equations give the exact result, see Eq. (*5.9*). In fact, this is a common feature of all equations based on the SPT-form of the correlation function $\mathscr{G}$. It can be also simply proved that Eqs (*5.38*) through (*5.40*) satisfy Eq. (*5.16*).

Percus–Yevick theory. Starting from the O–Z relation for mixtures, Eq. (*5.8*), and coupling it with the P–Y closure,

$$c_{\alpha\beta}(r) = f_{\alpha\beta}(r)\, y_{\alpha\beta}(r) \tag{5.41}$$

a set of integral equations results. Lebowitz[252] followed Wertheim's method used for the pure fluid and obtained the following analytic result for the direct correlation function of a mixture:

$$\begin{aligned} -c_{\alpha\alpha}(r) &= a_\alpha + b_\alpha r + dr^3\,, \quad r < \sigma_\alpha\,, \quad \alpha = 1, 2 \\ -c_{12}(r) &= a_1 \quad \text{for} \quad r < \lambda = (\sigma_2 - \sigma_1)/2\,, \quad \sigma_2 > \sigma_1 \\ &= a_1 + \frac{1}{r}\left[b(r - \lambda)^2 + 4\lambda d(r - \lambda)^3 + d(r - \lambda)^4\right] \\ &\qquad \text{for} \quad \lambda \leqq r \leqq \sigma_{12}\,, \end{aligned} \tag{5.42}$$

where b, d, a_α, and b_α are density-dependent parameters (see the original literature or ref.[25] for details). EOS follows immediately once the direct correlation function

TABLE XXXVII

Compressibility factors of equimolar mixtures of additive hard spheres evaluated from approximate theories

σ_1/σ_2	η	$\beta P/\varrho$					
		Eq. (*5.39*)	Eq. (*5.40*)	Eq. (*5.47*)	L–H–B[a]	vdW[b]	exact
0·9091	0·1296	1·73	1·73	1·73	1·73	1·73	1·71
	0·2334	2·82	2·83	2·80	2·81	2·82	2·83
	0·3107	4·19	4·20	4·15	4·17	4·19	4·19
	0·4073	7·20	7·22	7·15	7·13	7·19	7·06
	0·4589	9·88	9·90	9·91	9·75	9·85	9·83
0·60	0·2094	2·37	2·38	2·35	2·15	2·33	2·30
	0·3142	3·95	3·96	3·88	3·32	3·77	4·02
							4·16
	0·3864	5·82	5·84	5·70	4·56	5·40	5·86
	0·4451	8·20	8·22	8·06	6·00	7·37	8·19
0·3333	0·2333	2·37	2·37	2·37	1·77	2·23	2·37
	0·3106	3·36	3·36	3·38	2·16	2·99	3·36
	0·3808	4·76	4·78	4·83	2·62	3·97	4·76
	0·4393	6·57	6·58	6·74	3·10	5·08	6·57
	0·5068	9·90	9·89	10·51	3·77	6·87	9·77

[a] First-order perturbation theory with a pure hard sphere reference — Eq. (*5.53*). [b] First-order perturbation theory with a pure hard sphere reference — Eq. (*5.55*).

is known. The virial form reads as

$$\beta P/\varrho = \frac{1}{1-\eta} + \frac{3\zeta_1\zeta_2}{\zeta_0(1-\eta)^2} + \frac{3\zeta_2^3(1-\eta)}{\zeta_0(1-\eta)^3} \qquad \text{(v)} \qquad (5.43)$$

while the compressibility c-form is identical to the SPT equation (*5.38*).

A thorough analysis of the P–Y theory results was carried through by Lebowitz and Rowlinson[253]. Similarly to the case of pure HS, the P–Y (v) and (c) results bound the correct pressure with discrepancies not exceeding 5 per cent and both are exact for $\sigma_1/\sigma_2 \to 0$. The excess volume V^E is always negative when the c-form is used but it becomes positive at high pressures if it is evaluated from the v-form. However, G^E is always negative and no phase separation thus takes place. Concerning the consistency expressed by Eq. (*5.16*), both the c- and v-forms satisfy this equation.

Extended Andrews' EOS. Andrews and Ellerby[254] followed the same ideas which had lead to Eq. (*4.65*) for pure HS. They introduce a quantity w_α which is a volume occupied by all particles when they are jammed together so that there is no space available for a test particle of type α. Volume w_α enables one to express the conditional probability that, provided that there is a free space in vicinity of a molecule of type β to absorb a point, there is also an additional space to absorb a test particle of type α. After realizing that the probability that a randomly chosen point lies outside all hard spheres equals one minus the fraction of the unoccupied space, *i.e.* $(1 - \Sigma N_\alpha \mathscr{V}_\alpha / V)$, the residual chemical potential of species α can be written as

$$\exp\left[-\beta\mu_{\text{res},\alpha}\right] = \left(1 - \frac{\pi}{6}\varrho \sum_\beta x_\beta \sigma_\beta^3\right) \exp\left\{-\frac{\pi\varrho}{6(1-\varrho w_\alpha)} \sum_\beta x_\beta\left[(\sigma_\alpha+\sigma_\beta)^3 - \sigma_\beta^3\right]\right\}. \qquad (5.44)$$

Volume w_α depends slightly on density and Andrews and Ellerby approximate this dependence by a linear function,

$$w_\alpha = w_{0,\alpha} + d(w_{c,\alpha} - w_{0,\alpha}), \qquad (5.45)$$

where d is a reduced density (*cf.* Subsection 4.4.2.),

$$d = \frac{1}{\sqrt{2}} \varrho\sigma^3 \Sigma x_\alpha t_\alpha^3 \equiv \frac{1}{\sqrt{2}} \varrho\varepsilon\sigma^3, \qquad (5.46)$$

σ is the smallest diameter, and $t_\alpha = \sigma_\alpha/\sigma$. Parameter $w_{c,\alpha}$ is given by w_α at the close-packed volume and $w_{0,\alpha}$ can be determined from the third virial coefficient; for both these quantities approximate expressions were used. The EOS corresponding to (*5.44*) assumes then the form

$$\beta P/\varrho = \Sigma x_\alpha \left\{ \frac{b_\alpha d}{1 - (1 + \Delta_\alpha)\, d + \Delta_\alpha d^2} - \frac{6}{\pi \sqrt{2} d} \ln\left(1 - \frac{\pi \sqrt{2} d}{6}\right) - \right.$$

$$\left. - \frac{b_\alpha (1 + \Delta_\alpha)}{2\Delta_\alpha (1 - \Delta_\alpha)\, d} \ln\left(\frac{1 - d\Delta_\alpha}{1 - d}\right) - \frac{b_\alpha}{2d\Delta_\alpha} \ln\left[1 - (1 + \Delta_\alpha)\, d + \Delta_\alpha d^2\right] \right\}. \quad (5.47)$$

Here

$$b_\alpha = \frac{\pi \sqrt{2}}{6\varepsilon} \sum_\beta x_\beta [(t_\alpha + t_\beta)^3 - t_\beta^3] \quad (5.48)$$

$$\Delta_\alpha = \frac{29\pi \sqrt{2}}{84\varepsilon} \sum_\beta x_\beta a_{\alpha\beta} t_\beta^3 - 1 \quad (5.49)$$

and

$$a_{\alpha\beta} = 1 \quad \text{for} \quad t_\alpha / t_\beta \geqq 1\,,$$

$$a_{\alpha\beta} = \frac{14}{29} + \frac{15 t_\alpha}{29 t_\beta} \quad \text{for} \quad t_\alpha / t_\beta \leqq 1\,. \quad (5.50)$$

Examining Table XXXVII one can see that Eq. (*5.47*) yields results comparable or, at higher densities, inferior to Eq. (*5.39*).

One fluid approach. In addition to the above extensions of the pure fluid theories there are also methods developed solely for mixtures. They all have two factors in common: (i) to first order, the properties of a mixture, apart from the ideal entropy of mixing, are estimated by a suitably defined pure fluid reference and (ii) they enjoy considerable flexibilily in choosing the parameter of expansion. A review on most of these theories can be found in ref.[255]. It is also worth mentioning that a number of theories, at least in the lowest order, coincide for HS mixtures.

