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Self Similarity, Scaling and Renormalization Group Theory Used to Generate Equations of State for Hard-Particle Fluids*

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An approach based on the concept of functional self-similarity is used to derive equations of state for two- and three-dimensional hard-particle fluids. Calculations indicate that this procedure works quite well, producing estimates of the compressibility factor that closely agree with the results of computer simulation.

Key words: fluids, hard particle model, equation of state, simulation

I. Introduction

The equation of state of a fluid composed of structureless particles with repulsive, hard-core interactions always can be written in the form

$$p = \frac{k_B T}{V} N\phi(\mathrm{N};\mathrm{g}) \tag{1.1}$$

Here T is the absolute temperature and ϕ the compressibility factor. Because of the impenetrable, hard-core interactions, this function ϕ is independent of temperature. Finally, N denotes the total number of particles and g is the dimensionless ratio of the excluded volume per particle to V, the volume of the container to which the fluid is confined. If the fluid is *ideal*, $g = 0$, $\phi(N;0) = 1$ and (1.1) reduces to the perfect gas equation of state. However, when the hard cores of the particles are of finite size, the pressure exceeds that of the corresponding perfect gas and the value of the compressibility factor is greater than unity. The compressibility factor frequently is represented by a virial series of the form

$$\phi(\eta) = 1 + \sum_{j\geq 1} \overline{B}_{j+1}\eta^j \tag{1.2}$$

Here $\eta = Ng$ is the volume (or packing) fraction of the hard-core particles and the $\overline{B}_j$ are dimensionless virial coefficients. It should be noted that the formula (1.2) is appropriate to the thermodynamic limit in which $N \to \infty$ and $g \to 0$ with $Ng = \eta$ and V fi-

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[*] Dedicated to Prof. Jan Stecki on the occasion of his 70th birthday.

nite. For finite values of N the compressibility factor $\phi(N;g)$ is a polynomial of finite order in g with coefficients that are complicated functions of N [1].

At the present time only seven of the coefficients $\overline{B}_j$ have been evaluated for hard-core particle systems in two and three dimensions [2]. As we soon shall demonstrate [see Figures 2 and 3], the associated seventh order polynomial approximations for the compressibility factor do, in fact, agree quite well at sufficiently low densities with the results of computer simulations for hard discs and hard spheres. Nevertheless, it is of interest to produce alternatives to the simple perturbation series (1.2). Specifically, we want to construct the sum of this infinite series based upon a knowledge of only the first few terms. A number of techniques have been proposed for this purpose [3–5]. One of the most successful is that of Carnahan and Starling [4], according to which the exact hard-sphere virial coefficients [see Table 1, below] are replaced with the integral approximations 4, 10, 18, 28, 40, 56 and 70 given by the simple formula $\overline{B}_j(D = 3) = j^2 + j - 2$. The corresponding, modified virial series then can be summed over *all* values of j to produce the well-known Carnahan-Starling equation of state

$$\phi_{CS}(\eta) = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}; \qquad D = 3 \tag{1.3}$$

This same procedure can be applied to the fluid of hard discs, in which case we replace the first seven virial coefficients with the integer approximations $\overline{B}_j(D = 2) = j$ [see Table 1]. The sum of the virial series associated with this approximation is given by the same formula

$$\phi(\eta) = \frac{1}{(1 - \eta)^2}; \qquad D = 2 \tag{1.4}$$

as that obtained by Helfand *et al.* [6] using the scaled-particle method.

