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Hard-Particle Fluids.
I. General Scaled-Particle-Like Descriptions

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The Kirkwood–Salsburg equation for the many-particle distribution function is generalized to mixtures of anisotropic particles which can form ordered (e.g., liquid crystal or solid) phases. We extend similarly various statements of the "zero-separation" theorem. This allows us to obtain the small- and large-"scaled" particle limits in which a single particle is scaled to zero and infinite size, respectively. Simple interpolation between the corresponding solutions to the Kirkwood–Salsburg equation leads directly to the generalized scaled particle theory (SPT). Distribution functions as well as thermodynamic properties are considered. As special cases we treat first the single-component, hard-sphere system in its disordered and ordered states; an additional (gas ⇔ liquid) phase transition fails to appear when attractions are added. We then consider mixtures of particles, including those which interact via nonadditive hard cores. The SPT relations describing order states and isotropic phases of mixtures of *differently shaped* particles are found to violate certain of the Maxwell relations. This thermodynamic inconsistency, inherent in the SPT because of its having afforded special status to a single particle, is absent altogether in the alternative description of hard-particle fluids which is presented in an accompanying paper.

KEY WORDS: Kirkwood–Salsburg equation; zero-separation theorem; scaled particle theory; distribution functions; equations of state; hard-core particles; nonadditive pair potential; thermodynamic inconsistency.

1. INTRODUCTION

Recently we have been concerned with hard-particle fluids, in particular as models for thermotropic liquid crystals. A generalized van der Waals theory was used[(1–3)] to separate the effects of repulsive and attractive intermolecular

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forces: the attractions are mean-field-averaged, and the repulsions define a hard-particle reference system. The statistical thermodynamics of the hard-particle fluid has been treated alternatively by scaled particle theory (SPT)(4–7) and, more recently, by a resummed virial series (the "y-expansion").(8,9) In this and the following paper we present critical discussions of, and general improvements upon, these two approaches to hard-particle-fluid equations of state.

The scaled particle theory was first formulated twenty years ago for the particular case of hard-sphere fluids.(4) Since then, many investigators have considered its generalization to fluids of anisotropic hard particles(5–7,22) and attracting particles.(4b) These latter efforts have been less successful than those involving hard-sphere fluids, for a variety of reasons. In the present paper we discuss a general derivation of the scaled particle theory which includes previous developments as special cases. Our aim is to expose the strengths and weaknesses of this approach by checking thermodynamic consistency and equation of state data for each particular application.

The paper consists of two parts. In Sections 2, 3, and 4.1–4.3 we present our derivation of the scaled particle equations [Eqs. (45)–(49)]. We begin with the generalized Kirkwood–Salsburg (KS) and zero-separation-theorem (ZST) equations and evaluate them in the small- and large-scaled-particle limits. Interpolation leads directly to Eqs. (45)–(49). We do not need to consider the geometric arguments featured in earlier work(4,5) and, in addition, use of the KS and ZST equations permits us to treat the distribution functions as well as the thermodynamic properties. The second part of this paper is comprised of Section 4.4. Here we illustrate Eqs. (45)–(49) by specializing to the case of hard-sphere and attracting-hard-sphere systems (both fluid and solid phases, including nonadditive mixtures), and isotropic and anisotropic phases of arbitrary shaped particles. In case of an ordered state we are particularly concerned with the thermodynamic inconsistency which is inherent in SPT.

Part I, Sections 2, 3, and 4.1–4.3 can be skipped by readers interested primarily in the applications (strengths and weaknesses) of the SPT. Part II, with Eqs. (45)–(49), provides a self-contained discussion of SPT results.

2. THE KIRKWOOD–SALSBURG (KS) EQUATION

We consider a ν-component mixture of arbitrary shaped particles which comprise either an isotropic or anisotropic fluid (e.g., a liquid crystal with long-range orientational order) or a solid. The particles are assumed to be rigid; the internal degrees of freedom are separable and do not affect the intermolecular interactions. Let

$$\rho_\alpha = N_\alpha / V \tag{1}$$

be the number density of species α. The position and orientation of each molecule are characterized by $\mathbf{X} = r, \boldsymbol{\Omega}$, where $r \equiv |\mathbf{X}|$ is its distance from the origin and $\boldsymbol{\Omega}$ is its set of angle coordinates (Euler angles and the polar and azimuthal angles of the radius vector from the origin). The activity of species α is defined in the usual way by

$$z_\alpha = \rho_\alpha \exp(\beta\mu_\alpha^{\mathrm{ex}}) \tag{2}$$

where

$$\mu_\alpha^{\mathrm{ex}} = \mu_\alpha - \mu_\alpha^{\mathrm{ideal}} \tag{3}$$

is the excess (over that of an ideal gas) chemical potential; $\mu_\alpha^{\mathrm{ideal}} = \mu_\alpha{}^0 + kT \ln \rho_\alpha$, where $\mu_\alpha{}^0$ is the standard chemical potential. Then the probability of observing any n_1 out of N_1 molecules of species 1, n_2 out of N_2 of species 2,..., and n_ν out of N_ν of species ν in the configuration

$$\mathbf{X}^{(n)} \equiv \{\mathbf{X}_{i_\gamma};\, i_\gamma = 1,\ldots, n_\gamma;\, \gamma = 1,\ldots, \nu\}$$

within

$$d\mathbf{X}^{(n)} = \prod_{\gamma=1}^{\nu} \prod_{i_\gamma=1}^{n_\gamma} d\mathbf{X}_{i_\gamma}$$

is$^{(10)}$

$$\rho_{n_1,\ldots,n_\nu}^{(n)}(\mathbf{X}^{(n)}) = \frac{1}{\Xi} \sum_{N_1 \geqslant n_1} \cdots \sum_{N_\nu \geqslant n_\nu} \prod_{\gamma=1}^{\nu} \frac{z_\gamma^{N_\gamma}}{(N_\gamma - n_\gamma)!} \int \underset{V}{\cdots} \int e^{-\beta U_N}\, d\mathbf{X}^{(N-n)} \tag{4}$$

Here $n = \sum_{\gamma=1}^{\nu} n_\gamma$, $N = \sum_{\gamma=1}^{\nu} N_\gamma$, and $d\mathbf{X}$ has been normalized so that $\int d\mathbf{X} = V$; $\rho^{(n)}$ is the generic n-particle distribution,$^{(10)}$ with Ξ the grand canonical partition function.

Assume now that the intermolecular interactions are pairwise additive, and write

$$\Psi_{n_1-s_1,\ldots,n_\nu-s_\nu}^{(s,n)} = U_n - U_{n-s} \tag{5}$$

for the potential energy associated with a subgroup s ($s = \sum_{\alpha=1}^{\nu} s_\alpha$) of n. This allows us to express the total potential energy as ($s = 1$)

$$U_N = \Psi^{(1,n)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu} + \Psi^{(1,N-n+1)}_{N_1-n_1,\ldots,N_\nu-n_\nu} + U_{N-1}$$

The first term here describes the interaction of particle 1 (of species α) with the $n - 1$ particles in the group of n; the second term includes its potential in the field of the remaining $N - n$; and U_{N-1} is of course the total interaction energy in the absence of 1. Accordingly we can write

$$\begin{aligned} \exp(-\beta U_N) &= \exp(-\beta\Psi^{(1,n)}) \exp(-\beta U_{N-1}) \prod_{\gamma=1}^{\nu} \prod_{i_\gamma=n_\gamma+1}^{N_\gamma} [1 + f_{\alpha\gamma}(\mathbf{X}_{i_\alpha=1}, \mathbf{X}_{i_\gamma})] \\ &= \exp(-\beta\Psi^{(1,n)}) \exp(-\beta U_{N-1}) \\ &\quad \times \sum_{k_1=0}^{N_1-n_1} \cdots \sum_{k_\nu=0}^{N_\nu-n_\nu} \prod_{\gamma=1}^{\nu} \binom{N_\gamma - n_\gamma}{k_\gamma} \prod_{i_\gamma=n_\gamma+1}^{n_\gamma+k_\gamma} f_{\alpha\gamma}(\mathbf{X}_{i_\alpha=1}, \mathbf{X}_{i_\gamma}) \end{aligned} \tag{6}$$

where as usual

$$f_{\alpha\gamma}(\mathbf{X}_\alpha, \mathbf{X}_\gamma) = f_{\alpha\gamma}(\mathbf{X}_{\alpha\gamma}) \equiv \exp(-\beta u_{\alpha\gamma}) - 1 \tag{7}$$

with $u_{\alpha\gamma}(\mathbf{X})$ the interaction energy between two molecules of species α and γ whose relative position and orientation is $\mathbf{X}$. Inserting this into (4) gives

$$\begin{aligned}\rho^{(n)} = {} & \frac{1}{\Xi} \exp(-\beta \Psi^{(1,n)}) \sum_{N_1=n_1}^{\infty} \cdots \sum_{N_\nu=n_\nu}^{\infty} \sum_{k_1=0}^{N_1-n_1} \cdots \sum_{k_\nu=0}^{N_\nu-n_\nu} \\ & \times \left[\prod_{\gamma=1}^{\nu} \frac{z_\gamma^{N_\gamma}}{k_\gamma!\,(N_\gamma - n_\gamma - k_\gamma)!}\right] \int \underset{V}{\cdots} \int d\mathbf{X}^{(N-n)} \exp(-\beta U_{N-1})\, K^{(k,\alpha)}\end{aligned} \tag{8}$$

Here the kernel $K^{(k,\alpha)}$ is defined by ($k = \sum_{\gamma=1}^{\nu} k_\gamma$)

$$\begin{aligned} & K^{(k,\alpha)}_{k_1,\ldots,k_\nu}(\mathbf{X}_{i_\alpha=1}; \mathbf{X}^{(k)} \equiv \{\mathbf{X}_{i_\gamma}; i_\gamma = 1 + \delta_{\alpha\gamma},\ldots, k_\gamma + \delta_{\alpha\gamma}; \gamma = 1,\ldots, \nu\}) \\ & \quad = \prod_{\gamma=1}^{\nu} \prod_{i_\gamma=1+\delta_{\alpha\gamma}}^{k_\gamma+\delta_{\alpha\gamma}} f_{\alpha\gamma}(\mathbf{X}_{i_\alpha=1}, \mathbf{X}_{i_\gamma})\end{aligned} \tag{9}$$

Reversing the order of summation yields the Kirkwood–Salsburg equation[3]:

$$\begin{aligned} & \rho^{(n)}_{n_1,\ldots,n_\alpha,\ldots,n_\nu}(\mathbf{X}^{(n)} \equiv \{\mathbf{X}_{i_\gamma}; i_\gamma = 1,\ldots, n_\gamma; \gamma = 1,\ldots, \nu\}) \\ & \quad = z_\alpha \exp[-\beta \Psi^{(1,n)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}(\mathbf{X}_{i_\alpha=1}; \mathbf{X}^{(n-1)})] \\ & \qquad \times \sum_{k_1=0}^{\infty} \cdots \sum_{k_\nu=0}^{\infty} \left(\frac{1}{\prod_{\gamma=1}^{\nu} k_\gamma!}\right) \\ & \qquad \times \int_V \cdots \int K^{(k,\alpha)}_{k_1,\ldots,k_\nu}(\mathbf{X}_{i_\alpha=1}; \mathbf{X}^{(k)} \equiv \{\mathbf{X}_{i_\gamma}; i_\gamma = n_\gamma + 1, \ldots, n_\gamma + k_\gamma\}) \\ & \qquad \times \rho^{(n+k-1)}_{n_1+k_1,\ldots,n_\alpha+k_\alpha-1,\ldots,n_\nu+k_\nu}(\mathbf{X}^{(n+k-1)} \equiv \{\mathbf{X}_{i_\gamma}; i_\gamma = 1 + \delta_{\alpha\gamma},\ldots, n_\gamma + k_\gamma\}) \\ & \qquad \times \prod_{\gamma=1}^{\nu} \prod_{i_\gamma=n_\gamma+1}^{n_\gamma+k_\gamma} d\mathbf{X}_{i_\gamma}\end{aligned} \tag{8a}$$