One-fluid reference perturbation theory has been developed by Leonard and coworkers[256] as an extension of the Barker–Henderson theory[257], but the results for HS mixtures were obtained already earlier by Henderson and Barker[258]. Up to the first order, the free energy is given by

$$\beta(F - F_0)/N = \sum x_\alpha \ln x_\alpha + 12\eta g_{\mathrm{HS}}(\sigma_0 +)\, \Delta\,, \quad (5.51)$$

where subscript zero denotes properties of a pure fluid HS reference and, in general,

$$\Delta = \sigma_0^n - \sum x_\alpha x_\beta \sigma_{\alpha\beta}^n\,. \quad (5.52)$$

In the simplest version, the expansion is performed directly in powers of $\sigma_{\alpha\beta} - \sigma_0$ (*i.e.* $n = 1$) and the diameter of the reference HS is determined by anulling the first-order term of the expansion. The result is

$$\sigma_0 = \sum x_\alpha x_\beta \sigma_{\alpha\beta} \tag{5.53}$$

which for additive HS simplifies to

$$\sigma_0 = x_1\sigma_1 + x_2\sigma_2 . \tag{5.54}$$

One may expect that expansion in direct potential parameters will be inferior to other, more flexible choices. Smith[205] examined a family of conformal expansions and showed that the best result is achieved when the volume is taken as a variable. It means for spheres to expand in powers of $\sigma_{\alpha\beta}^3 - \sigma_0^3$. With this choice the diameter of the reference HS is given by

$$\sigma_0^3 = \sum x_\alpha x_\beta \sigma_{\alpha\beta}^3 \tag{5.55}$$

which is identical to the original van der Waals (vdW) one-fluid theory and the conformal solution theory (for details see ref.[255]).

Table XXXVII also shows the results given by the first-order one-fluid theories $n = 1$ and 3. It is seen that the choice $n = 3$ is clearly better, but yet inferior to Eqs (*5.39*) and (*5.40*). However, if these theories are extended to second order then the reverse is true and the choice $n = 1$ yields quite accurate results[255]. This may indicate that this choice has better convergence properties.

The expansion in powers of $\sigma_{\alpha\beta} - \sigma_0$ is not the only choice but besides simplicity it has also the virtue of annulling the most complex term in the second-order expansion.

It is known that for hard body mixtures the excess volume V^E is very small, $V^E \approx 0$. One may therefore define σ_0 so that $V^E = 0$ in zero order[255]. This may be a better choice but the theory would be definitely more complex and we are not aware of any result based on this assumption. Another possibility of utilizing the finding $V^E \approx 0$ is to use it directly for evaluating the EOS[246]. If $V^E = 0$ at constant pressure is assumed (*i.e.* ideal mixing), EOS of a mixture is given by those of pure components:

$$\beta P/\varrho = \sum x_\alpha z_\alpha , \tag{5.56}$$

where z_α is the compressibility factor of component α with $x_\alpha N$ particles at the pressure P. The results obtained from Eq. (*5.56*) are very good, with largest discrepancies appearing at low density[246]. Nevertheless, if the density is considered as an independent variable (which is usually the choice), then evaluation of $\beta P/\varrho$ is not straightforward and we may look upon this equation rather as a way of estimating the mixture compressibility factor by using those of pure components than a true EOS of a mixture.

Looking for an expansion parameter in a conformal theory it is tempting to choose the difference

$$\Delta_{\alpha\beta} = u_{\alpha\beta} - u_{\mathrm{ref}}\,, \tag{5.57}$$

where u_{ref} is an undefined reference potential. For HB fluids the perturbation $\Delta_{\alpha\beta}$ may become infinite and better would be to take thus the difference of the Mayer functions[259],

$$\Delta f_{\alpha\beta} = f_{\alpha\beta} - f_{\mathrm{ref}}\,.$$

On requiring again that the first order contribution to the Helmholtz free energy be zero we get

$$f_{\mathrm{ref}} = \sum x_\alpha x_\beta f_{\alpha\beta} \tag{5.58}$$

or, equivalently,

$$\beta u_{\mathrm{ref}} = -\ln \sum x_\alpha x_\beta \exp\left[-\beta u_{\alpha\beta}\right]. \tag{5.59}$$

The reference potential given by this equation is called the pseudopotential[260] and for the HS mixture (with $\sigma_1 < \sigma_2$) it reads as

$$\beta u_{\mathrm{ref}}(r) = \begin{array}{ll} \infty & \text{for} \quad r < \sigma_1 \\ -\ln x_1^2 & \text{for} \quad \sigma_1 < r < \sigma_{12} \\ -\ln\left(x_1^2 + 2x_1x_2\right) & \text{for} \quad \sigma_{12} < r < \sigma_2 \\ 0 & \text{for} \quad r < \sigma_2\,. \end{array} \tag{5.60}$$

Barker and coworkers[261] made MC simulations of the pure fluid given by (5.60), $x_1 = x_2 = 0{\cdot}5$, and $\sigma_1/\sigma_2 = 0{\cdot}6$, but the results were rather discouraging.

5.4.2. Non-additive Hard Spheres

There are several reasons making studies of this system appealing:

(i) within the context of perturbation theories an advantage would be gained if the diameter σ_{12} could be treated as an adjustable one. (For instance, in the Barker–Henderson theory with a multicomponent reference fluid the first-order term could be made to vanish with a suitable choice of σ_{12}).

(ii) Experimental data on the structure of certain liquid binary alloys (*e.g.* Cu–Sn) show that the partial structure factor of unlike ions does not fall midway between the other two. The simplest system exhibiting the same type of behaviour is just that of non-additive HS.

(iii) The non-additive system with $\delta < 0$ exhibits a fluid separation at higher densities; in a special case of $\sigma_1 = \sigma_2 = 0$ the system is isomorphic to the Widom--Rowlinson penetrable sphere model.

The non-additive HS mixtures with both $\delta < 0$ and $\delta > 0$ have been attacked by various theoretical methods: the P–Y theory, SPT, perturbation and conformal theories, and Padé approximants.

For mixtures with positive departure from additivity, Lebowitz and coworkers, in addition to the exact solution[262] in one dimension for $\delta \leqq (\sigma_2 - \sigma_1)/(\sigma_2 + \sigma_1)$, $\sigma_2 < \sigma_1$, solved also analytically the P–Y equation in three dimensions[263]. In a general case the equation was not solved explicitly because of its complexity. However, for $\sigma_1 = \sigma_2 = 0$ (*i.e.* for the Widom–Rowlinson model) they obtained the EOS in a closed form. The same model was also investigated by Melnyk and coworkers[234] by means of a Padé analysis based on the first seven terms (*cf.* Eq. (*5.20*)). Both approaches agree in locating the critical density at about $\varrho_c = 1{\cdot}674$ if the compressibility equation is used. The virial form of the EOS yields $\varrho_c = 1{\cdot}788$. It is also worth noting that there does not exist a solution of the P–Y equation beyond a certain maximum density.

A more general mixture with positive departure from additivity was investigated by Melnyk and Sawford[240]. They considered the case $\sigma_1 = \sigma_2 = \sigma$, $\delta = 0{\cdot}2$, and two variants of the perturbation theory: one with a pure HS and the other with an additive HS mixture reference. In the first case the free energy of the studied system is up to the first order term given by Eq. (*5.51*) with

$$\sigma_0^n = \sum x_\alpha x_\beta \sigma_{\alpha\beta}^n \tag{5.61}$$

and n is taken either 1 or 3 (*cf.* the preceding subsection). Employing the C–S equation of state, F_0 has the form

$$\beta F_0/N = \ln \varrho - 1 + (4\eta_0 - 3\eta_0^2)/(1 - \eta_0)^2 \,, \tag{5.62}$$

where $\eta_0 = \pi\varrho\sigma_0^3/6$ is the packing fraction of the HS reference. Due to the non-zero value of δ, $\delta > 0$, beginning from a critical density, ϱ_c, a demixing of the non-additive HS mixture into two phases, each with predominant content of molecules of one kind, occurs. Obviously, because of symmetry the critical point appears at $x_1 = x_2 = 0{\cdot}5$.

The condition of the critical point is

$$(\partial^2 F/\partial x_\alpha^2)_{T,\eta} = 0 \,. \tag{5.63}$$

Thus, on taking into account the relation between η (the packing fraction of the studied mixture) and η_0,

$$\eta_0/\eta = \{1 + 2x_1x_2[(1 + \delta)^n - 1]^{3/n}\}, \tag{5.64}$$

the dependence of the critical density on δ can be determined:

$$12\eta_{0,c}(2 - \eta_{0,c})/(1 - \eta_{0,c})^3 = n[(1 + \delta)^n + 1]/[(1 + \delta)^n - 1]. \tag{5.65}$$

For $n = 1$, $\eta_{0,c} = 0{\cdot}234$ and hence $\eta_c = 0{\cdot}176$ and for $n = 3$, $\eta_{0,c} = 0{\cdot}236$ which implies $\eta_c = 0{\cdot}173$. None of these values agrees with the simulation result of $\eta_c = 0{\cdot}22$.