The predictions of these two equations of state, (1.3) and (1.4), are in better agreement with the results of computer simulations than predictions based on the corresponding 7-term virial polynomials. Further improvements can be obtained by using the truncated virial series as input polynomials for constructing Padé approximants. This approach was proposed by Ree and Hoover [7], who obtained the expressions

$$\phi_{RH}(\eta) = 1 + 2\eta\,\frac{1 - 0.3934406\eta + 0.026076\eta^2}{1 - 1.957406\eta + 0.95768\eta^2}; \qquad D = 2 \tag{1.5}$$

and

$$\phi_{RH}(\eta) = 1 + 4\eta\,\frac{1 - 0.254028\eta + 0.277264\eta^2}{1 - 2.245972\eta + 1.301008\eta^2}; \qquad D = 3 \tag{1.6}$$

for 2D hard discs and 3D hard spheres, respectively. Compressibility factors computed from these formulas are in very good agreement with simulation data, *cf.* Tables

2 and 3. In addition to the Carnahan-Starling formulas and the Padé approximants, other semiempirical equations of state (*e.g.*, [8,9]) have been reported that generate values of the compressibility factor which agree better with computer simulations than do the virial polynomials.

While the success of these essentially empirical procedures are undeniable, one might prefer a more physically motivated approach. It is in this spirit that we propose an alternative method of resummation, which exploits the notions of scaling invariance and functional self similarity. Our procedure provides an illustration of the renormalization group (RG) method that has been applied usefully to other problems of statistical physics. It is essential in this context to recognize that the RG method is applicable to many very different physical problems, *e.g.*, field theory, polymer physics and critical phenomena. According to Shirkov [8], "the RG method is the regular method of improving perturbation theory results with the help of renorm-group Lie equations...." Although Shirkov's statement was made in the context of quantum electrodynamics and with implied reference to series in power of the fine structure constant, $e^2/\hbar c$, the RG method also has been used in connection with the magnetization of the Ising model, represented by a power series in the exchange energy, and to properties of self-avoiding polymer chains expressed in powers of a parameter related to the excluded-volume interaction energy. In each of these applications the physical aspects of the specific system were incorporated within "initial data" represented by perturbation series. To exploit these data by means of the RG method one must identify a system property to which the assumption of self similarity is appropriate. This invariably is accomplished by identifying a property of the corresponding ideal system that exhibits strict self similarity. In the study presented here, the RG method is applied to the pressure of a hard-particle fluid and the input, "initial data" are provided by truncated virial series. No claim can be made that results generated by this method are exact, for were that so we would have succeeded in solving an incredibly difficult many-body problem. The success of the procedure is determined by how well it works. To establish this we compare our predictions with the results of Monte Carlo computer simulations.

Many efforts have been made in recent years (*cf.*, [11–14]) to improve the predictability of the local structure of inhomogeneous hard-sphere particles by using nontraditional integral equations, some of which [15,16] generalize and extend the ideas of the scaled-particle theory. Not only is the approach used in these studies very different from ours, but so also are the objectives. The integral equation methods contend with subtle and detailed features of the fluid microstructure, whereas we focus exclusively on the macroscopic equation of state.

In the following section we provide an outline of the basic principles of the RG method, as they apply to the equation of state of a hard-particle fluid. Section III is devoted to the one-dimensional system of hard rods, thereby testing the efficacy of this RG method. In Section IV we examine the hard-disc ($D = 2$) and hard-sphere ($D = 3$) fluids. The paper concludes with a discussion of results.

II. Self similarity and scaling

The concepts of functional self similarity and scaling invariance are best conveyed by means of a simple example. For this purpose we consider the equation of state of a perfect gas, according to which the pressure is a linear function of the number of gas particles and can be written as

$$p = p(N;\, k_B T/V) = N\frac{k_B T}{V} = Np(1;\, k_B T/V) \tag{2.1}$$

One easily verifies that the function defined by (2.1) satisfies the simple scaling relation

$$p(N;\, k_B T/V) = \frac{N}{K}\, p(K;\, k_B T/V) \tag{2.2}$$

and this, in turn, can be rewritten as a functional equation,

$$p(N;\, k_B T/V) = p\left[\frac{N}{K};\, p(K; k_B T/V\right] \tag{2.3}$$

that expresses scaling invariance.