Consider now the distribution function

$$\hat{\rho}^{(n)} = \rho^{(n)} \exp(\beta U_n) \tag{10}$$

which has the same meaning as $\rho^{(n)}$ except that the interactions between the n

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[3] This derivation of (8a) from (4) is a straightforward generalization of the discussion given by Hill (see pp. 251–257 of Ref. 10). Cotter and Martire(11a) and Morriss and Smith(11b) do not recognize that their $\rho^{(1)}$ is the KS equation (8a) with $n = 1$ and derive it independently using probabalistic considerations(11a) or the graphical decomposition theorem.(11b)

particles have been "removed." Equation (8a) can then be rewritten in terms of $\hat{\rho}^{(n)}$:

$$\begin{aligned}
&\hat{\rho}^{(n)}_{n_1,\ldots,n_\alpha,\ldots,n_\nu}(X^{(n)} \equiv \{\mathbf{X}_{i_\gamma};\, i_\gamma = 1,\ldots, n_\gamma\}) \\
&\quad = z_\alpha \sum_{k_1 \geqslant 0} \cdots \sum_{k_\nu \geqslant 0} \left(\frac{1}{\prod_{\gamma=1}^{\nu} k_\gamma!}\right) \\
&\qquad \times \int \underset{V}{\cdots} \int K^{(k,\alpha)}_{k_1,\ldots,k_\nu}(\mathbf{X}_{i_\alpha=1};\, \mathbf{X}^{(k)} \equiv \{\mathbf{X}_{i_\gamma};\, i_\gamma = n_\gamma + 1,\ldots, n_\gamma + k_\gamma\}) \\
&\qquad \times \exp[-\beta\Psi'^{(k,n+k-1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}(\mathbf{X}^{(k)};\, \mathbf{X}^{(n-1)})] \\
&\qquad \times \hat{\rho}^{(n+k-1)}_{n_1+k_1,\ldots,n_\alpha+k_\alpha-1,\ldots,n_\nu+k_\nu}(\mathbf{X}^{(n+k-1)})\, d\mathbf{X}^{(k)} \\
&\quad = z_\alpha \Bigg\{ \hat{\rho}^{(n-1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}(\mathbf{X}^{(n-1)}) \\
&\qquad + \sum_{\gamma=1}^{\nu} \int_V f_{\alpha\gamma}(\mathbf{X}_{i_\alpha=1}, \mathbf{X}_\gamma) \exp[-\beta\Psi'^{(1,n)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}(\mathbf{X}_\gamma;\, \mathbf{X}^{(n-1)})] \\
&\qquad \times \hat{\rho}^{(n)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\gamma+1,\ldots,n_\nu}(\mathbf{X}^{(n-1)}, \mathbf{X}_\gamma)\, d\mathbf{X}_\gamma \\
&\qquad + \sum_{\gamma_1,\gamma_2=1}^{\nu} \int_V \int f_{\alpha\gamma_1}(\mathbf{X}_{i_\alpha=1}, \mathbf{X}_{\gamma_1}) f_{\alpha\gamma_2}(\mathbf{X}_{i_\alpha=1}, \mathbf{X}_{\gamma_2}) \\
&\qquad \times \exp[-\beta\Psi'^{(2,n+1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}(\mathbf{X}_{\gamma_1}, \mathbf{X}_{\gamma_2};\, \mathbf{X}^{(n-1)})] \\
&\qquad \times \hat{\rho}^{(n+1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_{\gamma_1}+1,\ldots,n_{\gamma_2}+1,\ldots,n_\nu}(\mathbf{X}^{(n-1)}, \mathbf{X}_{\gamma_1}, \mathbf{X}_{\gamma_2})\, d\mathbf{X}_{\gamma_1}\, d\mathbf{X}_{\gamma_2} + \cdots \Bigg\}
\end{aligned} \tag{8b}$$

The first term in curly brackets corresponds to $k = 0$, the second to $k = 1$, the third to $k = 2$, and so on.

It is also convenient to use the singlet distribution function $\rho_\gamma^{(1)}$ to define a new function

$$y^{(n)} = \hat{\rho}^{(n)} \Big/ \prod_{\gamma=1}^{\nu} \prod_{i_\gamma=1}^{n_\gamma} \rho_\gamma^{(1)}(\mathbf{X}_{i_\gamma}) \tag{11}$$

which is related to the more familiar correlation

$$g^{(n)} = \rho^{(n)} \Big/ \prod_{\gamma=1}^{\nu} \prod_{i_\gamma=1}^{n_\gamma} \rho_\gamma^{(1)}(\mathbf{X}_{i_\gamma}) \tag{12}$$

via

$$y^{(n)} = g^{(n)} \exp(\beta U_n) \tag{13}$$

The KS equation for $y^{(n)}$ is

$$y^{(n)} = \frac{z_\alpha}{\rho_\alpha^{(1)}(\mathbf{X}_{i_\alpha=1})} \sum_{k_1 \geqslant 0} \cdots \sum_{k_\nu \geqslant 0} \left(\frac{1}{\prod_{\gamma=1}^{\nu} k_\gamma!}\right) \int \underset{V}{\cdots} \int K^{(k,\alpha)}$$
$$\times \exp(-\beta\Psi^{(k,n+k-1)})\, y^{(n+k-1)} \prod_{\gamma=1}^{\nu} \prod_{i_\gamma=n_\gamma+1}^{n_\gamma+k_\gamma} \rho_\gamma^{(1)}(\mathbf{X}_{i_\gamma})\, d\mathbf{X}_{i_\gamma} \qquad \text{(8c)}$$

$g^{(n)}$ satisfies a similar equation.

3. THE ZERO-SEPARATION THEOREM (ZST)

Let us now consider pair potentials having the form of a hard core plus "cutoff" attraction (here **X** denotes the position and orientation of γ relative to α):

$$u_{\alpha\gamma}(\mathbf{X}) = \begin{cases} +\infty, & r < d_{\alpha\gamma} \\ \varphi_{\alpha\gamma}(\mathbf{X}), & d_{\alpha\gamma} < r < a_{\alpha\gamma} \\ 0, & a_{\alpha\gamma} < r \end{cases} \qquad (14)$$

$d_{\alpha\gamma} = d_{\alpha\gamma}(\mathbf{\Omega})$ and $a_{\alpha\gamma} = a_{\alpha\gamma}(\mathbf{\Omega})$ are convex surfaces and $\varphi_{\alpha\beta}$ is an arbitrary function. More explicitly, $d_{\alpha\gamma}$ describes a surface—depending on the relative orientation $\mathbf{\Omega}$, and enclosing a particle α inside which the center of particle γ cannot be found (due to the hard-core repulsions). In turn $a_{\alpha\gamma}$ encloses $d_{\alpha\gamma}$ and has the property that α and γ no longer attract each other when the center of γ is outside it; the cluster sums over the k_γ in (8) then terminate after a relatively small number of terms (determined by the ratio $a_{\alpha\gamma}/d_{\alpha\gamma}$).

We introduce the quantity

$$S_\tau^{(\alpha)}(\mathbf{\Omega}_\alpha, \mathbf{\Omega}_\tau) = \min_{\mathbf{\Omega}_\gamma, \gamma=1,\ldots,\nu} (d_{\tau\gamma} - a_{\alpha\gamma}) \qquad (15)$$

and suppose that there are two components α and τ such that $S_\tau^{(\alpha)}$ is nonnegative for a given relative orientation $\mathbf{\Omega}_{\tau\alpha}$ of τ and α particles. Then $r_{\tau\alpha} \leq S_\tau^{(\alpha)}$ defines a volume $R_\tau^{(\alpha)}$, containing α, such that any particle γ cannot get closer than $a_{\alpha\gamma}$ to α, because of the hard core $d_{\tau\gamma}$ (α is actually "inside" τ; see Fig. 1A). This means that the corresponding Mayer function $f_{\alpha\gamma}$ vanishes, and hence all $k \geqslant 1$ terms are zero in Eqs. (8b) and (8c). Thus we can write

$$\hat{\rho}^{(n)}_{n_1,\ldots,n_\alpha,\ldots,n_\tau,\ldots,n_\nu}[\mathbf{r}_{i_\alpha=1,i_\tau=1} \in R_\tau^{(\alpha)}] = z_\alpha \hat{\rho}^{(n-1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\tau,\ldots,n_\nu} \qquad \text{(16a)}$$

and

$$y^{(n)}_{n_1,\ldots,n_\alpha,\ldots,n_\tau,\ldots,n_\nu}[\mathbf{r}_{i_\alpha=1,i_\tau=1} \in R_\tau^{(\alpha)}] = \frac{z_\alpha}{\rho_\alpha^{(1)}(\mathbf{X}_{i_\alpha=1})}\, y^{(n-1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\tau,\ldots,n_\nu} \qquad \text{(16b)}$$

This last equation has the form of the zero-separation theorem given by

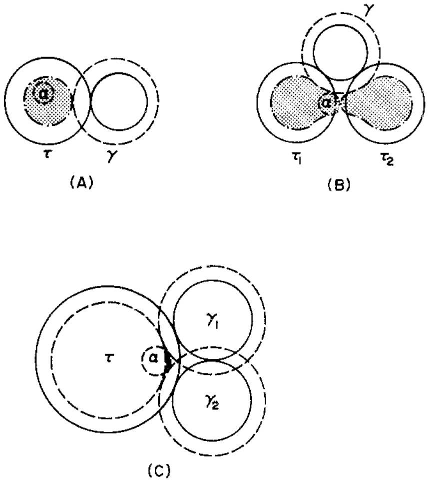

Fig. 1. In configurations (A) and (B), corresponding to $\mathbf{r}_\alpha \in R_\tau^{(\alpha)}$ and $\mathbf{r}_\alpha \in R_{\tau_1\tau_2}^{(\alpha)}$, respectively, particle γ cannot overlap the shadowed area which comprises the sphere of interaction with particle α; in (C), for $\mathbf{r}_\alpha \in D_\tau^{(\alpha)}$, particle γ_2 cannot overlap the shadowed area if γ_1 interacts with α. The solid and dashed curves denote the d and a particle boundaries and the dot-dashed curve shows the "interaction sphere" (for simplicity we depict here figures appropriate to the case of additive diameters).

Barboy and Tenne(12); the latter investigators considered an isotropic fluid and hence have $\rho_\alpha^{(1)}(\mathbf{X}_\alpha) = \rho_\alpha = N_\alpha/V$ on the right-hand side of (16b).[4]

The range of validity of (16) is actually larger than $R_\tau^{(\alpha)}$. Even when $S_\tau^{(\alpha)}$ is negative, or $r_{\tau\alpha} > S_\tau^{(\alpha)} > 0$, some configuration may exist such that α cannot interact with a molecule from "outside" (i.e., a particle not included in the original group n). More explicitly, for a given configuration of the $n - 1$ particles and a given orientation of $i_\alpha = 1$, there exists a nonzero volume $R_{\tau_1,\dots,\tau_{n-1}}^{(\alpha)}$ having the property that

$$f_{\alpha\gamma} \exp(-\beta\Psi^{(1,n)}) = \{\exp[-\beta u_{\alpha\gamma}(\mathbf{X}_{i_\alpha=1}, \mathbf{X}_\gamma)] - 1\} \times \prod_{\tau=1}^{\nu} \prod_{i_\tau=1+\delta_{\alpha\tau}}^{n_\tau} \exp[-\beta u_{\gamma\tau}(\mathbf{X}_{i_\tau}, \mathbf{X}_\gamma)] = 0 \qquad (17)$$

whenever $i_\alpha = 1$ is confined according to $\mathbf{r}_{i_\alpha=1} \in R_{\tau_1,\dots,\tau_{n-1}}^{(\alpha)}$ (see Fig. 1b). It then follows that Eqs. (16) hold.