In the case when the mixture of additive HS is chosen as a reference, $\eta_0 = \eta$ and $\beta(F - F_0)/N$ is – within the first order perturbation theory – given by the contribution of a pair of unlike molecules:

$$\beta(F - F_0)/N = 4\pi\varrho\sigma^3 x_1 x_2 g_{12}(\sigma)\,\delta. \tag{5.66}$$

Since $\sigma_1 = \sigma_2 = \sigma$, $g_{12}(\sigma)$ equals the contact value of the radial distribution of pure hard spheres which can be determined from an accurate EOS. For instance, from the C–S equation we get

$$g(\sigma) = (1 - \eta/2)/(1 - \eta)^3, \tag{5.67}$$

which in combination with (*5.63*) and (*5.66*) yields the following equation for η_c:

$$\eta_c^3 - 3(1 + 2\delta)\,\eta_c^2 + 3(1 + 4\delta)\,\eta_c - 1 = 0. \tag{5.68}$$

For $\delta = 0{\cdot}2$ the critical packing fraction is $\eta_c = 0{\cdot}221$, which perfectly agrees with the simulation result.

Melnyk and Sawford[240] also considered second order corrections to the above results but came to the conclusion that these were inferior to the first-order perturbation theory with the HS mixture reference.

Along with simulations for systems with negative departure from additivity, Adams and McDonald[241] did theoretical calculations using both the pure HS and additive HS mixture reference systems in the Barker–Henderson theory and one-fluid vdW theory.

Concerning the results based on a pure fluid reference and small values of δ, the Barker–Henderson theory is superior to the van der Waals theory within the first-order expansion. When the second-order terms are included, both methods yield, due to remarkable cancellations, very similar results over a wide range of ϱ. The expansion employing a mixture reference gives always good results provided that δ is small. However, none of the approximations discussed is useful at large values of δ except when the density is very low.

Recently Levesque and coworkers[264] and Nixon and Silbert[265] applied the P–Y theory to mixtures with negative departure from additivity and the results of their calculations exhibit an interesting trend: the more negative the non-additivity parameter, the better agreement between the P–Y and simulation results is obtained.

The system of non-additive HS was also investigated by means of the SPT by Bergmann[266–268]. Application of the SPT to non-additive HS is not straightforward because it requires changes in all three "ingredients" which make up the theory: (i) the choice of the interaction of the scaled particle with the other particles, (ii) the asymptotic limit, and (iii) the boundary conditions for very small values of the scaling parameter. Moreover, evaluation of the pressure is not unique and we refer readers to refs[266–268] and quotations therein for details.

5.5. *Theories of Nonspherical Body Mixtures*

From all the methods mentioned earlier only the SPT retains its importance also for nonspherical HB mixtures. Integral equations are (at least at present) out of game and one must be quite sceptical about the capacity of perturbation and conformal theories. The latter methods are therefore only briefly touched at the end of this section.

The SPT equation of mixtures was, similarly to pure nonspherical body fluids, first proposed by Gibbons[191] and then re-derived by Boublík[14] employing the correlation function formalism. The derivation follows the same pattern as that for pure nonspherical bodies and a HS mixture. There is only one difference, in comparison with HS mixtures, that the sort of a test particle must be explicitly considered from the very beginning. Let $\mathcal{G}^{\mathrm{av}}_{\alpha\beta}(\xi)$ be the average pair correlation function of a test particle α, characterized by a dilatation parameter ξ, which is in contact with particle β. Then for $\xi \leqq 0$ it holds (*cf.* Eq. (*5.32*))

$$\mathcal{G}^{\mathrm{av}}_{\alpha\beta}(\xi) = 1/[1 \sum_{\gamma} \varrho_{\gamma} \mathcal{V}_{\alpha+\gamma}(\xi)]\,, \quad \xi \leqq 0\,, \tag{5.69}$$

where

$$\mathcal{V}_{\alpha+\gamma}(\xi) = \mathcal{V}_{\gamma} + \xi \mathcal{S}_{\gamma} \mathcal{R}_{\alpha} + \xi^2 \mathcal{R}_{\gamma} \mathcal{S}_{\alpha} + \xi^3 \mathcal{V}_{\alpha}\,. \tag{5.70}$$

The function $\mathcal{G}^{\mathrm{av}}_{\alpha\beta}$ is then approximated by a polynomial whose coefficients are determined from the usual conditions:

$$\mathcal{G}^{\mathrm{av}}_{\alpha\beta}(\xi = 0) = 1/(1 - \sum \varrho_{\gamma} \mathcal{V}_{\gamma}) \tag{5.71}$$

$$\left(\frac{\partial \mathcal{G}^{\mathrm{av}}_{\alpha\beta}}{\partial \xi}\right)_{\xi=0} = \mathcal{R}_{\alpha} \sum \varrho_{\gamma} \mathcal{S}_{\gamma} / (1 - \sum \varrho_{\gamma} \mathcal{V}_{\gamma})^2 \tag{5.72}$$

$$\beta P_{\beta} = \varrho_{\beta} \mathcal{G}^{\mathrm{av}}_{\alpha\beta}(\xi \to \infty)\,. \tag{5.73}$$

The resulting EOS assumes then the form

$$\beta P/\varrho = \frac{1}{1-\eta} + \frac{rs}{\varrho(1-\eta)^2} + \frac{qs^2}{3\varrho(1-\eta)^3}\,, \tag{5.74}$$

where r, q, and s are geometric quantities of a mixture defined as follows:

$$r = \sum \varrho_\alpha \mathscr{R}_\alpha\,, \quad q = \sum \varrho_\alpha \mathscr{R}_\alpha^2\,, \quad s = \sum \varrho_\alpha \mathscr{S}_\alpha\,. \tag{5.75}$$

It can be proved that Eq. (*5.74*) satisfies the consistency conditions (Eq. (*5.16*)). In the case of HS Eq. (*5.74*) reduces to Eq. (*5.38*) and for a pure HB fluid to Eq. (*4.96*).

It is evident that one would like to have an equation which would reduce to the improved versions of the SPT in the above limiting cases. Such an equation has been derived by Boublík and it reads as

$$\beta P/\varrho = \frac{1}{1-\eta} + \frac{rs}{\varrho(1-\eta)^2} + \frac{qs^2(3-\eta)}{9\varrho(1-\eta)^3}\,. \tag{5.76}$$

This is at present the most universal EOS of HB fluids. It yields fairly accurate description of mixtures of CB with parameters $\alpha \lesssim 1\cdot2$ (see Table XXXVIII) and its accuracy increases with decreasing α. It is also the best equation of mixtures of FHS bodies (with the same limitations as those applying to pure FHS fluids) if these are described by means of the geometric functionals $\mathscr{R}$, $\mathscr{S}$, and $\mathscr{V}$ – see Subsection 4.5.2.

TABLE XXXVIII

Compressibility factors of equimolar mixtures of spheres and prolate spherocylinders with $\gamma = 2$ calculated from approximate equations of state

Conditions	η	$\beta P/\varrho$			
		Eq. (*5.76*)	Eq. (*5.79*)	Eq. (*5.81*)	exact
$\sigma_{HS} = \sigma_{PSC}$	0·20	2·52	2·50	2·51	2·50
	0·30	4·24	4·19	4·19	4·11
	0·40	7·54	7·34	7·36	7·31
	0·45	10·31	9·95	9·97	9·87
$\mathscr{V}_{HS} = \mathscr{V}_{PSC}$	0·20	2·54	2·54	2·54	2·52
	0·30	4·30	4·26	4·26	4·20
	0·40	7·65	7·52	7·49	7·39
	0·45	10·47	10·22	10·16	10·22

Eq. (*5.76*) represents an extension of Eq. (*4.105*) which is known to produce unsatisfactory results if the nonsphericity of particles becomes significant ($\alpha > 1{\cdot}2$). The same must then hold for mixtures, too. It is therefore natural to think about extending more accurate pure fluid equations to mixtures but this is in no way a simple problem. Formally such an extension can be made for any equation containing the geometric functionals $\mathscr{R}$, $\mathscr{S}$, and $\mathscr{V}$ by replacing them according to

$$\mathscr{R}^i \to \sum x_\alpha \mathscr{R}^i_\alpha \,, \quad \mathscr{S} \to \sum x_\alpha \mathscr{S}_\alpha \,, \quad \mathscr{V} \to \sum x_\alpha \mathscr{V}_\alpha \,, \tag{5.77}$$

which is equivalent to the change

$$\alpha \to \frac{1}{\varrho}\frac{rs}{3\eta}\,, \quad \alpha^2 \to \frac{1}{\varrho}\frac{qs^2}{9\eta^2}\,. \tag{5.78}$$

It can be easily shown that this transform brings the pure fluid EOS (*4.96*) and (*4.105*) to (*5.74*) and (*5.76*), respectively.