According to (2.3), the pressure of a perfect gas is a strictly self-similar object with respect to scaling of the particle number. Alternatively, one can interpret (2.3) as a statement that the pressure is invariant with respect to the scaling transformation

$$\begin{aligned} &N \to N' = N/K \\ &p(1;\, k_B T/V) \to p(K;\, k_B T/V) \end{aligned} \tag{2.4}$$

Incidentally, (2.2) can be identified as a form of the Dalton law, pertaining to the additivity of the partial pressures exerted by N/K subsystems, each at the same temperature and consisting of K particles confined to a common container of volume V.

Yet another interpretation of the situation is to identify (2.3) as the equation of evolution of a dynamical system, with the particle number N playing the role of a discrete time ($1 \le \mathrm{N} < \infty$). One then identifies the single-particle pressure $p(1;\, k_B T/V) = k_B T/V$ to be the “initial value” of the pressure.

The problem becomes more complex when excluded-volume interactions among the particles are taken into account. The pressure and the associated compressibility factor then become dependent on an additional variable g, which serves as a measure of the volume that has become inaccessible to the particle centers due to their impenetrable, hard cores. The pressure of this non-ideal fluid may be written as

$$\begin{aligned} p(N;\, g,\, k_B T/V) &= p(1;\, k_B T/V) N\phi(N;\, g) \\ &= \frac{N}{K}\,\frac{\phi(N; g)}{\phi(K; g)}\, p(1;\, k_B T/V) K\phi(K;\, g) \end{aligned}$$

$$= \frac{N}{K}\,\frac{\phi(N;g)}{\phi(K;g)}\,p(K;\,\mathrm{g},\,k_BT/V) \tag{2.5}$$

The last of these expressions can be recast in a form analogous to the right-hand side of (2.2), *provided* that we are able to find a function $\bar{g}(K;g)$, known as the effective (or running) coupling function, such that the relationship

$$\frac{\phi(N;g)}{\phi(K;g)} = \phi\left[\frac{N}{K};\bar{g}(K;g)\right] \tag{2.6}$$

is an identity. Equation (2.5) then would assume the form

$$p(N;\,g,\,k_BT/V) = \frac{N}{K}\,\phi\left[\frac{N}{K};\bar{g}(K;g)\right]p(K;\,g,\,k_BT/V) \tag{2.7}$$

and this can be rewritten as a functional equation

$$p(N;\,g,\,k_BT/V) = p\left[\frac{N}{K};\bar{g}(K;g),\,p(K,\,g,\,k_BT/V)\right] \tag{2.8}$$

which closely resembles the scaling invariance condition (2.3). Finally, by regrouping terms on the right-hand side of (2.5), this generalized scaling invariance condition for a *non-ideal* fluid can be recast in the form

$$p(N;\,g,\,k_BT/V) = p\left[K;g,\,p\left(\frac{N}{K};\bar{g}(K;g),\,k_BT/V\right)\right] \tag{2.9}$$

A few comments are in order, concerning the physical interpretation of the formalism presented above. First we note that the expression (2.7) describes a scaling of the pressure. The system of N particles is (virtually) separated into N/K subsystems, every one of which contains K interacting particles. Each of these subsystems occupies the entire volume V and contributes a partial pressure $p(K;\,g,\,k_BT/V)$. If it were permissible to neglect interactions among particles assigned to different subsystems, the total pressure would equal $(N/K)p(K;\,g,\,k_BT/V)$. However, particles belonging to different subsystems do indeed interact with one another, so that it is necessary to introduce a corrective factor, namely the renormalized compressibility factor $\phi(N/K;\,\bar{g}(K;g))$. Incorporation of this factor produces the equation (2.7), which clearly can be interpreted as a "scaled-up" form of the corresponding equation, (1.1). Equation (2.7) then has been rewritten in the form (2.8) of a functional equation, expressing the requirement that the value of the pressure be unaltered by the virtual subdivision of the system.