The zero-separation theorem can be generalized still further by imagining that *several* (s) of the n molecules do not interact with the rest ($N - n$) of the system because of the hard cores of the remaining $n - s$ molecules. Let the volume $R_{\tau_1,\dots,\tau_{n-s}}^{(\alpha_1,\dots,\alpha_s)}$ be defined by $\{\mathbf{X}_{i_\alpha}\}$ such that

$$\begin{aligned} &K_{s_1,\dots,s_\nu}^{(s,\gamma)}(\mathbf{X}_\gamma; \mathbf{X}^{(s)} \equiv \{\mathbf{X}_{i_\alpha}; i_\alpha = 1,\dots, s_\alpha\}) \\ &\quad \times \exp[-\beta\Psi_{n_1-s_1,\dots,n_\nu-s_\nu}^{(1,n-s+1)}(\mathbf{X}_\gamma; \mathbf{X}^{(n-s)} \equiv \{\mathbf{X}_{i_\tau}; i_\tau = s_\tau + 1,\dots, n_\tau\})] \\ &= \left[\prod_{\alpha=1}^{\nu} \prod_{i_\alpha=1}^{s_\alpha} f_{\alpha\gamma}(\mathbf{X}_{i_\alpha}, \mathbf{X}_\gamma)\right]\left[\prod_{\tau=1}^{\nu} \prod_{i_\tau=s_\tau+1}^{n_\tau} \exp[-\beta u_{\tau\gamma}(\mathbf{X}_{i_\tau}, \mathbf{X}_\gamma)]\right] = 0 \qquad (18) \end{aligned}$$

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[4] The ZST has been formulated and proved first by Hoover and Poirier(23) and later by Meeron and Siegert(24) for a hard sphere fluid. For generalizations and further applications of ZST see Refs. 18–20, 25–27.

Then we can write

$$\hat{\rho}^{(n)}_{n_1,\ldots,n_\nu}[\mathbf{r}^{(s)} \in R^{(\alpha_1,\ldots,\alpha_s)}_{\tau_1,\ldots,\tau_{n-s}}] = \left(\prod_{\alpha=1}^{\nu} z_\alpha^{s_\alpha}\right)\hat{\rho}^{(n-s)}_{n_1-s_1,\ldots,n_\nu-s_\nu} \tag{19a}$$

and

$$y^{(n)}_{n_1,\ldots,n_\nu}[\mathbf{r}^{(s)} \in R^{(\alpha_1,\ldots,\alpha_s)}_{\tau_1,\ldots,\tau_{n-s}}] = \left[\prod_{\alpha=1}^{\nu}\prod_{i_\alpha=1}^{s_\alpha} \frac{z_\alpha}{\rho_\alpha^{(1)}(\mathbf{X}_{i_\alpha})}\right] y^{(n-s)}_{n_1-s_1,\ldots,n_\nu-s_\nu} \tag{19b}$$

In the particular case where $s = n - 1$, all $n - 1$ molecules lie inside the hard core of one molecule, say $i_\alpha = 1$, so that

$$y^{(n)}_{n_1,\ldots,n_\nu}(\mathbf{r}_{i_\alpha=1,i_\tau} \in R^{(\tau)}_\alpha;\ i_\tau = 1 + \delta_{\alpha\tau},\ldots, n_\tau) = \frac{1}{z_\alpha}\prod_{\tau=1}^{\nu}\prod_{i_\tau=1}^{n_\tau}\frac{z_\tau}{\rho_\tau^{(1)}(\mathbf{X}_{i_\tau})} \tag{20a}$$

$$\hat{\rho}^{(n)}_{n_1,\ldots,n_\alpha,\ldots,n_\nu}(\mathbf{r}_{i_\alpha=1,i_\tau} \in R^{(\tau)}_\alpha;\ i_\tau = 1 + \delta_{\alpha\tau},\ldots, n_\tau) = \frac{\rho_\alpha^{(1)}(\mathbf{X}_{i_\alpha=1})}{z_\alpha}\prod_{\tau=1}^{\nu} z_\tau^{n_\tau} \tag{20b}$$

Finally we introduce a volume $D^{(\alpha)}_{\tau_1,\ldots,\tau_{n-1}}$ such that, although (17) is not satisfied for certain $\mathbf{X}_{i_\alpha=1}$, the equality

$$\begin{aligned} &f_{\alpha\gamma_1}(\mathbf{X}_{i_\alpha=1}, \mathbf{X}_{\gamma_1}) f_{\alpha\gamma_2}(\mathbf{X}_{i_\alpha=1}, \mathbf{X}_{\gamma_2}) \\ &\quad\times \exp[-\beta\Psi'^{(2,n+1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}(\mathbf{X}_{\gamma_1}, \mathbf{X}_{\gamma_2}; \mathbf{X}^{(n-1)} \equiv \{\mathbf{X}_{i_\tau};\ i_\tau = 1 + \delta_{\alpha\tau},\ldots, n_\tau\})] \\ &\quad = 0 \end{aligned} \tag{21}$$

holds nevertheless for each γ_1 and γ_2 (see Fig. 1C). It then follows from (8) that

$$\begin{aligned} &\hat{\rho}^{(n)}_{n_1,\ldots,n_\nu}(\mathbf{r}_{i_\alpha=1} \in D^{(\alpha)}_{\tau_1,\ldots,\tau_{n-1}}) \\ &\quad = z_\alpha\left\{\hat{\rho}^{(n-1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu} + \sum_\gamma \int_V f_{\alpha\gamma}\hat{\rho}^{(n)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\gamma+1,\ldots,n_\nu}\right. \\ &\qquad \left.\times \exp(-\beta\Psi'^{(1,n)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu})\, d\mathbf{X}_\gamma\right\} \end{aligned} \tag{22a}$$

$$\begin{aligned} &y^{(n)}_{n_1,\ldots,n_\nu}(\mathbf{r}_{i_\alpha=1} \in D^{(\alpha)}_{\tau_1,\ldots,\tau_n}) \\ &\quad = \frac{z_\alpha}{\rho_\alpha^{(1)}(\mathbf{X}_{i_\alpha=1})}\left\{y^{(n-1)}_{n_\nu,\ldots,n_\alpha-1,\ldots,n_\nu} + \sum_\gamma \int_V f_{\alpha\gamma}\hat{y}^{(n)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\gamma+1,\ldots,n_\nu}\right. \\ &\qquad \left.\times [\exp(-\beta\Psi'^{(1,n)})]\rho_\gamma^{(1)}(\mathbf{X}_\gamma)\, d\mathbf{X}_\gamma\right\} \end{aligned} \tag{22b}$$

Equations (16) and (22) provide the n-particle distribution function $\rho^{(n)}_{n_1,\ldots,n_\alpha,\ldots,n_\nu}$ for $\mathbf{r}_{i_\alpha} \in R^{(\alpha)}_{\tau_1,\ldots,n-1} + D^{(\alpha)}_{\tau_1,\ldots,\tau_{n-1}}$ as soon as we know the activity z_α and the $(n - 1)$-particle d.f. $\rho^{(n-1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}$. It remains only to determine $\rho^{(n)}$ outside of this range.

4. SCALED-PARTICLE THEORY (SPT)

4.1. Exact Results for Co-volumes

We begin by considering two convex[5] bodies α and γ having volumes $v_{0\alpha}$ and $v_{0\gamma}$, respectively. The points from which the center of body α is excluded by the hard core of γ *also* form a convex body, which we call the co-body of α and γ. Its volume (depending on the relative orientation of α and γ) can be represented by the following formal expression$^{(13)}$:

$$v_{\alpha\gamma} = v_{0\gamma} + C^{\text{h.c.}}_{\gamma\alpha} + C^{\text{h.c.}}_{\alpha\gamma} + v_{0\alpha} \tag{23}$$

Here $C^{\text{h.s.}}_{\alpha\gamma}$ is given by the integral

$$C^{\text{h.c.}}_{\alpha\gamma} = -\int\!\!\int d\theta\, d\varphi\, \mathbf{r}_\gamma(\pi - \theta, \pi + \varphi)\left[\frac{\partial \mathbf{r}_\alpha(\theta\varphi)}{\partial\theta} \times \frac{\partial \mathbf{r}_\alpha(\theta\varphi)}{\partial\varphi}\right] \tag{24}$$

The radius vector $\mathbf{r}_\alpha$ is defined as follows. For any direction $\theta\varphi$—referred to a coordinate system fixed to the center of α—there is one and only one plane which touches α and whose normal from the origin (center) lies along $\theta\varphi$. In the simplest case (i.e., convex bodies of "the first kind") this "supporting"$^{(13)}$ plane touches α at a single point: $\mathbf{r}_\alpha(\theta\varphi)$ is the vector from the origin to this point of contact. Similar definitions obtain for $\mathbf{r}_\gamma$ and $C^{\text{h.c.}}_{\gamma\alpha}$. Note that (24) obtains only for convex bodies of "the first kind."

Expression (23) holds even in the case of convex bodies whose supporting planes make contact along a line or plane. In the case of right circular cylinders of diameter D and length L, for example, we have$^{(14)}$

$$v_{0\alpha} = \tfrac{1}{4}\pi D_\alpha{}^2 L_\alpha \tag{25a}$$

and

$$\begin{aligned} C^{\text{h.c.}}_{\alpha\gamma} &= \tfrac{1}{4}\pi D_\alpha{}^2(D_\gamma|\sin\theta_{\alpha\gamma}| + L_\gamma|\cos\theta_{\alpha\gamma}|) \\ &\quad + D_\alpha L_\alpha[D_\gamma E(\sin\theta_{\alpha\gamma}) + L_\gamma|\sin\theta_{\alpha\gamma}|] \end{aligned} \tag{25b}$$

Here $E(\cdots)$ is the complete elliptic integral of the second kind and $\theta_{\alpha\gamma}$ is the angle between the cylinder axes. For *sphero*cylinders $C^{\text{h.c.}}_{\alpha\gamma}$ takes on a much simpler form,$^{(14)}$ and for additive hard spheres the co-volumes are trivial and well known. Hard spheres with *non*additive diameters, i.e.,

$$d_{\alpha\gamma} = \tfrac{1}{2}(d_{\alpha\alpha} + d_{\gamma\gamma})(1 + \Delta_{\alpha\gamma}), \qquad \Delta_{\alpha\gamma} \neq 0, \geqslant -1 \tag{26}$$

also allow $v_{\alpha\gamma}$ to be expressed in the form (23):

$$v^{(\gamma)}_{0\alpha} = \tfrac{1}{6}\pi d^3_{\alpha\alpha}(1 + \Delta_{\alpha\gamma})^3 \tag{27a}$$

and

$$C^{\text{h.c.}}_{\alpha\gamma} = \tfrac{1}{2}\pi d^2_{\alpha\alpha} d_{\gamma\gamma}(1 + \Delta_{\alpha\gamma})^3 \tag{27b}$$

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[5] A body is convex if any line segment whose end points lie inside it is wholly contained in the body.

(Note that $v_{0\alpha}$ depends here not only on α, but also on γ—hence the superscript.)