If the above scheme is applied to the Nezbeda equation (*4.117*), the resulting equation is accurate for mixtures of PSC and spheres, but it yields results inferior to those of the BMCSL equation for HS mixtures. Pavlíček and coworkers[269] devised therefore a method enabling one to extend any pure fluid EOS to mixtures under the constraint that for HS it reduces to the BMCSL equation. The method exploits certain relations of the SPT but yet it is not unique and at one step it requires an empirical guess. Pavlíček and coworkers[269] obtained the equation

$$\beta P/\varrho = \frac{1}{1-\eta} + \frac{rs}{\varrho(1-\eta)^2} + \frac{3qs^2 - 2r^2s^2/\varrho + 12r^2st/\varrho - 18rstw/\varrho + (12t - 5s)\,qs\eta}{9\varrho(1-\eta)^3}\,, \tag{5.79}$$

where t and w are additional geometric functionals,

$$t = \sum \varrho_\alpha \mathscr{V}_\alpha/\mathscr{R}_\alpha \,, \quad w = \sum \varrho_\alpha \mathscr{V}_\alpha/\mathscr{S}_\alpha \,. \tag{5.80}$$

Rather a complex form of this equation is an obvious consequence of the imposed constraint to contain the BMCSL equation as a special case. (One sees that the only "straightforward" extension of the BMCSL equation is Eq. (*5.76*)). In a later study Boublík[65] has therefore dropped this constraint and after employing expressions (*5.23*) and (*5.26*) for the third and fourth virial coefficients of CB mixtures he has derived an equation

$$\beta P/\varrho = \frac{1}{1 - \eta} + \frac{rs}{\varrho(1 - \eta)^2} + \frac{qs^2(1 - 2\eta) + 5rs\eta^2}{3\varrho(1 - \eta)^3} \qquad (5.81)$$

which is only slightly more complex then Eq. (*5.76*).

In Table XXXVIII we compare the compressibility factors given by Eqs (*5.76*) and (*5.79*) with simulation data for two equimolar mixtures of PSC and HS. It is seen that the results produced by Eq. (*5.79*) are in perfect agreement with the simulation data and the results of Eq. (*5.76*) are practically the same. Because of the lack of data for other CB mixtures we may only conjecture about the accuracy of the two equations in general but it is believed that they will perform similarly as their pure fluid predecessors. It should be only reminded that they are not suitable for FHS mixtures.

Concerning FHS mixtures, the only reasonable way of calculating their properties seems to be the same as that used for pure FHS fluids: the Boublík–Nezbeda method of defining the parameter of nonsphericity in combination with the improved SPT equation, *i.e.* Eq. (*5.76*). Wojcik and Gubbins[238] and Nezbeda and coworkers[121] applied this method to the available simulation data and found very good agreement (in most cases within experimental errors) for all systems but one: the mixture of heteronuclear dumbells and linear triatomics. This is the only mixture studied so far whose both components are nonspherical and qualitatively different. In accordance with our experience with pure FHS fluids, deterioration of the Boublík–Nezbeda method for such systems may be anticipated. It may be also interesting to note that this is the only mixture for which the Amagat law, *i.e.* the assumption of ideal mixing, fails to give an accurate compressibility factor.

Perturbation and conformal theories need a reference system to expand about. For nonspherical HB mixtures the only candidates are either a pure HS fluid or a multicomponent HS mixture. However, in Section 4.5. we have shown that the model of hard spheres is not able, in principle, to estimate accurately the properties of non-spherical bodies over a wide range of densities and this finding can in no way be encouraging to try this approach for mixtures. Few attempts made in this direction seem also to support this view and therefore we are not going to comment on them further.

5.6. *Discussion*

For HS mixtures the existing computer data cover the range of diameter ratios up to 1 : 3. Besides equimolar mixtures also concentration limits have been studied so that the data seem sufficient. Simple and accurate pure fluid equations, (*4.44*) and (*4.46*), have been extended to mixtures, Eqs (*5.39*) and (*5.40*), and they both yield very accurate description of HS mixtures over the entire density and concentration ranges. Other equations are inferior to these. Concerning the perturbation methods, the expansions must be considered up to the second order if accurate results are to be obtained. This requires numerical computations which disfavours these methods. On the other hand, they may be successfully applied to nontrivial mixtures like *e.g.* mixtures of non-additive HS.

For nonspherical body mixtures the situation is different. First, the only nonspherical shape of components considered up to now has been linear. Second, most mixtures contained only one nonspherical component with the other being hard spheres. Third, the data on nonspherical body mixtures are usually less accurate in comparison with those on pure fluids and HS mixtures. Finally, as one proceeds from the pure fluid of HS *via* pure nonspherical body fluids and mixtures of HS through mixtures of nonspherical bodies, the originally abundant number of theories and methods available shrinks to a few only. All these facts make any assessment of the theories quite difficult.

For CB mixtures the extended versions of Eqs (*4.117*) and (*4.118*), Eqs (*5.79*) and (*5.81*), compare very well with the existing data and the same can be expected if the component nonsphericities are only reasonably mild. However, nothing can be said about their performance if a mixture were made up of nonlinear components. A similar conclusion holds true also for FHS fluid mixtures. The Boublík–Nezbeda method provides results which in most cases agree with simulation data within experimental errors. However, the method fails for the mixture of linear triatomics and heteronuclear dumbells, the only mixture with both qualitatively different nonspherical components studied so far.

The excess volume is very small and usually within experimental errors which makes its direct determination very difficult. The indirect method, the assumption of ideal mixing, yields quite accurate results for all mixtures but, again, that of linear triatomics and heteronuclear dumbells. It is hard to say if this is going to be a rule unless further simulations on more complex mixtures are performed.

6. CONCLUDING REMARKS

With only few exceptions, the methods and results compiled in this review represent the output of studies initiated in the late 1960ieth by the finding that the structure of normal liquids is determined primarily by the repulsive forces acting between molecules. To judge to what extent the basic problems have been satisfactorily solved within these two decades and what remains to be done, depends on the point from which we view this field.

No doubt the greatest progress has been made towards description and understanding of fluids of spherical particles. For the pure hard sphere fluid the present situation is very satisfactory both from the theoretical and experimental points of view. Practically the same can be also said about hard sphere mixtures on condition that the ratio of the hard sphere diameters is not extremely small ($\frac{1}{3} \lesssim \sigma_2/\sigma_1 < 1$).

The main problems the theory faces are thus associated with nonsphericity of particles.

Practically all theoretical approaches to non-spherical hard body fluids either employ directly, or are somehow related to the convex body geometry. The mean excluded volume of a pair of identical convex particles can be characterized by a single parameter of nonsphericity, α, and this quantity emerges both in the expression for the second virial coefficient and in the equation of state resulting from the extended scaled particle theory. This theory provides also a functional form used for deriving more accurate equations of state and approximate expressions for higher virial coefficients.

With the exception of equations good for specific systems only, all general and accurate equations are based either on the scaled particle theory or on the resummation of the virial expansion. In contrast to the scaled particle theory, the virial expansion still possesses a capacity to push our understanding of hard body fluid properties forward if the geometric problem of clusters of at least three and four particles were exactly solved (approximate estimates may hardly help because they usually work on the level of two-particle clusters). This concerns the convex body models while for the fused-hard-sphere models the even more elementary problem of a pair of bodies has not been generally solved yet. The present approach to the fused-hard-sphere models makes use of the convex body results which seems the weakest point of the theory: Although the convex-like approach can produce reasonable, and very often quite accurate, results it is theoretically justified only for a limited class of models. Cracking the above mentioned geometrical problems may thus provide a clue to introducing rigorously a highly demanded second parameter of nonsphericity because semi-empirical methods have failed so far. Unless this is done we cannot expect any substantial breakthrough to take place.