Whether the pressure of a non-ideal fluid can indeed be treated as a functionally self-similar object depends on our success in finding an effective coupling function $\bar{g}(K;\,g)$ that makes (2.6) a mathematical identity. This equation can be written in the explicitly multiplicative form

$$\phi(NK;g) = \phi(K;g)\phi(N;\bar{g}(K;g)) \tag{2.10}$$

where, according to (2.5), $\phi(1;g) = 1$. Then, since (2.10) must be satisfied identically for $K = 1$, it follows that the initial condition for the effective coupling function is $\bar{g}(1;g) = g$. Our search for the effective coupling function is now completed, for it has been established elsewhere [17] that a function which conforms to this initial condition and obeys (2.10) is an invariant of the scaling transformation

$$\begin{aligned} N &\to N' = N/K \\ g &\to g' = \bar{g}(K;g) \end{aligned} \tag{2.11}$$

that satisfies the conservation equation

$$\bar{g}(\mathrm{N};\mathrm{g}) = \bar{g}[N/K;\bar{g}(K;g)] \tag{2.12}$$

The two functional equations, (2.10) and (2.12), form a self-consistent pair governing the evolution of the dynamical system under consideration. Identical equations arise in quantum field theory where they are identified as the functional equations of a multiplicative renormalization group [10,18]. Specifically, (2.10) is identical to the equation for the generalized propagator and (2.12) is the same as that satisfied by the invariant charge.

The utility of these functional equations of evolution, as well as the related differential (Lie) equations given below, is that they permit one to calculate the compressibility factor of a dense, many-body fluid of hard-core particles from information about the compressibility factors of similar systems consisting of only a relatively few particles. In particular, one can use a truncated virial polynomial, that certainly is accurate at low densities, to generate reliable estimates of the compressibility factor for much higher densities. It is important to recognize that the RG formula obtained for the object function (here $\phi(N;g)$) will be functionally dependent on the initial approximation that one has selected, *e.g.*, a specific truncated virial polynomial. Although it is reasonable to expect that convergence will result from the systematic consideration of a sequence of such initial approximations, each input set of data does, in principle, produce a different RG estimate of the object function and one which does as well satisfy the general conservation equation (here (2.8)).

Before proceeding to the calculational part of the paper we must attend to a technical problem associated with the use of the asymptotic $[N \to \infty, g \to 0; Ng = \eta$ finite$]$ series (1.2). In particular, the compressibility factor given by this series does not satisfy the condition $\phi(1;g) = 1$ and, thus, is not normalized to unity with respect to the generalized, time-like variable N. Instead of attempting to construct a modified expression for $\phi(N;\mathrm{g})$ that would be valid for all values of N (see [1] for a virial series correct to second order in g), we introduce the "transfer function" or normalized compressibility factor

$$\tilde{\phi}(N;g) = \phi(N;g)/\phi(1;g) \tag{2.13}$$

The conservation equation (2.8) then is rewritten as

$$p\left[N;g,\ \frac{k_BT}{V}\phi(1;g)\right]=p\left\{\frac{N}{K};g,p\left[K;\bar{g}\left(\frac{N}{K};g\right),\frac{k_BT}{V}\ \phi(1;g)\right]\right\} \tag{2.14}$$

thereby replacing (2.5) with

$$p\left[N;g,\ \frac{k_BT}{V}\phi(1;g)\right]=p\left(1;\ \frac{k_BT}{V}\phi(1;g)\right)N\ \tilde{\phi}(N;g) \tag{2.15}$$

and the initial condition $p(1;\, k_BT/V) = k_BT/V$ with

$$p\left[1;\frac{k_BT}{V}\ \phi(1;g)\right]=\frac{k_BT}{V}\phi(1;g) \tag{2.16}$$

The equation of evolution for the transfer function is identical with (2.10), namely

$$\tilde{\phi}(N;g)=\tilde{\phi}(K;g)\tilde{\phi}\left(\frac{N}{K};\bar{g}(K;g)\right) \tag{2.17}$$

and the effective coupling function continues to satisfy (2.12).