Let $S_{\alpha\gamma}$ denote the surface of the co-body $\alpha\gamma$. Then we can write

$$v_{\alpha\gamma} = \int d\mathbf{R}_{\alpha\gamma}\, H(S_{\alpha\gamma} - R_{\alpha\gamma}) \tag{28}$$

where $H(X)$ is the usual unit-step-function[6] and $\mathbf{R}_{\alpha\gamma}$ is the vector running from one center to the other. Consider now the second virial coefficient defined by

$$B_{\alpha\gamma} \equiv -\frac{1}{2}\int_V d\mathbf{r}\, f_{\alpha\gamma}(\mathbf{X}) \tag{29}$$

Since $f_{\alpha\gamma} = -H(S_{\alpha\gamma} - R_{\alpha\gamma})$ for the hard-core potential, it follows that

$$2B^{\text{h.c.}}_{\alpha\gamma} = v^{(\alpha)}_{0\gamma} + C^{\text{h.c.}}_{\gamma\alpha} + C^{\text{h.c.}}_{\alpha\gamma} + v^{(\gamma)}_{0\alpha} \tag{29c}$$

For the interaction potential (14), however, $f_{\alpha\gamma}$ is discontinuous along *two* surfaces: $S^{(1)}_{\alpha\gamma} = d_{\alpha\gamma}$ and $S^{(2)}_{\alpha\gamma} = a_{\alpha\gamma}$. Still more generally, it can be discontinuous along any number ($k - 2$, say) of surfaces between $d_{\alpha\gamma}$ and $a_{\alpha\gamma}$. As long as the discontinuities $\Delta f^{(i)}_{\alpha\gamma}$ of $f_{\alpha\gamma}$ along $S^{(i)}_{\alpha\gamma}$ are finite, then integration by parts allows the second virial coefficient to be expressed in the form(12b)

$$B_{\alpha\gamma} = \frac{1}{2}\sum_{i=1}^{k}\left\{v_{\alpha\gamma}(S^{(i)}_{\alpha\gamma})\,\Delta f^{(i)}_{\alpha\gamma} + \int_{f_{\alpha\gamma}(S^{(i)}_{\alpha\gamma}+)}^{f_{\alpha\gamma}(S^{(i+1)}_{\alpha\gamma}-)} df\, v_{\alpha\gamma}[S_{\alpha\gamma}(f)]\right\} \tag{30}$$

Here $\Delta f^{(i)}_{\alpha\gamma}$ is defined by

$$\Delta f^{(i)}_{\alpha\gamma} = \lim_{R_{\alpha\gamma}\to S^{(i)}_{\alpha\gamma}+} f_{\alpha\gamma} - \lim_{R_{\alpha\gamma}\to S^{(i)}_{\alpha\gamma}-} f_{\alpha\gamma} \equiv f_{\alpha\gamma}(S^{(i)}_{\alpha\gamma}+) - f_{\alpha\gamma}(S^{(i)}_{\alpha\gamma}-) \tag{31}$$

and the "equipotential" surface $S_{\alpha\gamma}(f)$ is determined from the functional equation

$$f_{\alpha\gamma}(\mathbf{X}_\alpha, \mathbf{X}_\gamma) = f \tag{32}$$

Alternatively, taking $f_{\alpha\gamma}$ out of the integral, we can write (29) as[7]

$$B_{\alpha\gamma} = -\tfrac{1}{2}f_{\alpha\gamma}(\xi_{\alpha\gamma})\int_V d\mathbf{r} H(a_{\alpha\gamma} - r) = -\tfrac{1}{2}f_{\alpha\gamma}(\xi_{\alpha\gamma})v_{\alpha\gamma}(a_{\alpha\gamma}) \tag{33}$$

Here $\xi_{\alpha\gamma}$ is some point inside the volume confined by surface $a_{\alpha\gamma}$.

Implicit in the above are five restrictions on $f_{\alpha\gamma}$ (or, equivalently, on $u_{\alpha\gamma}$): (i) finite k; (ii) finite $\Delta f^{(i)}_{\alpha\gamma}$; (iii) existence of a hard core, $f_{\alpha\gamma}(d_{\alpha\gamma} = S^{(1)}_{\alpha\gamma}-) = -1$; (iv) a cutoff character, $f_{\alpha\gamma}(a_{\alpha\gamma} = S^{(k)}_{\alpha\gamma}+) = 0$; and (v) $|\varphi_{\alpha\gamma}| < \infty$. Assume now

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[6] $H(X) = 1$ for $X \geqslant 0$ and vanishes otherwise.

[7] Strictly speaking, the mean-value theorem (33) is true for continuous $f_{\alpha\gamma}(\mathbf{r})$ only. But for our present purposes we can always deform slightly the original potential $u_{\alpha\gamma}$ so as to make $f_{\alpha\gamma}$ continuous: (33) holds for this "new" $f_{\alpha\gamma}$.

in addition that the volume $v_{\alpha\gamma}(a_{\alpha\gamma})$ can be expressed in the form (23). [Note that we have not restricted $d_{\alpha\gamma}$ (which can reduce to a point) or $a_{\alpha\gamma}$ (which can become arbitrarily large as long as it remains small compared to the system size) or the sign of $\varphi_{\alpha\gamma}$ (i.e., the interaction tail can describe either attraction or repulsion).] It then follows from (33) that

$$B_{\alpha\gamma} = \psi_\gamma{}^\alpha + C_{\gamma\alpha} + C_{\alpha\gamma} + \psi_\alpha{}^\gamma \tag{34a}$$

with

$$\psi_\alpha{}^\gamma = -\tfrac{1}{2} f_{\alpha\gamma}(\xi_{\alpha\gamma}) v_{0\alpha}(a_{\alpha\alpha}) \tag{34b}$$

and

$$C_{\alpha\gamma} = -\tfrac{1}{2} f_{\alpha\gamma}(\xi_{\alpha\gamma}) C_{\alpha\gamma}^{\text{h.c.}}(a_{\alpha\alpha}, a_{\gamma\gamma}) \tag{34c}$$

[the factor $f_{\alpha\gamma}(\xi_{\alpha\gamma})$ is determined via Eqs. (30) and (33)]. As we can see from (24)–(27) and (34), for $a_{\alpha\alpha} \ll a_{\gamma\gamma}$ each successive term in (34a) is smaller by a factor of $a_{\alpha\alpha}/a_{\gamma\gamma}$ than its predecessor. This analysis may be straightforwardly extended to the KS equation.

4.2. Small-Particle Limit of the KS Equation

The range of integration in the second ($k = 1$) term on the right-hand side of (8b) is an overlap of the volumes $v_{\alpha\gamma}(a_{\alpha\gamma})$ and $V - v^{(\gamma)}_{\tau_1,\dots,\tau_{n-1}}$, where the volume $v^{(\gamma)}_{\tau_1,\dots,\tau_{n-1}}$ is determined by the condition

$$\exp[-\beta\Psi'^{(1,n)}_{n_1,\dots,n_\alpha-1,\dots,n_\nu}(\mathbf{X}_\gamma; \mathbf{X}^{(n-1)})] = 0$$

If $v_{\alpha\gamma}(a_{\alpha\gamma})$ lies entirely inside $V - v^{(\gamma)}_{\tau_1,\dots,\tau_{n-1}}$ we have

$$\begin{aligned}\int d\mathbf{X}_\gamma f_{\alpha\gamma}\hat{\rho}^{(n)} \exp(-\beta\Psi'^{(1,n)}) \\ = \int d\mathbf{\Omega}_{\alpha\gamma}\, v_{\alpha\gamma}(\mathbf{\Omega}_{\alpha\gamma})\{f_{\alpha\gamma}\hat{\rho}^{(n)} \exp(-\beta\Psi'^{(1,n)})\}_{\mathbf{r}_\gamma=\xi_\gamma}\end{aligned} \tag{35}$$

$\xi_\gamma(\mathbf{\Omega}_{\alpha\gamma})$ is some point inside $v_{\alpha\gamma}$. This suggests that we write the left-hand side integral directly as the sum $-\bar{\psi}_\gamma^{\tau_1,\dots,\tau_n} - \bar{C}_{\gamma\alpha}^{\tau_1,\dots,\tau_n} - \bar{C}_{\alpha\gamma}^{\tau_1,\dots,\tau_n} - \bar{\psi}_\alpha^{\tau_1,\dots,\tau_n}$; here

$$\bar{\psi}_\gamma^{\tau_1,\dots,\tau_n} = -\int d\mathbf{X}_\gamma \frac{v_{0\gamma}(a_{\gamma\gamma})}{v_{\alpha\gamma}(a_{\alpha\gamma})} f_{\alpha\gamma}\hat{\rho}^{(n)} \exp(-\beta\Psi'^{(1,n)}) \tag{36}$$

and similarly for the remaining three terms $\bar{C}_{\gamma\alpha}^{\tau_1,\dots,\tau_n}$, $\bar{C}_{\alpha\gamma}^{\tau_1,\dots,\tau_n}$, and $\bar{\psi}_\alpha^{\tau_1,\dots,\tau_n}$ but with $v_{0\gamma}(a_{\gamma\gamma})$ in the integrand replaced by $C_{\gamma\alpha}^{\text{h.c.}}(a_{\gamma\gamma}, a_{\alpha\alpha})$, $C_{\alpha\gamma}^{\text{h.c.}}(a_{\gamma\gamma}, a_{\alpha\alpha})$, and $v_{0\alpha}(a_{\alpha\alpha})$, respectively. Obviously, even when the integration range in (35) is smaller than $v_{\alpha\gamma}$ the left-hand side can still be written as the same sum whose successive terms are vanishingly small (compared to their predecessors) in the small-α limit.

Consider now the $k \geqslant 2$ terms in (8b):

$$\int\cdots\int K^{(k,\alpha)}\hat{\rho}^{(n+k-1)}\exp(-\beta\Psi'^{(k,n+k-1)})\,d\mathbf{X}^{(k)}$$
$$= [K^{(k,\alpha)}\hat{\rho}^{(n+k-1)}\exp(-\beta\Psi'^{(k,n+k-1)})]_{\xi^{(k)}}\int\cdots\int d\mathbf{X}^{(k)}\,v_{\alpha\gamma_1\ldots\gamma_k} \qquad (37)$$

Here $v_{\alpha\gamma_1\ldots\gamma_k}$ is the volume associated with the overlap of the k co-bodies formed between particle α and each member of the k-set of impenetrable particles. Again we assume that the distances between α and the other members of the set n are big enough so that $\exp(-\beta\Psi'^{(k,n+k-1)}) > 0$. Here $\xi^{(k)}$ is a set of k coordinates $\mathbf{X}_{\gamma_i}$ inside $v_{\alpha\gamma_1\ldots\gamma_k}$ $[K^{(k,\alpha)}(\xi^{(k)}) \neq 0]$.

We examine first the case $k = 2$. Imagine (see Fig. 2) that the two co-bodies formed by pairs $\alpha\gamma_1$ and $\alpha\gamma_2$ touch each other at a point P, and let π be a tangent plane at this point. Imagine further two more planes π_1 and π_2, both parallel to π, such that π_1 touches α and γ_1 at P_1 and π_2 touches α and γ_2 at P_2. Now let particles γ_1 and γ_2 approach each other (with their orientations held fixed) in such a way that P_1 and P_2 move along lines PP_1 and PP_2 until both bodies are in contact at P. Let the parameter λ characterize their approach ($0 \leqslant \lambda \leqslant 1$). When α is sufficiently small ($a_{\alpha\alpha} \ll d_{\gamma_1\gamma_1}, d_{\gamma_2\gamma_2}$), the overlap of the co-bodies consists of two nearly spherical sectors. These sectors have heights $\lambda h_{\pi\pi_1}$ and $\lambda h_{\pi\pi_2}$ and base diameters $2(2\hat{R}_{\gamma_1}\lambda h_{\pi\pi_1})^{1/2}$ and $2(2\hat{R}_{\gamma_2}\lambda h_{\pi\pi_2})^{1/2}$, where $h_{\pi\pi_1}$ is the distance between the planes π and π_1 (similarly for $h_{\pi\pi_2}$) and $\hat{R}_{\gamma_1}$ and $\hat{R}_{\gamma_2}$ are the radii of mean curvature of the surfaces which touch at $P(\hat{R} \gg h)$. Hence $v_{\alpha\gamma_1\gamma_2}$ is of order $\lambda^2 h^2 \sim \lambda^2(a_{\alpha\alpha}/d_{\gamma\gamma})^2$ and

$$\int d\mathbf{X}_{\gamma_1}\int d\mathbf{X}_{\gamma_2}\,H(a_{\alpha\gamma_1} - R_{\alpha\gamma_1})H(a_{\alpha\gamma_2} - R_{\alpha\gamma_2})H(R_{\gamma_1\gamma_2} - d_{\gamma_1\gamma_2})$$
$$= \int_{v_{\alpha\gamma_1\gamma_2}}\int d\mathbf{X}_{\gamma_1}\,d\mathbf{X}_{\gamma_2} \sim (a_{\alpha\alpha}/d_{\gamma\gamma})^3 \sim (v_{0\alpha}/v_{0\gamma}) \qquad (38)$$

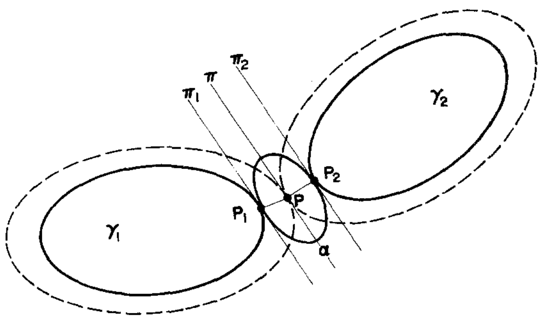

Fig. 2. Convex particles and co-bodies formed by them. See text for the definitions of points P, P_1, P_2, and planes π, π_1, and π_2.