On various occassions we have already mentioned the lack of data. One reason for that surely is the complexity once we have to deal with bodies different from spheres. To calculate the shortest distance between a pair of geometrical objects is a trivial matter for spheres, still simple and only more computer time consuming for fused-hard-sphere models but quite complicated for convex body models. For this reason the only convex shapes considered so far have been spherocylinders (both prolate and oblate) and ellipsoids. It is also possible to simulate properties of mixtures of bodies of one type but other possibilities cause considerable numerical complications and we doubt they will be considered in near future. The fused-hard-sphere models seem thus better candidates for computer studies which is already reflected by variety of the studied systems. This is, however, a rather paradoxical situation: convex body models possess a virtue of enabling us to study theoretically even extremal systems, like *e.g.* infinitely thin rods or discs, without additional effort and for this reason, and with respect to their fundamental role in developing the theory of nonspherical body fluids, more data for convex body fluids are highly demanded.

In addition to the general lack of data, another problem associated with simulations is the accuracy of the results. With the only exception of the pure hard sphere fluid, accuracy of no existing data matches the demanded standard. It is therefore impossible in many cases to differentiate between various methods which all agree with the data within wide error bars.

Despite a number of pending theoretical problems, some of which we have mentioned in the preceding paragraphs, the state-of-the-art of the liquid state is quite satisfactory from the engineering point of view. Nonsphericity of hard cores of real molecules falls practically always into the range $\alpha < 1{\cdot}2$ and this justifies the application of the accurate one-parameter equations of state to fluids made up of particles of any shape. Although there is not enough data to support it, we believe that the same can be said about mixtures, too. All these results constitute the necessary prerequisite for accomplishing a perturbation expansion leading to the so-called augmented van der Waals equations of state. In this type of equations with a sound theoretical basis, like *e.g.* BACK[270,271], YAS[272], chain-of-rotator equation[273], or the equation due to Chung and coworkers[131], the leading hard body term accounts correctly for the repulsive forces between molecules while the less important contribution due to attractive forces is treated empirically. These equations are gradually crawling into engineers' consciousness and are on its way to replace[274] until recently exclusively used purely empirical equations. All these facts only underline importance of studies of the hard body fluid properties.

We are very grateful to Dr K. Aim for careful reading the manuscript and to our students, J. Kolafa and R. Kantor, for checking the results showed in the Tables. Valuable discussions with our collegues, Drs S. Labík and A. Malijevský, are also acknowledged.

LIST OF IMPORTANT SYMBOLS

$c(1, 2)$	direct correlation function, convolution function
d	reduced density, $d = \varrho/\varrho_c$
e	Boltzmann factor
f	Mayer function, $f = e - 1$
$g(1, 2)$	pair correlation function
g_{klm}	spherical harmonic expansion coefficient
l_c	shortest core-to-core distance
s	surface-to-surface distance
$u(1, 2), u$	pair potential
v_f	free volume
w	average volume per particle
x	mole fraction
$y(1, 2)$	background correlation function
z	compressibility factor, $z = \beta P/\varrho$
B_i	virial coefficients (ϱ — expansion) of pure fluids
$B, C,$ *etc.*	virial coefficients (ϱ — expansion) of mixtures
F	Helmholtz free energy
G	Gibbs free energy, site–site correlation function
$\mathcal{G}$	certain pair correlation function

L	number of lattice sites, intramolecular distances
N	number of molecules
P	pressure
$P(\mathrm{m, n})$, P_{AH}, P_{φ}	Padé approximants
$\mathscr{R}$, $\mathscr{S}$, $\mathscr{V}$	geometrical functionals of hard bodies
T	absolute temperature
V	volume of a system
W	reversible work
Z	configuration integral
α	parameter of nonsphericity, $\alpha = \mathscr{R}\mathscr{S}/3\mathscr{V}$
β	$= 1/kT$
γ	length-to-breadth ratio of a convex body
δ	Dirac function, parameter of nonadditivity
ζ_i	parameters of a HS mixture
η	packing fraction, $\eta = \varrho\mathscr{V}$
μ	chemical potential
$\mathbf{v}$	normal of the supporting plane
ξ	dilatation parameter
ϱ	number density
σ	breadth of a body
τ, ζ	second parameters of nonsphericity

LIST OF ABBREVIATIONS

A–H	Alder–Hoover
BBGY	Bogolyubov–Born–Green–Yvon
B–G	Barboy–Gelbart
B–H	Barker–Henderson
BMCSL	Boublík–Mansoori–Carnahan–Starling–Leland
B–N	Boublík–Nezbeda
c	compressibility form, close-packed, critical, contact value
CB	convex body
CM	centre-of-mass
C–S	Carnahan–Starling
1-D, ...	one-dimensional, ...
E	excess
EOS	equation of state
E–W	Erpenbeck–Wood
FHS	fused-hard-sphere
HB	hard body
HNC	hypernetted chain
HOMO DB	homonuclear dumbell
HS	hard sphere
IS	interaction site
ISPT	improved scaled particle theory
MC	Monte Carlo
MD	molecular dynamics
med	median

N–L	Naumann–Leland
nonsph	nonspherical
OSC	oblate spherocylinder
O–Z	Ornstein–Zernike
PA	Padé approximant
PSC	prolate spherocylinder
P–Y	Percus–Yevick
RAM	reference average Mayer-function
ref	reference
RISM	reference interaction site model
SC	site–centred
SPT	scaled particle theory
v	virial form
vdW	van der Waals

REFERENCES

1. Hirschfelder J. O., Curtiss C. F., Bird R. B.: *Molecular Theory of Gases and Liquids.* Wiley, New York 1954.
2. Gray C. G., Gubbins K. E.: *Theory of Molecular Fluids.* Oxford Univ. Press, Oxford 1984.
3. Egelstaff P. A., Gray C. G., Gubbins K. E. in the book: *MPT Intl. Rev. Sci. Phys. Chem.* Ser. 2, (A. D. Buckingham, Ed.) Vol. 2, Chap. 8, Butterworths, London 1975.
4. Gray C. G.: in the book *Spec. Periodical Rep., Stat. Mech.* Vol. 2 (K. Singer, Ed.), Chap. 5. Chem. Soc., London 1975.
5. Streett W. R., Gubbins K. E.: Ann. Rev. Phys. Chem. *28*, 373 (1977).
6. Wertheim M. S.: Ann. Rev. Phys. Chem. *30*, 471 (1979).
7. Chandler D.: Advan. Chem. Phys. *31*, 1 (1980).
8. Stell G., Patey G. N., Hoye J. S.: Advan. Chem. Phys. *48*, 183 (1981).
9. Smith W. R., Nezbeda I.: Advan. Chem. Ser. (Am. Chem. Soc.) *204*, 235 (1983).
10. Lippert E., Chatzidimitriou-Dreismann C. A., Naumann K. H.: Advan. Chem. Phys. *57*, 311 (1984).
11. Boublík T.: Advan. Chem. Ser. (Am. Chem. Soc.) *204*, 173 (1983).
12. Kihara T.: Advan. Chem. Phys. *5*, 147 (1963).
13. Hadwiger H.: *Altes und Neues über konvexe Körper.* Birkhauser, Basel 1955.
14. Boublík T.: Mol. Phys. *27*, 1415 (1974).
15. Nezbeda I.: Mol. Phys. *33*, 1287 (1977).
16. Nezbeda I., Smith W. R.: Chem. Phys. Lett. *81*, 79 (1981).
17. Tildesley D. J., Streett W. B., Wilson D. S.: Chem. Phys. *36*, 63 (1979).
18. Tildesley D. J., Streett W. B., Steele W. A.: Mol. Phys. *39*, 1169 (1980).
19. Kamerlingh-Onnes H.: Comm. Phys. Lab. Leiden. No 71, 1901.
20. Mayer J. E., Mayer M. G.: *Statistical Mechanics.* Wiley, New York 1940.
21. McQuarrie D. A.: *Statistical Mechanics.* Harper-Row, New York 1976.
22. Hill T.: *Statistical Mechanics.* McGraw-Hill, New York 1956.
23. Hála E., Boublík T.: *Einführung in die statistische Thermodynamik.* Academia, Prag 1970.
24. Stell G. in the book: *The Equilibrium Theory of Classical Fluids* (H. L. Frisch, J. L. Lebowitz, Eds) p. II—171. Benjamin, New York 1964.
25. Boublík T., Nezbeda I., Hlavatý K.: *Statistical Thermodynamics of Simple Liquids and their Mixtures.* Elsevier, Amsterdam 1980.