It previously has been demonstrated [17] that the Lie differential equations

$$\frac{\partial\ln\tilde{\phi}(N;g)}{\partial\ln N}=\gamma[\bar{g}(N;g)] \tag{2.18}$$

$$\frac{\partial\bar{g}(N;g)}{\partial\ln N}=\beta[\bar{g}(N;g)] \tag{2.19}$$

can be obtained directly from the functional equations (2.12) and (2.17). The objects $\gamma(g)$ and $\beta(g)$ appearing in these equations are the infinitesimal generators of the RG transformation, defined here by the formulas

$$\gamma(g)=\left.\frac{\partial\,\tilde{\phi}(N;g)}{\partial N}\right|_{N=1} \tag{2.20}$$

and

$$\beta(g)=\left.\frac{\partial\,\bar{g}(N;g)}{\partial N}\right|_{N=1} \tag{2.21}$$

As mentioned previously, the effective coupling function is not an independent quantity but a functional of the object function $\tilde{\phi}(N;\,g)$ which must be determined self-consistently in order to insure the validity of the conservation equation (2.14).

To accomplish this we first differentiate (2.18) with respect to *N*, thereby obtaining the expression

$$\frac{\partial}{\partial N}\left[\frac{\partial \ln \tilde{\phi}}{\partial \ln N}\right] = \frac{\partial \gamma[\bar{g}(N;g)]}{\partial \bar{g}(N;g)} \frac{\partial \bar{g}(N;g)}{\partial N} \tag{2.22}$$

Next, by taking the limit of (2.22) for $N \to 1$ we obtain the formula

$$\beta(g) = \frac{\left.\dfrac{\partial}{\partial N}\left[\dfrac{\partial \ln \tilde{\phi}}{\partial \ln N}\right]\right|_{N=1}}{\dfrac{\partial \gamma}{\partial g}} = \frac{\left.\gamma(g) - \gamma(g)^2 + \dfrac{\partial^2 \tilde{\phi}}{\partial N^2}\right|_{N=1}}{\dfrac{\partial \gamma}{\partial g}} \tag{2.23}$$

which provides an explicit relationship between the so-called Gell-Mann and Low function $\beta(g)$ and the derivatives of the object function, evaluated for the initial value ($N = 1$) of the group parameter.

By taking into account the definition (2.13) of the normalized compressibility factor and the relationship $\phi(N; g) = \phi(\eta)$ between the compressibility factor itself and the virial series of (1.1) one can express the generators directly in terms of the compressibility factor, *viz*.

$$\gamma(g) = \frac{g}{\phi(g)} \frac{d\phi(g)}{dg} \tag{2.24}$$

and

$$\beta(g) = \frac{\gamma(g) - \gamma(g)^2 + \dfrac{g^2}{\phi(g)} \dfrac{d^2\phi}{dg^2}}{\dfrac{d\gamma}{dg}} \tag{2.25}$$

Next, by using (2.24) to calculate $d\gamma/dg$ we find that

$$\beta(g) = g$$

From this last result it can be seen that (2.19) reduces to the simple differential equation $\partial\bar{g}(N; g)/\partial \ln N = \bar{g}(N; g)$, the solution of which is

$$\bar{g}(N; g) = Ng \tag{2.27}$$

The Lie equation (2.18) consequently can be written in the form

$$\tilde{\phi}(N; g) = \exp \int_1^N dN\, \gamma(Ng) / N \tag{2.28}$$

Suppose, now, that our choice for the initial approximation is the virial *polynomial* (truncated series)

$$\phi_M(g) = 1 + \sum_{j=1}^{M} \overline{B}_{j+1} g^j \tag{2.29}$$

From (2.24) we then obtain the corresponding approximation

$$\gamma_M(g) = \frac{\sum_{j=1}^{M} j\overline{B}_{j+1} g^j}{1 + \sum_{j=1}^{M} \overline{B}_{j+1} g^j} = \sum_{j\geq 1} \Gamma_{j+1} g^j \tag{2.30}$$

with

$$\begin{aligned} \Gamma_2 &= \overline{B}_2 \\ \Gamma_3 &= 2\overline{B}_3 - \overline{B}_2^2 \\ \Gamma_4 &= 3\overline{B}_4 - 3\overline{B}_2\overline{B}_3 + \overline{B}_2^3 \\ &\vdots \end{aligned} \tag{2.31}$$