[In cases where the tangent plane π makes contact with γ_1 and γ_2 along a line or plane, there exist relative orientations of the particles for which $v_{\alpha_1\gamma_1\gamma_2} \sim (\lambda a_{\alpha\alpha}/d_{\gamma\gamma})^{3/2}$ or $\sim \lambda a_{\alpha\alpha}/d_{\gamma\gamma}$; but these orientations make negligible contribution to the $\int\int d\mathbf{X}_{\gamma_1}\, d\mathbf{X}_{\gamma_2}$ in (38).] (For *non*additive pair interactions, the above analysis becomes more complicated.)

The integrals over $\mathbf{X}^{(k)}$ in (37) with $k > 2$ are infinitesimal, i.e., they go to zero faster than $v_{0\alpha}/v_{0\gamma}$ in the small-α limit. Thus the $k \geqslant 2$ sum (henceforth called F_2) from the right-hand side of (8b)—and all its first and second derivatives with respect to $a_{\alpha\alpha}$—vanish as $a_{\alpha\alpha} \to 0$.[8,9]

The $k \leqslant 1$ sum, on the other hand, remains nonzero and finite. It follows that $\ln(\hat\rho^{(n)}/z_\alpha\hat\rho^{(n-1)})$ can be expanded for small $a_{\alpha\alpha}$ in the following Taylor functional series:

$$\begin{aligned}
\ln \frac{\hat\rho^{(n)}_{n_1,\ldots,n_\alpha,\ldots,n_\nu}}{z_\alpha \hat\rho^{(n-1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}}
&= \ln\left(1 - \sum_{\gamma=1}^{\nu} \rho_\gamma \psi_\gamma^{\tau_1,\ldots,\tau_n}\right) - \frac{\sum_{\gamma=1}^{\nu} \rho_\gamma (C_{\gamma\alpha}^{\tau_1,\ldots,\tau_n} + C_{\alpha\gamma}^{\tau_1,\ldots,\tau_n})}{1 - \sum_{\gamma=1}^{\nu} \rho_\gamma \psi_\gamma^{\tau_1,\ldots,\tau_n}} \\
&\quad - \frac{1}{2} \frac{\sum_{\gamma_1=1}^{\nu} \sum_{\gamma_2=1}^{\nu} \rho_{\gamma_1}\rho_{\gamma_2} C_{\gamma_1\alpha}^{\tau_1,\ldots,\tau_n} C_{\gamma_2\alpha}^{\tau_1,\ldots,\tau_n}}{(1 - \sum_{\gamma=1}^{\nu} \rho_\gamma \psi_\gamma^{\tau_1,\ldots,\tau_n})^2} + O\left(\frac{v_{0\alpha}}{v_{0\gamma}}\right) \qquad (39)
\end{aligned}$$

Here

$$\begin{aligned}
\psi_\gamma^{\tau_1,\ldots,\tau_n} &\equiv -\int d\mathbf{X}_\gamma \frac{v_{0\gamma}(a_{\gamma\gamma})}{v_{\alpha\gamma}(a_{\alpha\gamma})} f_{\alpha\gamma} \exp(-\beta\Psi^{(1,n)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}) \frac{\hat\rho^{(n)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\gamma+1,\ldots,n_\nu}}{\rho_\gamma \hat\rho^{(n-1)}_{n_1,\ldots,n_\alpha-1,\ldots,n_\gamma,\ldots,n_\nu}} \\
&= \frac{\bar\psi_\gamma^{\tau_1,\ldots,\tau_n}}{\rho_\gamma \hat\rho^{(n-1)}} \qquad (40a)
\end{aligned}$$

$$\begin{aligned}
C_{\alpha\gamma}^{\tau_1,\ldots,\tau_n} &\equiv -\int d\mathbf{X}_\gamma \frac{C_{\alpha\gamma}^{\text{h.c.}}(a_{\alpha\alpha}, a_{\gamma\gamma})}{v_{\alpha\gamma}(a_{\alpha\gamma})} f_{\alpha\gamma} \exp(-\beta\Psi^{(1,n)}) \frac{\hat\rho^{(n)}}{\rho_\gamma \hat\rho^{(n-1)}} \\
&= \frac{\bar C_{\alpha\gamma}^{\tau_1,\ldots,\tau_n}}{\rho_\gamma \hat\rho^{(n-1)}} \qquad (40b)
\end{aligned}$$

and similarly for $\psi_\alpha^{\tau_1,\ldots,\tau_n}$ and $C_{\gamma\alpha}^{\tau_1,\ldots,\tau_n}$. Whereas ψ_α is proportional to the particle volume $v_{0\alpha}$, $C_{\alpha\gamma}$ is proportional to the product of the surface area S_α associated with α and the orientationally averaged radius of curvature $\hat R_\gamma$ associated with γ.

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[8] If the integration range in (37) is smaller than $v_{\alpha\gamma_1\ldots\gamma_k}$, i.e., $\exp(-\beta\Psi^{(k,n+k-1)}) = 0$ at some points inside, F_2 and its first and second derivatives vanish at $a_{\alpha\alpha} > 0$.

[9] Cotter,(15) in pursuing SPT for fluids of L, D spherocylinders, has claimed (details unpublished) that F_2, $\partial F_2/\partial L$, $\partial F_2/\partial D$, $\partial^2 F_2/\partial L\, \partial D$, and $\partial^2 F_2/\partial D^2$ all vanish as L, $D \to 0$ but that $\partial^2 F_2/\partial L^2$ does not: this contradicts the general arguments which we provide in the text.

4.3. Large-Particle Limit and Interpolation: SPT

Consider now the opposite limit, in which the $d_{\alpha\gamma}$, $\gamma = 1,\ldots,\nu$, grow to macroscopic size, so that each of the remaining $n-1$ molecules in $\rho^{(n)}$ is inside the $R_\alpha^{(\tau_i)}$, $i = 1,\ldots, n-1$. Suppose further that in this limit the difference $a_{\alpha\gamma} - d_{\alpha\gamma}$ remains finite ($a_{\alpha\gamma} - d_{\alpha\gamma} \ll d_{\alpha\gamma}$) and that the system (whose size is still large compared to $d_{\alpha\gamma}$) is in a single phase. From Eqs. (2) and (20) we have

$$\ln \frac{\hat{\rho}^{(n)}}{z_\alpha} = \sum_{i=1}^{n-1} \ln z_{\tau_i} - \beta\mu_\alpha^{\text{ex}} \tag{41}$$

[Note that for a macroscopically large scaled particle, $\rho_\alpha^{(1)}(\mathbf{X}_\alpha)$ is independent of $\mathbf{X}_\alpha$, i.e., $\rho_\alpha^{(1)} \to \rho_\alpha$.] Here μ_α^{ex} is the reversible work necessary to create a large cavity in the system, plus terms proportional to the cavity surface.

In general, the surfaces $d_{\alpha\gamma}$ (and $a_{\alpha\gamma}$) for different γ do not coincide with one another since $d_{\alpha\gamma} \neq \frac{1}{2}(d_{\alpha\alpha} + d_{\gamma\gamma})$. [For *additive* diameters, $d_{\alpha\gamma} = \frac{1}{2}d_{\alpha\alpha} + O(d_{\gamma\gamma}/d_{\alpha\alpha})$ and we have essentially one surface, $\frac{1}{2}d_{\alpha\alpha}$.] That is, $d_{\alpha\gamma}$ is impenetrable for molecules of species γ but not for particles of other species: the surface $d_{\alpha\gamma}$ acts as a semipermeable membrane.[10] The intersecting $\{d_{\alpha\gamma}, \gamma = 1,\ldots,\nu\}$ form $m \geqslant \nu + 1$ different spatial areas (see Fig. 3 for the case $\nu = 3$). Each shell is macroscopically large and thus the work μ_α^{ex} is

$$\mu_\alpha^{\text{ex}} = \sum_{i=1}^{m-1} \sum_{j=1}^{k_i} v_{\alpha 0}^{(i)} \frac{S_{\alpha 0}^{(ij)}}{S_{\alpha 0}^{(i)}} (P^{(j)} - P^{(i)}) \tag{42}$$

$v_{\alpha 0}^{(i)}$ is the volume of the ith shell (area) ($v_{\alpha 0}^{(m)} = V - \sum_{i=1}^{m-1} v_{\alpha 0}^{(i)}$) and $S_{\alpha 0}^{(ij)}$ is the surface dividing the areas with pressures $P^{(i)}$ and $P^{(j)}$. [$P^{(m)}$ is the system pressure P and $P^{(1)} = 0$; $P^{(j)} - P^{(i)}$ is the osmotic pressure across the surface $S_{\alpha 0}^{(ij)}$.] The volume $v_{\alpha 0}^{(i)}$ is in general confined by k_i such surfaces;

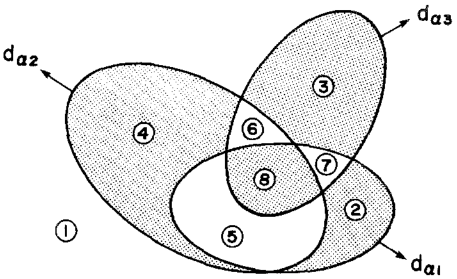

Fig. 3. Schematic drawing of the eight volumes formed by the three "membranes" $d_{\alpha\gamma}$, $\gamma = 1, 2, 3$. Volume (1) contains all three species; (2), (3), and (4) each contains two (2, 3; 1, 2; and 1, 3; respectively); (5), (6), and (7) each contains one (3; 1; and 2; respectively); and (8) contains none.

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[10] This idea has been extensively elaborated upon over the last several years by Bergmann and Tenne.[16]

$S_{\alpha 0}^{(i)} = \sum_{j=1}^{k_i} S_{\alpha 0}^{(ij)}$ is the overall surface confining $v_{\alpha 0}^{(i)}$. The $v_{\alpha 0}^{(i)}$ $S_{\alpha 0}^{(ij)}$ can be referenced to either $d_{\alpha\gamma}$ or $a_{\alpha\gamma}$.

Membrane equilibrium determines the number density $\rho_\gamma^{(i)}$ of species γ and pressure in the ith shell ($i = 1, 2,\ldots, m$). Writing $\mu_\gamma^{(i)}$ for the chemical potential of species γ in the ith shell, we have

$$\mu_\gamma(\rho_1,\ldots, \rho_\gamma,\ldots, \rho_\nu) = \mu_\gamma^{(i)}(\rho_{\varphi_1}^{(i)},\ldots, \rho_\gamma^{(i)},\ldots, \rho_{\varphi_{\nu(i)}}^{(i)}) \tag{43a}$$

and

$$\frac{\partial P^{(i)}}{\partial \rho_{\varphi_n}^{(i)}} = \sum_{j=1}^{\nu^{(i)}} \rho_{\varphi_j}^{(i)} \frac{\partial \mu_{\varphi_j}^{(i)}}{\partial \rho_{\varphi_n}^{(i)}}, \qquad n = 1,\ldots, \nu^{(i)} \tag{43b}$$

where $\nu^{(i)}$ is the total number of components in the ith shell ($\nu^{(m)} = \nu$ and $\nu^{(1)} = 0$). The explicit expressions for functions $\mu_\gamma^{(i)}$ may be obtained with the help of, say, SPT for a $\nu^{(i)}$ $(<\nu)$ component mixture. For $m = 2$, Eq. (42) reduces to $\mu_\alpha^{\text{ex}} = v_{0\alpha} P$ and no additional information is necessary. In general, however, we write

$$\ln \frac{\hat{\rho}_{n_1,\ldots,n_\alpha,\ldots,n_\nu}^{(n)}}{z_\alpha \hat{\rho}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}^{(n-1)}} = -\beta \sum_{i=1}^{m-1} \sum_{j=1}^{k_i} v_{\alpha 0}^{(i)} \frac{S_{\alpha 0}^{(ij)}}{S_{\alpha 0}^{(i)}} (P^{(j)} - P^{(i)}) + O\left(\frac{a_{\gamma\gamma}^2}{a_{\alpha\alpha}^2}\right) \tag{44}$$