26. Ree F. H., Hoover W. G.: J. Chem. Phys. *40*, 939 (1964).
27. Kilpatrick J. F.: Advan. Chem. Phys. *20*, 39 (1971).
28. Isihara A.: J. Chem. Phys. *19*, 397 (1951).
29. Wertheim M. S.: J. Chem. Phys. *78*, 4625 (1983).
30. Kratky K. W.: Physica *87A*, 584 (1977).
31. Malijevský A., Labík S.: Mol. Phys. *55*, 411 (1985).
32. Rigby M.: J. Chem. Phys. *53*, 1021 (1970).
33. Wojcik M., Gubbins K. E.: Mol. Phys. *53*, 397 (1984).
34. Nezbeda I.: Czech J. Phys. B *35*, 752 (1985).
35. Mulder B. M., Frenkel D.: Mol. Phys. *55*, 1193 (1985).
36. Lado F.: Mol. Phys. *47*, 283 (1982).
37. van Laar J. J.: Proc. R. Acad. Sci. Amsterdam *1*, 273 (1899).
38. Boltzmann L.: Proc. R. Acad. Sci. Amsterdam *1*, 398 (1899).
39. Nijboer B. R. A., van Hove L.: Phys. Rev. *85*, 771 (1952).
40. Rowlinson J. S.: Mol. Phys. *6*, 517 (1963).
41. Powell M. J. O.: Mol. Phys. *7*, 591 (1964).
42. Kim S., Henderson D.: Chem. Phys. Lett. *27A*, 379 (1968).
43. Rowlinson J. S.: Proc. R. Soc. A *279*, 147 (1964).
44. Katsura S., Abe Y.: J. Chem. Phys. *39*, 2068 (1963).
45. Ree F. H., Keeler R. N., McCarthy S. L.: J. Chem. Phys. *44*, 3407 (1966).
46. Barker J. A., Henderson D.: Can. J. Phys. *45*, 3959 (1967).
47. Kihara T., Miyoshi K.: J. Stat. Phys. *13*, 337 (1975).
48. Freasier B. C., Bearman R. J.: Mol. Phys. *32*, 551 (1976).
49. Perram J. W., Wertheim M. S.: J. Comp. Phys. *1*, 1 (1985).
50. Nezbeda I.: Czech. J. Phys. B *26*, 355 (1976).
51. Nezbeda I., Smith W. R., Boublík T.: Mol. Phys. *37*, 985 (1979).
52. Nezbeda I.: Chem. Phys. Lett. *41*, 55 (1976).
53. Monson P. A., Rigby M.: Mol. Phys. *35*, 1337 (1978).
54. Nezbeda I., Boublík T.: Czech. J. Phys. B *27*, 953 (1977).
55. Frenkel D., Eppenga R.: Phys. Rev. Lett. *49*, 1089 (1982).
56. Eppenga R., Frenkel D.: Mol. Phys. *52*, 1303 (1984).
57. Nezbeda I., Boublík T.: Mol. Phys. *51*, 1443 (1984).
58. Wertheim M. S.: J. Chem. Phys. *78*, 4619 (1983).
59. Boublík T.: Mol. Phys. *44*, 1369 (1981).
60. Nezbeda I., Labík S.: Mol. Phys. *47*, 1087 (1982).
61. Boublík T., Nezbeda I.: Chem. Phys. Lett. *46*, 315 (1977).
62. Nezbeda I., Boublík T.: Czech. J. Phys. B *27*, 1071 (1977).
63. Nezbeda I., Vörtler H. L.: Mol. Phys. *57*, 909 (1986).
64. Nezbeda I.: unpublished results.
65. Boublík T.: Mol. Phys. *42*, 209 (1981).
66. Gibbons R. M.: Mol. Phys. *17*, 81 (1969).
67. Naumann K. H., Leland T. W.: Fluid Phase Equilibria *18*, 1 (1984).
68. Tsykalo A. L., Selevanyuk V. I.: Teplofiz. Vys. Temp. (High Temp. Phys.) *8*, 659 (1970).
69. Labík S., Nezbeda I.: Mol. Phys. *48*, 97 (1983).
70. Nezbeda I., Pavlíček J., Labík S.: This Journal *44*, 3555 (1979).
71. Freasier B. C.: Mol. Phys. *39*, 1273 (1980).
72. Freasier B. C., Jolly D., Bearman R. J.: Mol. Phys. *31*, 255 (1976).
73. Jolly D., Freasier B. C., Bearman R. J.: Chem. Phys. Lett. *46*, 75 (1977).
74. Streett W. B., Tildesley D. J.: Faraday Disc. Chem. Soc. *66*, 27 (1978).

75. Boublík T., Nezbeda I., Trnka O.: Czech. J. Phys. B *26*, 1081 (1976).
76. Nezbeda I.: Czech. J. Phys. B *25*, 843 (1975).
77. Freasier B. C.: Chem. Phys. Lett. *35*, 280 (1975).
78. Aviram I., Tildesley D. J., Streett W. B.: Mol. Phys. *34*, 881 (1977).
79. Bearman R. J.: Mol. Phys. *34*, 1687 (1977).
80. Vieillard-Baron J.: J. Chem. Phys. *56*, 4729 (1972).
81. Vieillard-Baron J.: Mol. Phys. *28*, 809 (1974).
82. Perram J. W., Wertheim M. S., Lebowitz J. L., Williams G. O.: Chem. Phys. Lett. *105*, 277 (1984).
83. Steele W. A.: J. Chem. Phys. *39*, 3197 (1963).
84. Nezbeda I., Smith W. R.: J. Chem. Phys. *75*, 4060 (1981).
85. Wood W. W. in the book: *Physics of Simple Liquids* (H. N. V. Temperley, J. S. Rowlinson, G. S. Rushbrook, Eds), Chap. 5. North-Holland, Amsterdam 1968.
86. McDonald I. R.: Mol. Phys. *23*, 41 (1972).
87. Vesely F.: *Computerexperimente an Flüssigkeitsmodellen.* Physik Verlag, Weinheim 1978.
88. Ree F. H. in the book: *Physical Chemistry — An Advanced Treatice* (D. Henderson, Ed.), Vol. VIIIA, Chap. 5. Academic, New York 1971.
89. Valleau J. P., Whittington S. G. in the book: *Modern Theoretical Chemistry,* Vol. 5, *Statistical Mechanics*, Part A (B. J. Berne, Ed.), Chap. 4. Plenum Press, New York 1977.
90. Valleau J. P., Torrie G. N. in the book: *Modern Theoretical Chemistry.* Vol. 5. *Statistical Mechanics*, Part A (B. J. Berne, Ed.), Chap. 5. Plenum Press, New York 1977.
91. Levesque D., Weis J. J., Hansen J. P. in the book: *Topics in Current Physics.* Vol. 7. *Monte Carlo Method* (K. Binder, Ed.), Chap. 2. Springer, Berlin 1984.
92. Levesque D., Weis J. J., Hansen J. P. in the book: *Topics in Current Physics.* Vol. 36. *Applications of Monte Carlo Method* (K. Binder, Ed.), Chap. 2. Springer, Berlin 1984.
93. Shing K. S., Gubbins K. E.: Advan. Chem. Ser. (Am. Chem. Soc.) *204*, 73 (1983).
94. Hoover W. G., Ladd A. J. C., Hoover V. N.: Advan. Chem. Ser. (Am. Chem. Soc.) *204*, 29 (1983).
95. *Computer Modeling of Matter.* (P. Lykos, Ed.): Advan. Chem. Ser. (Am. Chem. Soc.) *86* (1978).
96. Metropolis N., Rosenbluth A. W., Rosenbluth M. N., Teller A. H.: J. Chem. Phys. *21*, 1087 (1953).
97. Streett W. B., Tildesley D. J.: Proc. R. Soc. A *348*, 485 (1976).
98. Tildesley D. J., Streett W. B.: Mol. Phys. *41*, 85 (1980).
99. Nezbeda I.: Czech. J. Phys. B *30*, 601 (1980).
100. Smith E. B., Wells B. H.: Mol. Phys. *53*, 701 (1984).
101. Labík S., Malijevský A.: Czech. J. Phys. B *33* 128 (1983).
102. McDonald I. R., Singer K. J.: J. Chem. Phys. *47*, 4766 (1967).
103. Bennett C. H.: J. Comp. Phys. *22*, 245 (1977).
104. Valleau J. P., Card D. N.: J. Chem. Phys. *57*, 5457 (1972).
105. Torrie G. M., Valleau J. P.: Chem. Phys. Lett. *28*, 578 (1974).
106. Widom B. J.: J. Chem. Phys. *39*, 2808 (1963).
107. Rebertus D. W., Sando K. M.: J. Chem. Phys. *67*, 2585 (1977).
108. Chapela G. A., Martinez-Casas S. E., Alejandre J.: Mol. Phys. *53*, 139 (1984).
109. Alder B. J., Wainwright T. E.: J. Chem. Phys. *31*, 459 (1959).
110. Erpenbeck J. J., Wood W. W.: J. Stat. Phys. *35*, 321 (1984).
111. Hoover W. G., Ree F. H.: J. Chem. Phys. *47*, 4873 (1967).
112. Hoover W. G., Ree F. H.: J. Chem. Phys. *49*, 3609 (1968).
113. Barker J. A., Henderson D.: Mol. Phys. *21*, 187 (1971).