The transfer function $\tilde{\phi}(N; g)$ of (2.28) now can be evaluated. If only terms to second order in g are retained, the result is

$$\tilde{\phi}(N; g) = \exp\left[\overline{B}_2 g(N-1) + \frac{1}{2}(2\overline{B}_3 - \overline{B}_2^2) g^2 (N^2 - 1)\right] \tag{2.32}$$

In the limit $N \to \infty$, $g \to 0$, $Ng = \eta$ finite, this produces a formula for the compressibility factor,

$$\phi(\eta) = \exp\left[\overline{B}_2 \eta + \frac{1}{2}(2\overline{B}_3 - \overline{B}_2^2)\eta^2\right] \tag{2.33}$$

that constitutes a generalization of the Shinomoto [5] equation of state to systems of hard-core particles in spaces of arbitrary dimensions.

More generally, RG calculations using virial polynomials (2.29) for the initial approximation, produce transfer functions of the form

$$\tilde{\phi}(N; g) = \exp\left\{\sum_{j\geq 1} \Gamma_{j+1} g^j \frac{1}{j}(N^j - 1)\right\} \tag{2.34}$$

and these, in turn, yield the corresponding cumulant [19] approximations

$$\phi(\eta) = \exp\left\{\sum_{j\geq 1} \Gamma_{j+1} \frac{1}{j} \eta^j\right\} \tag{2.35}$$

for the compressibility factor.

III. One-dimensional, hard-rod fluid

The so-called Tonks gas [20], consisting of hard particles (rods) confined to a line segment of length L, is an exactly solvable model which therefore can be used to test the RG method outlined in the preceding section. Tonks showed that the pressure of this hard-rod system was given by the formula

$$p = \frac{k_B T}{L} N \frac{1}{1 - Ng} \tag{3.1}$$

where the "bare coupling parameter" $g = \sigma/L$ equals the ratio of σ, the length of a single rod, to L, the length of the line segment. The corresponding compressibility factor

$$\phi(\eta) = \frac{1}{1 - \eta} \tag{3.2}$$

with $\eta = gN$, then can be represented by the virial series (1.2), all coefficients of which have the common value $\overline{B}_j = 1$.

We now assume that the exact formula (3.2) is not known and that the only information available to us is the polynomial approximation

$$\phi_k(\eta) = 1 + \sum_{s=1}^{k} \eta^s = (1 - \eta^{k+1}) / (1 - \eta) \tag{3.3}$$

The corresponding, approximate infinitesimal generator $\gamma_k(g)$ is then

$$\gamma_k(g) = \frac{g}{1 - g}\left[1 - (k+1)\frac{(1-g)g^k}{1 - g^{k+1}}\right] = g + g^2 + g^3 + \cdots + g^k + \cdots \tag{3.4}$$

In the limit $k \to \infty$ this series approaches the exact result, namely,

$$\gamma(g) = \lim_{k \to \infty} \gamma_k(g) = \frac{g}{1 - g} \tag{3.5}$$

The Shinomoto-like, exponential approximation for the compressibility factor of the Tonks gas is

$$\phi(\eta) \cong \exp\left(\eta + \frac{1}{2}\eta^2\right) \tag{3.6}$$

In Figure 1, predictions based on this simple approximation are compared with results obtained from the exact formula (3.2). The other curves included in this figure illustrate that by using progressively higher order approximations one obtains correspondingly more accurate estimates of the compressibility factor. The general formula (2.35), with all coefficients Γ_i set equal to unity, obviously converges to the exact formula (3.2) in the limit k → ∞, *viz.*,

$$\phi(\eta) = \lim_{k\to\infty} \exp\left[\sum_{j=1}^{k} \frac{1}{j}\eta^j\right] = \exp\left[\ln \frac{1}{1-\eta}\right] = \frac{1}{1-\eta} \tag{3.7}$$