for the large-α limit. Comparing (44) with (39) suggests an interpolation formula for $\ln(\hat{\rho}^{(n)}/z_\alpha)$ in terms of $\hat{\rho}^{(n)}$ and $\hat{\rho}^{(n-1)}$, which includes both the small- and large-$a_{\alpha\alpha}$ limits:

$$\begin{aligned} \ln & \frac{\hat{\rho}_{n_1,\ldots,n_\alpha,\ldots,n_\nu}^{(n)}(\mathbf{r}_{i_\alpha=1} \notin R_{\tau_1,\ldots,\tau_{n-1}}^{(\alpha)})}{z_\alpha \hat{\rho}_{n_1,\ldots,n_\alpha-1,\ldots,n_\nu}^{(n-1)}} \\ & \approx \ln\left(1 - \sum_{\gamma=1}^{\nu} \rho_\gamma \psi_\gamma^{\tau_1,\ldots,\tau_n}\right) \\ & \quad - \frac{\sum_{\gamma=1}^{\nu} \rho_\gamma (C_{\gamma\alpha}^{\tau_1,\ldots,\tau_n} + C_{\alpha\gamma}^{\tau_1,\ldots,\tau_n})}{1 - \sum_{\gamma=1}^{\nu} \rho_\gamma \psi_\gamma^{\tau_1,\ldots,\tau_n}} - \frac{1}{2} \frac{\sum_{\gamma_1=1}^{\nu} \sum_{\gamma_2=1}^{\nu} \rho_{\gamma_1}\rho_{\gamma_2} C_{\gamma_1\alpha}^{\tau_1,\ldots,\tau_n} C_{\gamma_2\alpha}^{\tau_1,\ldots,\tau_n}}{(1 - \sum_{\gamma=1}^{\nu} \rho_\gamma \psi_\gamma^{\tau_1,\ldots,\tau_n})^2} \\ & \quad - \beta \sum_{i=1}^{m-1} \sum_{j=1}^{k_i} v_{\alpha 0}^{(i)} \frac{S_{\alpha 0}^{(ij)}}{S_{\alpha 0}^{(i)}} (P^{(j)} - P^{(i)}) \end{aligned} \tag{45}$$

Equivalently, in terms of the functions $y^{(n)}$,

$$\begin{aligned} \ln & \frac{y^{(n)}(\mathbf{r}_{i_\alpha=1} \notin R_{\tau_1,\ldots,\tau_n}^{(\alpha)})}{y^{(n-1)}} \\ & \approx \ln\left(1 - \sum_{\gamma=1}^{\nu} \rho_\gamma \psi_\gamma^{\tau_1,\ldots,\tau_n}\right) \\ & \quad - \frac{\sum_{\gamma=1}^{\nu} \rho_\gamma (C_{\gamma\alpha}^{\tau_1,\ldots,\tau_n} + C_{\alpha\gamma}^{\tau_1,\ldots,\tau_n})}{1 - \sum_{\gamma=1}^{\nu} \rho_\gamma \psi_\gamma^{\tau_1,\ldots,\tau_n}} - \frac{1}{2} \frac{\sum_{\gamma_1=1}^{\nu} \sum_{\gamma_2=1}^{\nu} \rho_{\gamma_1}\rho_{\gamma_2} C_{\gamma_1\alpha}^{\tau_1,\ldots,\tau_n} C_{\gamma_2\alpha}^{\tau_1,\ldots,\tau_n}}{(1 - \sum_{\gamma=1}^{\nu} \rho_\gamma \psi_\gamma^{\tau_1,\ldots,\tau_n})^2} \\ & \quad + \beta(\mu_\alpha - {\mu_\alpha}^0) - \ln \rho_\alpha^{(1)}(\mathbf{X}_{i_\alpha=1}) - \beta \sum_{i=1}^{m-1} \sum_{j=1}^{k_i} v_{\alpha 0}^{(i)} \frac{S_{\alpha 0}^{(ij)}}{S_{\alpha 0}^{(i)}} (P^{(j)} - P^{(i)}) \end{aligned} \tag{46}$$

Here ψ_γ and $C_{\alpha\gamma}$ are defined as in (40a), (40b) but with $y^{(n)}\rho_\gamma^{(1)}/y^{(n-1)}$ replacing $\hat{\rho}^{(n)}/\hat{\rho}^{(n-1)}$. [Note that the ranges of validity (45), (46), and (22) overlap, so that we can check the approximate equations (45) and (46) with the help of the exact (22) for each given z_α.]

For $n = 1$ we have ($y^{(1)} = y^{(0)} = 1$)

$$\beta(\mu_\alpha - \mu_\alpha{}^0) = \ln \frac{\rho_\alpha^{(1)}(\mathbf{X}_\alpha)}{1 - \sum_{\gamma=1}^{v} \bar{\psi}_\gamma{}^\alpha} + \frac{\sum_{\gamma=1}^{v} (\bar{C}_{\gamma\alpha}^{\alpha} + \bar{C}_{\alpha\gamma}^{\alpha})}{1 - \sum_{\gamma=1}^{v} \bar{\psi}_\gamma{}^\alpha}$$
$$+ \frac{1}{2} \frac{\sum_{\gamma_1=1}^{v} \sum_{\gamma_2=1}^{v} \bar{C}_{\gamma_1\alpha}^{\alpha} \bar{C}_{\alpha_2\alpha}^{\alpha}}{(1 - \sum_{\gamma=1}^{v} \bar{\psi}_\gamma{}^\alpha)^2} + \beta \sum_{i=1}^{m-1} \sum_{j=1}^{k_i} v_{\alpha 0}^{(i)} \frac{S_{\alpha 0}^{(ij)}}{S_{\alpha 0}^{(i)}} (P^{(j)} - P^{(i)}) \tag{47}$$

The pressure can be eliminated from the right-hand side of (47) via the Gibbs–Duhem relation

$$\frac{\delta P}{\delta \rho_\alpha^{(1)}(\mathbf{X}_\alpha)} = \frac{1}{V} \sum_{\gamma=1}^{v} \int d\mathbf{X}_\gamma\, \rho_\gamma^{(1)}(\mathbf{X}_\gamma) \frac{\delta \mu_\gamma}{\delta \rho_\alpha^{(1)}(\mathbf{X}_\alpha)} \tag{48}$$

Since neither the chemical potential nor the pressure depends on $\mathbf{X}$, we obtain

$$\ln \frac{\rho_\alpha^{(1)}(\mathbf{X}_\alpha)}{1 - \sum_{\gamma=1}^{v} \bar{\psi}_\gamma{}^\alpha(\mathbf{X}_\alpha)} + \frac{\sum_{\gamma=1}^{v} [\bar{C}_{\gamma\alpha}^{\alpha}(\mathbf{X}_\alpha) + \bar{C}_{\gamma\alpha}^{\alpha}(\mathbf{X}_\alpha)]}{1 - \sum_{\gamma=1}^{v} \bar{\psi}_\gamma{}^\alpha(\mathbf{X}_\alpha)}$$
$$+ \frac{1}{2} \left(\frac{\sum_{\gamma=1}^{v} \bar{C}_{\gamma\alpha}^{\alpha}(\mathbf{X}_\alpha)}{1 - \sum_{\gamma=1}^{v} \bar{\psi}_\gamma{}^\alpha(\mathbf{X}_\alpha)} \right)^2 = \ln \lambda \tag{49}$$

where λ is a normalization constant assuring

$$\frac{1}{V} \int d\mathbf{X}\, \rho_\alpha^{(1)}(\mathbf{X}) = \rho_\alpha \tag{49a}$$

The quantities $\bar{\psi}_\gamma$ and $\bar{C}_{\alpha\gamma}$ are defined by

$$\bar{\psi}_\gamma{}^\alpha(\mathbf{X}_\alpha) = -\int d\mathbf{X}_\gamma \frac{v_{0\gamma}}{v_{\alpha\gamma}(\mathbf{\Omega}_{\alpha\gamma})} f_{\alpha\gamma}(\mathbf{X}_\alpha, \mathbf{X}_\gamma) \rho_\gamma^{(1)}(\mathbf{X}_\gamma) \tag{36a}$$

$$\bar{C}_{\alpha\gamma}^{\alpha}(\mathbf{X}_\alpha) = -\int d\mathbf{X}_\gamma \frac{C_{\alpha\gamma}^{\text{h.c.}}(\mathbf{\Omega}_{\alpha\gamma})}{v_{\alpha\gamma}(\mathbf{\Omega}_{\alpha\gamma})} f_{\alpha\gamma}(\mathbf{X}_\alpha, \mathbf{X}_\gamma) \rho_\gamma^{(1)}(\mathbf{X}_\gamma) \tag{36b}$$

where $v_{0\gamma}$ and $C_{\alpha\gamma}^{\text{h.c.}}$ can be calculated either at $a_{\alpha\alpha}$, $a_{\gamma\gamma}$ or $d_{\alpha\alpha}$, $d_{\gamma\gamma}$.

Note that instead of using (48) we could have chosen to eliminate the pressure from (47) via the virial relation, or the compressibility, or energy equations,$^{(10)}$ etc. Each of these alternatives leads in general to different thermodynamic results, for example, to ones which violate the Gibbs–Duhem relation. We feel it is more important to satisfy this *thermodynamic* relation (otherwise the free energy as a function of state cannot be calculated) than to require that additional *statistical mechanical* (e.g., virial, compressibility, or energy) relations be obeyed exactly.

The closed set of equations (47)–(49) comprises the SPT and can be solved to provide the pressure, chemical potential, and the distribution $\rho_\gamma^{(1)}$ as functions of the temperature T and densities ρ_γ. The higher distributions $y^{(n)}$ and $\rho^{(n)}$, $n > 1$, are given by (45), (46), (22), and (16).

4.4. Illustrations: Successes and Failures

4.4.1. Hard-Sphere, Isotropic Fluid. We consider first a single-component system of hard spheres. If it is isotropic, then

$$\rho^{(1)}(\mathbf{X}) = \rho, \qquad \bar{\psi}_\gamma{}^\alpha = \rho v_0, \qquad \bar{C}^\alpha_{\alpha\gamma} = \bar{C}^\alpha_{\gamma\alpha} = 3\rho v_0 \tag{50}$$

and

$$\beta\mu = \beta\mu_0 + \ln\frac{\rho}{1 - v_0\rho} + 6\frac{v_0\rho}{1 - v_0\rho} + \frac{9}{2}\left(\frac{v_0\rho}{1 - v_0\rho}\right)^2 + v_0\beta P \tag{51}$$

In conjunction with (48) this yields the familiar equation of state

$$v_0\beta P = \frac{v_0\rho}{1 - v_0\rho} + 3\left(\frac{v_0\rho}{1 - v_0\rho}\right)^2 + 3\left(\frac{v_0\rho}{1 - v_0\rho}\right)^3 \tag{52}$$

which has been obtained earlier by the scaled-particle,(4) Percus–Yevick,(17) and y-expansion(8) theories.