114. Labík S., Malijevský A.: Mol. Phys. *42*, 739 (1981).
115. Few G. A., Rigby M.: Chem. Phys. Lett. *20*, 433 (1973).
116. Nezbeda I., Boublík T.: Czech. J. Phys. B *28*, 353 (1978).
117. Monson P. A., Rigby M.: Chem. Phys. Lett. *58*, 122 (1978).
118. Frenkel D., Mulder B. M., McTague J. P.: Phys. Rev. Lett. *52*, 287 (1984).
119. Frenkel D., Mulder B. M.: Mol. Phys. *55*, 1171 (1985).
120. Streett W. B., Tildesley D. J.: J. Chem. Phys. *68*, 1275 (1978).
121. Nezbeda I., Reddy M. R., Smith W. R.: Mol. Phys. *55*, 447 (1985).
122. Boublík T.: Czech. J. Phys. B *33*, 121 (1983).
123. Kirkwood J. G.: J. Chem. Phys. *18*, 380 (1950).
124. Barker J. A.: *Lattice Theories of the Liquid State.* Pergamon, Oxford 1963.
125. Hoover W. G., Hoover N. E., Hanson K.: J. Chem. Phys. *70*, 1837 (1979).
126. Hoover W. G., Ashurst W. T., Grover R.: J. Chem. Phys. *57*, 1259 (1972).
127. Speedy R. J.: J. Chem. Soc., Faraday Trans. II *76*, 693 (1980).
128. Tonks L.: Phys. Rev. *50*, 955 (1936).
129. Vörtler H. L., Heybey J., Haberlandt R.: Physica A *99*, 217 (1979).
130. Vörtler H. L., Heybey J.: Mol. Phys. *51*, 73 (1984).
131. Chung T. H., Khan M. M., Lee L. L., Starling K. E.: Fluid Phase Equilibria *17*, 351 (1984).
132. Sugiyama M.: Progr. Theor. Phys. *63*, 1484 (1980).
133. Shinomoto S.: Progr. Theor. Phys. *70*, 687 (1983).
134. Lebowitz J. L., Penrose O.: J. Math. Phys. *5*, 841 (1964).
135. Ree F. H.: Phys. Rev. *155*, 84 (1967).
136. Woodcock L. V., Angell C. A.: Phys. Rev. Lett. *47*, 1129 (1981).
137. Angell C. A., Clarke J. H. R., Woodcock L. V.: Advan. Chem. Phys. *48*, 397 (1981).
138. Carnahan N. F., Starling K. E.: J. Chem. Phys. *51*, 635 (1969).
139. Kolafa J.: unpublished results.
140. Baker G. A., Graves-Morris P. in the book: *Pade Approximants Encycloped. Math. and its Applications* (G. C. Rota, Ed.), Vols 13, 14. Addison-Wesley, New York 1981.
141. Baker G. A. jr., Gutierrez G., de Llano M.: J. Chem. Phys. *153*, 283 (1984).
142. Aguilera-Navaro V. C., Fortes M., De Llano M., Plastino A.: J. Chem. Phys. *76*, 749 (1982).
143. Aguilera-Navaro V. C., Fortes M., De Llano M., Plastino A.: Del Rio J., Rojo O.: J. Stat. Phys. *32*, 95 (1983).
144. Alder B. J., Hoover W. G. in the book: *Physics of Simple Liquids* (H. N. V. Temperley, J. S. Rowlinson, G. S. Rushbrook, Eds.), Chap. 4. North-Holland, Amsterdam 1968.
145. Devore J. A., Schneider E.: J. Chem. Phys. *77*, 1067 (1982).
146. Hall K. R.: J. Chem. Phys. *57*, 2252 (1972).
147. Le Fevre E. J.: Nature *20*, 235 (1972).
148. Woodcock L. V.: J. Chem. Soc., Faraday Trans. II *72*, 731 (1976).
149. Hoste R., Van Dael W.: J. Chem. Soc., Faraday Trans. 2, *80*, 477 (1984).
150. Levin D.: Inter. J. Computer Meth. B *3*, 371 (1973).
151. Baram A., Luban M.: J. Phys. C.: Solid. State Phys. *12*, L 659 (1979).
152. Barboy B., Gelbart W. M.: J. Chem. Phys. *71*, 3035 (1979).
153. Reiss H., Frisch H. L., Lebowitz J. L.: J. Chem. Phys. *31*, 369 (1959).
154. Reiss H.: Adv. Phys. Chem. *9*, 1 (1966).
155. Lebowitz J. L., Helfand E., Preastgaard E.: J. Chem. Phys. *43*, 774 (1965).
156. Tully-Smith D. M., Reiss H.: J. Chem. Phys. *53*, 4015 (1970).
157. Reiss H., Casberg K. V.: J. Chem. Phys. *61*, 1107 (1974).
158. Andrews F. C.: J. Chem. Phys. *62*, 272 (1975).
159. Speedy R. J.: J. Chem. Soc., Faraday Trans. 2, *73*, 714 (1977).

160. Speedy R. J.: J. Chem. Soc., Faraday Trans. 2, *75*, 1643 (1979).
161. Meeron E., Siegert J. F.: J. Chem. Phys. *48*, 3139 (1968).
162. Hoover W. G., Poirier J. C.: J. Chem. Phys. *37*, 1041 (1962).
163. Ballance J. A., Speedy R. J.: Mol. Phys. *54*, 1035 (1985).
164. Labík S., Malijevský A.: Mol. Phys. *53*, 381 (1984).
165. Speedy R. J.: Physica *121* B, 153 (1983).
166. Shinomoto S.: Phys. Lett. *89A*, 19 (1982).
167. Shinomoto S.: J. Stat. Phys. *32*, 105 (1983).
168. Kirkwood J. G.: J. Chem. Phys. *3*, 300 (1935).
169. Bogolyubov N. N.: J. Phys. (U.S.S.R.) *10*, 257 (1946).
170. Yvon J.: *Actualitees Scientifiques et Industrielles*, No 203. Hermann, Paris 1935.
171. Born M., Green H. S.: Proc. R. Soc. A *188*, 10 (1946).
172. Fisher I. Z., Kopeliovich B. L.: Dokl. Akad. Nauk SSSR *133*, 81 (1960).
173. Ree F. H., Lee Y. T., Ree T. J.: J. Chem. Phys. *55*, 234 (1971).
174. Percus J. K., Yevick G. J.: Phys. Rev. *110*, 1 (1958).
175. Hansen J. P., McDonald I. R.: *Theory of Simple Liquids*. Academic, London 1976.
176. Thiele E.: J. Chem. Phys. *39*, 474 (1963).
177. Wertheim M. S.: J. Math. Phys. *5*, 643 (1964).
178. Baxter R. J.: Phys. Rev. *154*, 170 (1967).
179. Nezbeda I.: Czech. J. Phys. B *24*, 55 (1974).
180. Verlet L.: Physica *30*, 95 (1964).
181. Verlet L.: Physica *31*, 959 (1965).
182. Wertheim M. S.: J. Math. Phys. *8*, 927 (1967).
183. Rowlinson J. S.: Mol. Phys. *9*, 217 (1965).
184. Hutchinson P., Conkie W. R.: Mol. Phys. *21*, 881 (1971).
185. Hutchinson P., Conkie W. R.: Mol. Phys. *24*, 567 (1972).
186. Verlet L.: Mol. Phys. *42*, 1291 (1981).
187. Martynov G. A., Sarkisov G. N.: Mol. Phys. *49*, 1495 (1983).
188. Verlet L.: Mol. Phys. *41*, 183 (1980).
189. Malijevský A., Labík S., Sýs J., Pick J.: *Molekulární teorie jednoduchých tekutin a jejich aplikace*. Academia, Prague 1985.
190. Ritchie A. B.: J. Chem. Phys. *46*, 618 (1967).
191. Gibbons R. M.: Mol. Phys. *18*, 809 (1970).
192. Kirkwood J. G., Buff F. P.: J. Chem. Phys. *17*, 338 (1949).
193. Boublík T.: J. Chem. Phys. *63*, 4084 (1975).
194. Boublík T.: J. Chem. Phys. *53*, 471 (1970).
195. Cotter M. A., Martire D. E.: J. Chem. Phys. *53*, 4500 (1970).
196. Lasher G.: J. Chem. Phys. *53*, 4141 (1970).
197. Cotter M. A.: J. Chem. Phys. *66*, 1098 (1977).
198. Savithramma K. L., Madhusudana N. V.: Mol. Cryst. Liquid Cryst. *74*, 243 (1981).
199. Boublík T.: Mol. Phys. *51*, 1429 (1984).
200. Rigby M.: Mol. Phys. *32*, 575 (1976).
201. Abascal J. L. F., Lago S.: J. Mol. Liquids *30*, 133 (1985).
202. Lustig R.: Mol. Phys. *55*, 305 (1985).
203. Smith W. R.: *Specialist Periodical Report, Statistical Mechanics* (*Chemical Society*) Vol. 1, Chap. 2. London 1977.
204. Lebowitz J. L., Percus J. K.: J. Chem. Phys. 79, 443 (1983).
205. Smith W. R.: Mol. Phys. *22*, 105 (1971).
206. Williams G. O., Lebowitz J. L., Percus J. K.: J. Chem. Phys. *81*, 2070 (1984).

207. Williams G. O., Lebowitz J. L., Percus J. K.: J. Phys. Chem. *88*, 6488 (1984).
208. Nezbeda I., Leland T. W.: J. Chem. Soc., Faraday Trans. 2, *75*, 193 (1979).
209. Bellemans A.: Phys. Rev. Lett. *21*, 527 (1968).
210. Naumann K. H., Lippert E.: Ber. Bunsenges. Phys. Chem. *85*, 650 (1981).
211. Nezbeda I., Smith W. R.: Mol. Phys. *45*, 681 (1982).
212. Labík S., Nezbeda I., Smith W. R.: Mol. Phys. *52*, 815 (1984).
213. Andersen H. C., Weeks J. D., Chandler D.: Phys. Rev. A *4*, 1597 (1971).
214. Sung S., Chandler D.: J. Chem. Phys. *56*, 4989 (1972).
215. Nezbeda I.: Czech. J. Phys. B *28*, 1071 (1978).
216. Steele W. A., Sandler S. I.: J. Chem. Phys. 1315 (1974).
217. MacRury T. B., Steele W. A.: J. Chem. Phys. *66*, 2262 (1977).
218. Perram J. W., White L. R.: Mol. Phys. *28*, 527 (1974).
219. Smith W. R.: Can. J. Phys. *52*, 2022 (1974).
220. Labík S., Malijevský A., Nezbeda I.: Czech. J. Phys. B *31* 8 (1981).
221. Smith W. R., Nezbeda I.: Chem. Phys. Lett. *82*, 96 (1981).
222. Smith W. R., Nezbeda I.: Mol. Phys. *44*, 347 (1981).
223. Nezbeda I., Smith W. R.: J. Chem. Phys. *75*, 4060 (1981).
224. Andersen H. C., Chandler D.: J. Chem. Phys. *57*, 1930 (1972).
225. Chen Y. D., Steele W. A.: J. Chem. Phys. *54*, 703 (1971).
226. Lado F.: Mol. Phys. *47*, 283 (1982).
227. Lado F.: Mol. Phys. *47*, 299 (1982).
228. Lowden L. J., Chandler D.: J. Chem. Phys. *59*, 6587 (1974).
229. Gubbins K. E., Shing K. S., Streett W. B.: J. Phys. Chem. *87*, 4573 (1983).
230. Boublík T., Nezbeda I.: Czech. J. Phys. B *30*, 121 (1980).
231. Rowlinson J. S., Swinton F. C.: *Liquids and Liquid Mixtures*. Butterworths, London 1982.
232. Rigby M., Smith E. B.: J. Chem. Soc., Faraday Trans. 2, *59*, 2469 (1963).
233. McLelan A. G., Alder B. J.: J. Chem. Phys. *24*, 115 (1956).
234. Melnyk T. W., Rowlinson J. S., Sawford B. L.: Mol. Phys. *24*, 809 (1972).
235. Stillinger F. H., Helfand E.: J. Chem. Phys. *41*, 2495 (1964).
236. Helfand E., Stillinger F. H.: J. Chem. Phys. *49*, 1232 (1968).
237. Aviram I., Tildesley D. J.: Mol. Phys. *35*, 365 (1978).
238. Wojcik M., Gubbins K. E.: Mol. Phys. *49*, 1401 (1983).
239. Smith E. B., Lea K. R.: J. Chem. Soc., Faraday Trans. II *59*, 1535 (1963).
240. Melnyk T. W., Sawford B. L.: Mol. Phys. *29*, 891 (1975).
241. Adams D. J., McDonald I. R.: J. Chem. Phys. *63*, 1900 (1975).
242. Widom B., Rowlinson J. S.: J. Chem. Phys. *52*, 1670 (1970).
243. Nezbeda I., Boublík T.: Czech. J. Phys. B *30*, 953 (1980).
244. Monson P. A., Rigby M.: Mol. Phys. *39*, 977 (1980).
245. Nezbeda I., Reddy M. R., Smith W. R.: Mol. Phys. *39*, 977 (1980).
246. Alder B. J.: J. Chem. Phys. *40*, 2724 (1964).
247. Rotenberg A.: J. Chem. Phys. *43*, 4377 (1965).
248. Lee L. L., Levesque D.: Mol. Phys. *26*, 1351 (1973).
249. Fries P. H., Hansen J. P.: Mol. Phys. *48*, 891 (1983).
250. Mansoori G. A., Carnahan N. F., Starling K. E., Leland T. W.: J. Chem. Phys. *54*, 1523 (1971).
251. Boublik T.: unpublished results.
252. Lebowitz J. L.: Phys. Rev. *133*, A895 (1964).
253. Lebowitz J. L., Rowlinson J. S.: J. Chem. Phys. *41*, 133 (1964).
254. Andrews F. C., Ellerby H. M.: J. Chem. Phys. *75*, 3542 (1981).

255. Henderson D., Leonard P. J. in the book: *Physical Chemistry — An Advanced Treatise* (D. Henderson, Ed.), Vol. 8B, Chap. 7. Academic Press, New York 1971.
256. Leonard P. J., Henderson D., Barker J. A.: J. Chem. Soc., Faraday Trans. 2, *66*, 2439 (1970).
257. Barker J. A., Henderson D.: J. Chem. Phys. *47*, 2856 (1967).
258. Henderson D., Barker J. A.: J. Chem. Phys. *49*, 3377 (1968).
259. Barker J. A.: Proc. R. Soc. A *241*, 547 (1957).
260. Salzburg Z. W.: J. Chem. Phys. *36*, 1974 (1962).
261. Barker J. A., Rigby M., Smith E. B.: J. Chem. Soc., Faraday Trans. II *62*, 3039 (1966).
262. Lebowitz J. L., Zomick D.: J. Chem. Phys. *54*, 3335 (1971).
263. Ahn S., Lebowitz J. L.: J. Chem. Phys. *60*, 523 (1974).
264. Levesque D., Nixon J. H., Silbert M., Weis J. J.: J. Phys. (Paris), *41*, C8—317 (1980).
265. Nixon J. H., Silbert M.: Mol. Phys. *52*, 207 (1984).
266. Bergmann E.: Mol. Phys. *32*, 237 (1976).
267. Bergmann E.: Acta Phys. Austriaca *44*, 151 (1976).
268. Bergmann E., Tenne R.: Chem. Phys. Lett. *56*, 310 (1978).
269. Pavlíček J., Nezbeda I., Boublík T.: Czech. J. Phys. B *29*, 1061 (1979).
270. Chen S. S., Kreglewski A.: Ber. Bunsenges. Phys. Chem. *81*, 1049 (1977).
271. Kreglewski A., Chen S. S.: Advan. Chem. Ser. (Am. Chem. Soc.) *182*, 197 (1979).
272. Yokoyama C., Arai K., Saito S.: J. Chem. Eng. Jpn. *16*, 345 (1983).
273. Chien C. H., Greenkorn R. A., Chao K. C.: AIChE J. *29*, 560 (1983).
274. Henderson D.: Advan. Chem. Ser. (Am. Chem. Soc.) *182*, 1 (1979).