For $n = 2$, Eqs. (23) and (40) give

$$C^{\alpha\tau}_{\alpha\gamma} = C^{\alpha\tau}_{\gamma\alpha} = 3\psi(r_{12}) \tag{53}$$

$$\begin{aligned} \psi_\gamma^{\alpha\tau} &= \frac{1}{8}\int d\mathbf{r}_3\, H(d - r_{13})H(r_{23} - d)y^{(2)}(r_{23}) \\ &= \frac{\pi}{8r_{12}}\int_{\max(d, r_{12} - d)}^{r_{12} + d} t\,dt\,(d^2 - r_{12}^2 + 2tr_{12} - t^2)y^{(2)}(t) \equiv \psi(r_{12}) \end{aligned} \tag{54}$$

and hence

$$\begin{aligned} \ln y^{(2)}(r_{12}) = \ln\frac{1 - \rho\psi(r_{12})}{1 - \rho v_0} &+ \left[\frac{\rho v_0}{1 - \rho v_0} - \frac{\rho\psi(r_{12})}{1 - \rho\psi(r_{12})}\right] \\ &\times \left[6 + \frac{9}{2}\frac{\rho v_0}{1 - \rho v_0} + \frac{9}{2}\frac{\rho\psi(r_{12})}{1 - \rho\psi(r_{12})}\right] \end{aligned} \tag{55}$$

Since

$$\psi(r \to 0) \sim r\pi y^{(2)}(d)d^2 \to 0 \tag{54a}$$

we have

$$y^{(2)}(r \to 0) = \exp[\beta(\mu^{\mathrm{ex}} - v_0 P)] \tag{55a}$$

but, from the zero-separation theorem,

$$y^{(2)}(r = 0) = \exp[\beta(\mu^{\mathrm{ex}})] \tag{56}$$

This jump of $y^{(2)}$ at $r = 0$ is a consequence of the discontinuity of the pair potential at $r = d$. The fact that $y^{(2)}(r \to 0) < y^{(2)}(r = 0)$ must be taken into account when using $y^{(2)}(r \to 0)$ from an approximate theory—instead of $y^{(2)}(r = 0)$—in the zero-separation theorem. In the Percus–Yevick theory, for example, $y^{(2)}(r \to 0)$ is too low(18) and leads via the zero-separation theorem to a poor equation of state for the hard-sphere fluid.(19)

4.4.2. Hard-Sphere, Anisotropic System (Solid). If the hard sphere system of interest is anisotropic, it follows from Eqs. (23) and (49) that

$$\bar{\psi}_\gamma{}^\alpha = \frac{1}{8}\int d\mathbf{t}\, \rho^{(1)}(\mathbf{t}) H(d - |\mathbf{r} - \mathbf{t}|) \equiv \bar{\psi}(\mathbf{r}) \tag{57a}$$

$$\bar{C}^\alpha_{\alpha\gamma} = \bar{C}^\alpha_{\gamma\alpha} = 3\bar{\psi}(\mathbf{r}) \tag{57b}$$

and

$$\rho^{(1)}(\mathbf{r}) = \lambda[1 - \bar{\psi}(\mathbf{r})] \exp\left[-6\frac{\bar{\psi}(\mathbf{r})}{1 - \bar{\psi}(\mathbf{r})} - \frac{9}{2}\left(\frac{\bar{\psi}(\mathbf{r})}{1 - \bar{\psi}(\mathbf{r})}\right)^2\right] \tag{57c}$$

with

$$\lambda = \rho V\left\{\int d\mathbf{t}\, [1 - \psi(\mathbf{t})] \exp\left[-6\frac{\bar{\psi}(\mathbf{t})}{1 - \bar{\psi}(\mathbf{t})} - \frac{9}{2}\left(\frac{\bar{\psi}(\mathbf{t})}{1 - \bar{\psi}(\mathbf{t})}\right)^2\right]\right\}^{-1} \tag{57d}$$

For

$$\rho^{(1)}(\mathbf{r}) = \sum_{\nu_1, \nu_2, \nu_3} \delta[\mathbf{r} - \mathbf{l}(\nu_1, \nu_2, \nu_3)] \tag{58}$$

with $\delta(\mathbf{r})$ the Dirac delta function and the $\mathbf{l}$'s running over a three-dimensional lattice,

$$\bar{\psi}(\mathbf{r}) = \frac{1}{8}\sum_{\nu_1, \nu_2, \nu_3} H[d - |\mathbf{r} - \mathbf{l}(\nu_1, \nu_2, \nu_3)|] = \begin{cases} \frac{1}{8}, & |\mathbf{r} - \mathbf{l}| < d \\ 0, & \text{otherwise} \end{cases} \tag{57a$'$}$$

Thus

$$\lambda = \rho/[1 + \tfrac{1}{6}\pi d^3 \rho(\tfrac{7}{8}e^{-93/98} - 1)] = \rho/(1 - 0.6613 v_0 \rho)$$

$(v_0 = \frac{1}{6}\pi d^3)$ and

$$\rho^{(1)}(\mathbf{r}) = \begin{cases} \frac{7}{8}\lambda e^{-93/98}, & |\mathbf{r} - \mathbf{l}(\nu_1, \nu_2, \nu_3)| < d \\ \lambda, & \text{otherwise} \end{cases} \tag{57c$'$}$$

in contradiction to (58). Thus only a periodic function with broad enough peaks can be a solution to the integral equation (57c)—but it is not clear whether such a function can represent the singlet distribution of hard spheres in the solid state.

4.4.3. Attracting Hard Spheres: $g \leftrightarrow l$ and $l \leftrightarrow s$ Transitions.

Consider now a pair potential in the form of a square well (d, ϵ, a). For *isotropic* states of the system, we have $(n = 1)$

$$\bar{\psi}_\gamma^\alpha = v_0\rho(1 - \chi) \equiv \psi\rho, \qquad \bar{C}^\alpha_{\alpha\gamma} = \bar{C}^\alpha_{\gamma\alpha} = 3\psi\rho \tag{59}$$

where

$$\chi = (1 - d^3/a^3)e^{\beta\epsilon}, \qquad v_0 = \tfrac{1}{6}\pi a^3 \tag{60}$$

Then

$$\beta\mu = \beta\mu_0 + \ln\frac{\rho}{1 - \psi\rho} + 6\frac{\rho\psi}{1 - \rho\psi} + \frac{9}{2}\left(\frac{\rho\psi}{1 - \rho\psi}\right)^2 + v_0\beta P \tag{61}$$

and

$$\begin{aligned} v_0\beta P = {} & -\frac{(3 - 2\chi)^2}{\chi^3}\ln\left(1 - \frac{\chi}{1 - \chi}\frac{\rho\psi}{1 - \rho\psi}\right) \\ & - 3\frac{3 - \chi}{\chi^2}\frac{\rho\psi}{1 - \rho\psi} - \frac{9}{2\chi}\left(\frac{\rho\psi}{1 - \rho\psi}\right)^2 \end{aligned} \tag{62a}$$

with

$$\frac{\partial\beta P}{\partial\rho} = \frac{(1 + 2\psi\rho)^2}{(1 - \psi\rho)^3(1 - v_0\rho)}\begin{cases} \geqslant 0 & 0 < \rho < 1/v_0 \\ \leqslant 0 & \rho > 1/v_0 \end{cases} \tag{62b}$$

Define the temperature T_0 by $-\epsilon/k\ln(1 - d^3/a^3)$, so that $0 < \psi < v_0$ when $T > T_0$ and $\psi < 0$ when $T < T_0$. Then the pressure is seen to be a nondecreasing function of the density when $\rho < 1/v_0$, and decreasing when $1/v_0 < \rho$ ($< 1/\psi$ if $T > T_0$—μ and P diverge at $\rho = 1/\psi$). That is, $\rho = 1/v_0$ is the largest density for which the pressure behaves in a physically reasonable way [if v_0 on the right-hand side of (61) is replaced by $v_0 d^3/a^3$, $\rho_{\max} = a^3/v_0 d^3$ or $1/\psi$] and SPT fails to describe a gas–liquid phase transition.

For $n = 2$, Eqs. (23) and (40) lead again to Eq. (55) but with

$$\begin{aligned} \psi(r_{12}) = \frac{1}{8}\int d\mathbf{r}_3\, y^{(2)}(r_{23})[H(d - r_{13})e^{\beta\epsilon} + H(a - r_{13})(1 - e^{\beta\epsilon})] \\ \times [H(r_{23} - d)e^{\beta\epsilon} + H(r_{23} - a)(1 - e^{\beta\epsilon})] \end{aligned} \tag{63a}$$

and hence

$$\psi(r \to 0) = -\tfrac{1}{2}\pi e^{\beta\epsilon}(e^{\beta\epsilon} - 1)\int_b^a dt\, t^2 y^{(2)}(t) \tag{63b}$$

Thus $y^{(2)}(r \to 0) > \exp[\beta(\mu^{\text{ex}} - v_0 P)]$ and $y^{(2)}(r \to 0)$ may be closer to $y^{(2)}(r = 0)$ than in the case of hard spheres without attraction: for intermediate temperatures the use of $y^{(2)}(r \to 0)$ in the zero-separation theorem should give reasonable results. This is consistent with the result of Barboy and

Tenne, who have shown$^{(20)}$ that the Percus–Yevick theory and zero-separation theorem give a respectable equation of state for the "sticky hard sphere" fluid (i.e., for $\epsilon \to \infty$ with χ held fixed).

For an *an*isotropic phase of the square-well fluid the singlet distribution $\rho^{(1)}(\mathbf{r})$ is again described by Eqs. (57c) and (57d), but instead of (57a), $\bar{\psi}(\mathbf{r})$ is now defined by

$$\bar{\psi}(\mathbf{r}) = \frac{1}{8}\int d\mathbf{t}\, \rho^{(1)}(\mathbf{t})[H(d - |\mathbf{r} - \mathbf{t}|)e^{\beta\epsilon} + H(a - |\mathbf{r} - \mathbf{t}|)(1 - e^{\beta\epsilon})] \tag{64}$$

For a density of the form (58),

$$\begin{aligned} \bar{\psi}(\mathbf{r}) &= \frac{1}{8}\sum_{\nu_1,\nu_2,\nu_3} [H(d - |\mathbf{r} - \mathbf{l}|)e^{\beta\epsilon} + H(a - |\mathbf{r} - \mathbf{l}|)(1 - e^{\beta\epsilon})] \\ &= \begin{cases} \frac{1}{8}, & |\mathbf{r} - \mathbf{l}| < d \\ \frac{1}{8}(1 - e^{\beta\epsilon}), & d < |\mathbf{r} - \mathbf{l}| < a \\ 0, & a < |\mathbf{r} - \mathbf{l}| \end{cases} \end{aligned} \tag{64'}$$

Thus

$$\begin{aligned} \lambda &= \rho\Big/\left\{1 + v_0\rho\left[\chi_1\left(1 - \frac{d^3}{a^3}\right) + \frac{d^3}{a^3}\chi_2 - 1\right]\right\} \\ \chi_1 &= (1/8)(7 + e^{\beta\epsilon})\exp[3(31 + e^{\beta\epsilon})(e^{\beta\epsilon} - 1)/2(7 + e^{\beta\epsilon})^2] \\ \chi_2 &= (7/8)e^{-93/98} \end{aligned}$$

and

$$\rho^{(1)}(\mathbf{r}) = \begin{cases} \chi_2\lambda, & |\mathbf{r} - \mathbf{l}| < a \\ \chi_1\lambda, & d < |\mathbf{r} - \mathbf{l}| < a \\ \lambda, & a < |\mathbf{r} - \mathbf{l}| \end{cases}$$

in contradiction to (58). Again, though, a periodic function with broad peaks can be a solution to (57c) (see, however, Section 4.4.4b below).

4.4.4. Mixtures and Anisotropic Systems: Thermodynamic Inconsistencies.

(a) Isotropic Phases. We discuss first the case of multicomponent mixtures of hard spheres with nonadditive diameters. For $n = 1$ we have

$$\begin{aligned} \bar{\psi}_\gamma{}^\alpha &= \tfrac{1}{6}\pi d_{\gamma\gamma}^3(1 + \Delta_{\alpha\gamma})^3\rho_\gamma \\ \bar{C}_{\alpha\gamma}^\alpha &= \tfrac{1}{2}\pi d_{\alpha\alpha}^2 d_{\gamma\gamma}(1 + \Delta_{\alpha\gamma})^3\rho_\gamma \\ \bar{C}_{\gamma\alpha}^\alpha &= \tfrac{1}{2}\pi d_{\gamma\gamma}^2 d_{\alpha\alpha}(1 + \Delta_{\alpha\gamma})^3\rho_\gamma \end{aligned} \tag{65}$$

and

$$\begin{aligned}\beta\mu_\alpha = {} & \beta\mu_\alpha{}^0 + \ln \frac{\rho_\alpha}{1 - \frac{1}{6}\pi \sum_\gamma \rho_\gamma d_{\gamma\gamma}^3 (1 + \Delta_{\alpha\gamma})^3} + \pi \frac{\sum_\gamma \rho_\gamma d_{\alpha\alpha} d_{\gamma\gamma} d_{\alpha\gamma} (1 + \Delta_{\alpha\gamma})^2}{1 - \frac{1}{6}\pi \sum_\gamma \rho_\gamma d_{\gamma\gamma}^3 (1 + \Delta_{\alpha\gamma})^3} \\ & + \frac{\pi^2}{8} d_{\alpha\alpha}^2 \left[\frac{\sum_\gamma \rho_\gamma d_{\gamma\gamma}^2 (1 + \Delta_{\alpha\gamma})^3}{1 - \frac{1}{6}\pi \sum_\gamma \rho_\gamma d_{\gamma\gamma}^3 (1 + \Delta_{\alpha\gamma})^3}\right]^2 \\ & + \frac{\beta\pi}{6} d_{\alpha\alpha}^3 \sum_{i=2}^{\nu} \frac{(1 + \Delta_{\alpha\gamma_i})^3 - (1 + \Delta_{\alpha\gamma_{i-1}})^3}{(1 + \Delta_{\alpha\gamma_i})^2 + (1 + \Delta_{\alpha\gamma_{i-1}})^2} \\ & \times [(1 + \Delta_{\alpha\gamma_i})^2 (P^{(i+1)} - P^{(i)}) - (1 + \Delta_{\alpha\gamma_{i-1}})^2 (P^{(i)} - P^{(i-1)})] \qquad (66)\end{aligned}$$

where $\Delta_{\alpha\gamma_1} < \Delta_{\alpha\gamma_2} < \cdots < \Delta_{\alpha\gamma_\nu}$.

For simplicity consider a binary mixture ($\nu = 2$). In this case the last term on the right-hand side of (66) is

$$\beta \frac{\pi}{6} d_{\alpha\alpha}^3 |\Delta| (3 + 3\Delta + \Delta^2) \left[\frac{(1 + \Delta^1)^2}{1 + (1 + \Delta)^2} P - P^{(2)}\right] \qquad (67)$$

where $\Delta = \Delta_{12}$,

$$\beta v_{0\tau} P^{(2)} = \frac{v_{0\tau}\rho_\tau^{(2)}}{1 - v_{0\tau}\rho_\tau^{(2)}} + 3\left(\frac{v_{0\tau}\rho_\tau^{(2)}}{1 - v_{0\tau}\rho_\tau^{(2)}}\right)^2 + 3\left(\frac{v_{0\tau}\rho_\tau^{(2)}}{1 - v_{0\tau}\rho_\tau^{(2)}}\right)^3 \qquad (68)$$

$v_{0\tau} = \frac{1}{6}\pi d_{\tau\tau}^3$ and

$$\Delta^1 = \Delta H(\Delta) = \begin{cases} \Delta, & \Delta > 0 \\ 0, & \Delta < 0 \end{cases}$$

$\rho_\tau^{(2)}$ is calculated from the equation

$$\begin{aligned}\ln \frac{\rho_\tau^{(2)}}{1 - v_{0\tau}\rho_\tau^{(2)}} + 6 \frac{v_{0\tau}\rho_\tau^{(2)}}{1 - v_{0\tau}\rho_\tau^{(2)}} + \frac{9}{2}\left(\frac{v_{0\tau}\rho_\tau^{(2)}}{1 - v_{0\tau}\rho_\tau^{(2)}}\right)^2 & \\ + v_{0\tau}\beta P^{(2)} = \beta\mu_\tau - \beta\mu_\tau{}^0 & \qquad (69)\end{aligned}$$

and $\tau = \alpha$ if $\Delta > 0$ and $\tau \neq \alpha$ if $\Delta < 0$ ($\tau, \alpha = 1, 2$). To eliminate the pressure we use the Gibbs–Duhem relations

$$\frac{\partial P}{\partial \rho_\gamma} = \sum_{\alpha=1}^{2} \rho_\alpha \frac{\partial \mu_\alpha}{\partial \rho_\gamma}, \qquad \frac{\partial P^{(2)}}{\partial \rho_\gamma} = \rho_\tau^{(2)} \frac{\partial \mu_\tau}{\partial \rho_\gamma}$$

When $\Delta_{\alpha\gamma} = 0$ this procedure leads to the known generalization of (51) and (52) for mixtures of hard spheres with additive diameters(21)

$$\frac{\pi}{6}\beta P = \frac{\xi_0}{1 - \xi_3} + 3\frac{\xi_1\xi_2}{(1 - \xi_3)^2} + 3\left(\frac{\xi_2}{1 - \xi_3}\right)^3$$

$$\begin{aligned}\beta\mu_\alpha = {} & \beta\mu_\alpha{}^0 + \ln\frac{\rho_\alpha}{1 - \xi_3} + 3\frac{d_{\alpha\alpha}}{1 - \xi_3}(\xi_2 + d_{\alpha\alpha}\xi_1) \\ & + \frac{9}{2}\left(\frac{d_{\alpha\alpha}\xi_2}{1 - \xi_3}\right)^2 + \frac{\pi}{6} d_{\alpha\alpha}^3 \beta P \qquad (70)\end{aligned}$$

where

$$\xi_k = \frac{\pi}{6} \sum_{\gamma=1}^{\nu} \rho_\gamma d_{\alpha\alpha}^k \tag{70a}$$

But if $\Delta_{\alpha\gamma} \neq 0$, eliminating the pressure from the right-hand side of (66) yields a fundamental thermodynamic inconsistency:

$$\partial\mu_\alpha/\partial\rho_\gamma \neq \partial\mu_\gamma/\partial\rho_\alpha \tag{71}$$

More generally, for isotropic states of anisotropic hard particles, we find ($\bar{\psi}_\gamma{}^\alpha = v_{0\gamma}\rho_\gamma$ and $\bar{C}_{\alpha\gamma}^\alpha = C_{\alpha\gamma}^{\text{h.c.}}\rho_\gamma = S_\alpha \hat{R}_\gamma \rho_\gamma$)

$$\begin{aligned}\frac{\partial\beta\mu_\alpha}{\partial\rho_\tau} = {} & \frac{\delta_{\alpha\tau}}{\rho_\alpha} + \frac{v_{\tau\alpha}}{1 - \sum_\gamma \rho_\gamma v_{0\gamma}} + \frac{\sum_\gamma \rho_\gamma [v_{0\tau}(v_{\alpha\gamma} - v_{0\gamma}) + v_{0\alpha}(v_{\tau\gamma} - v_{0\gamma}) - v_{0\tau}v_{0\alpha}]}{(1 - \sum_\gamma \rho_\gamma v_{0\gamma})^2} \\ & + \frac{v_{0\tau}v_{0\alpha} \sum_{\gamma,\delta} \rho_\gamma\rho_\delta (C_{\gamma\delta}^{\text{h.c.}} + C_{\delta\gamma}^{\text{h.c.}})}{(1 - \sum_\gamma \rho_\gamma v_{0\gamma})^3} + \frac{v_{0\tau}v_{0\alpha} \sum_{\gamma,\delta,\varphi} \rho_\gamma\rho_\delta\rho_\varphi C_{\gamma\varphi}^{\text{h.c.}} C_{\delta\varphi}^{\text{h.c.}}}{(1 - \sum_\gamma \rho_\gamma v_{0\gamma})^4} \\ & + \left\{\frac{\sum_\gamma \rho_\gamma C_{\tau\alpha}^{\text{h.c.}} C_{\gamma\alpha}^{\text{h.c.}}}{(1 - \sum_\gamma \rho_\gamma v_{0\gamma})^2} + \frac{\sum_{\gamma,\delta} \rho_\gamma\rho_\delta (v_{0\tau} C_{\gamma\alpha}^{\text{h..c}} C_{\delta\alpha}^{\text{h.c.}} + v_{0\alpha} C_{\tau\delta}^{\text{h.c.}} C_{\gamma\delta}^{\text{h.c.}})}{(1 - \sum_\gamma \rho_\gamma v_{0\gamma})^3}\right\}\end{aligned} \tag{72}$$

The term in curly brackets leads to the inequality (71), unless$^{(22)}$ all the particles in the mixture have the same shape, differing only in size:

$$(v_{0\alpha}/v_{0\gamma})^{1/3} = (S_\alpha/S_\gamma)^{1/2} = \hat{R}_\alpha/\hat{R}_\gamma$$

(*b*) *Anisotropic Phases* (*Liquid Crystals and Solids*). Differentiation of (47) and subsequent use of the Gibbs–Duhem relation (48) gives

$$\begin{aligned}\frac{\delta\beta\mu_\alpha}{\delta\rho_\tau^{(1)}(\mathbf{X}_\tau)} = {} & \frac{\delta_{\alpha\tau}(\mathbf{X}_\alpha, \mathbf{X}_\tau)}{\rho_\alpha^{(1)}(\mathbf{X}_\alpha)} - \frac{f_{\alpha\tau}(\mathbf{X}_\alpha, \mathbf{X}_\tau)}{v_{\alpha\tau}(\mathbf{\Omega}_{\alpha\tau})} \left\{\frac{v_{\alpha\tau}(\mathbf{\Omega}_{\alpha\tau}) - v_{0\alpha}}{1 - \sum_\gamma \bar{\psi}_\gamma{}^\alpha(\mathbf{X}_\alpha)}\right. \\ & + \frac{v_{0\tau} \sum_\gamma [\bar{C}_{\gamma\alpha}^\alpha(\mathbf{X}_\alpha) + \bar{C}_{\alpha\gamma}^\alpha(\mathbf{X}_\alpha)] + C_{\tau\alpha}^{\text{h.c.}} \sum_\gamma \bar{C}_{\gamma\alpha}^\alpha(\mathbf{X}_\alpha)}{[1 - \sum_\gamma \bar{\psi}_\gamma{}^\alpha(\mathbf{X}_\alpha)]^2} \\ & \left. + \frac{v_{0\tau} \sum_{\gamma,\delta} \bar{C}_{\gamma\alpha}^\alpha(\mathbf{X}_\alpha) \bar{C}_{\delta\alpha}^\alpha(\mathbf{X}_\alpha)}{[1 - \sum_\gamma \bar{\psi}_\gamma{}^\alpha(\mathbf{X}_\alpha)]^3}\right\} + \frac{v_{0\alpha}}{V} \sum_\gamma \int d\mathbf{X}_\gamma\, \rho_\tau^{(1)}(\mathbf{X}_\gamma) \frac{\delta\beta\mu_\gamma}{\delta\rho_\tau^{(1)}(\mathbf{X}_\tau)}\end{aligned} \tag{73}$$

where the symbolic $\delta_{\alpha\tau}(\mathbf{X}_\alpha, \mathbf{X}_\tau)$ is defined as a linear functional

$$\frac{1}{V} \sum_{\alpha=1}^{\nu} \int d\mathbf{X}_\alpha\, \varphi_\alpha(\mathbf{X}_\alpha)\, \delta_{\alpha\tau}(\mathbf{X}_\alpha, \mathbf{X}_\tau) = \varphi_\tau(\mathbf{X}_\tau) \tag{74}$$

on a set of ν arbitrary functions $\{\varphi_\alpha(\mathbf{X}_\alpha)\}_{\alpha=1,\ldots,\nu}$. Therefore we see that

$$\delta\mu_\alpha/\delta\rho_\tau^{(1)} \neq \delta\mu_\tau/\delta\rho_\alpha^{(1)} \tag{75}$$

or, for a pure system,

$$\delta\mu/\delta\rho^{(1)}(\mathbf{X}_1) \neq \delta\mu/\delta\rho^{(1)}(\mathbf{X}_2) \tag{75a}$$

that is, the functional derivative $\delta\mu/\delta\rho^{(1)}$ varies from point to point (direction to direction), in violation of the thermodynamic behavior.

We note, in conclusion, that in two-dimensional systems the quadratic (third) term on the right-hand side of Eqs. (45)–(49) does not appear, and as a consequence (71) becomes an equality for the case considered in Eq. (72).

Lasher$^{(6)}$ and Cotter and Martire$^{(5)}$ have developed slightly different versions of the SPT; we recover their results upon replacing $\bar{\psi}_\gamma{}^\alpha$ by $v_{0\gamma}\rho_\gamma$ in the denominators of (47) and (49). But these minor differences do not change the fundamental difficulties pointed out above for the liquid crystal phase transitions. Henceforth we do not consider the various versions of SPT which have been offered recently to deal with fluids of anisotropic particles. Instead, in the accompanying paper, we treat further the y-expansion approach proposed by us earlier.

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