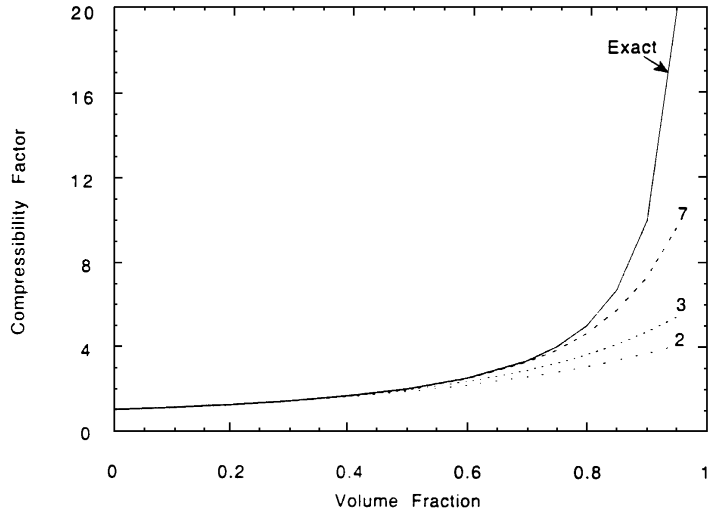

Figure 1. The compressibility factor of a one-dimensional hard-rod fluid. The continuous curve (labeled "exact") is a plot of the Tonks equation (3.1). The labels 2, 3 and 7 of the broken curves indicate the number of virial coefficients used to construct the corresponding RG approximations.

The one-dimensional, hard-rod system clearly is exceptional. In all other cases one is unable to solve the problem exactly. Indeed, this is precisely why it is necessary to develop an effective approximation procedure, such as the RG method described above, which permits one to construct the object function from limited information (here the behavior of the compressibility factor at low densities).

IV. Hard discs and hard spheres

For hard-core fluids in two and three dimensions the available information about the compressibility factor is limited to seven coefficients of the virial series (1.2). The relevant data are presented in Table 1.

From these data and (2.33) one obtains the Shinomoto 2D and 3D, second order cumulant approximations

$$\phi_{2D}^{Sh}(\eta) = \exp(2\eta + 1.128\eta^2) \tag{4.1}$$

and

$$\phi_{3D}^{Sh}(\eta) = \exp(4\eta + 2\eta^2) \tag{4.2}$$

respectively. Corresponding to these are the seventh order cumulant approximations

$$\phi_{2D}(\eta) = \exp(2\eta+1.128\eta^2+0.6686\eta^3+0.4409\eta^4+0.3465\eta^5+0.3043\eta^6+0.2892\eta^7) \tag{4.3}$$

and

$$\phi_{3D}(\eta) = \exp(4\eta+2\eta^2 - 0.3020\eta^3+0.7653\eta^4+1.8302\eta^5-0.2013\eta^6+0.7146\eta^7) \tag{4.4}$$

obtained by using all seven of the presently available virial coefficients.

Values of the compressibility factor predicted by these and several other approximate formulas are presented graphically in Figure 2 (2D) and Figure 3 (3D), where they also are compared with results generated by computer simulations. Indicated in these figures by the symbols η_{RCP} and η_{OCP} are the packing fractions specific to random (RCP) and ordered (OCP) closest packing of the discs and spheres. The current best estimates of these densities [21] are $\eta_{RCP}(2D) \cong 0.82$ and $\eta_{OCP}(2D) \cong 0.907$ for discs and $\eta_{RCP}(3D) \cong 0.64$ and $\eta_{OCP}(3D) \cong 0.74$ for spheres. Finally, numerical values of the compressibility factor obtained from several approximation formulas are collected in Table 2 (2D) and Table 3 (3D).

Table 1. Virial coefficients $\overline{B}_j$ and the corresponding cumulant coefficients Γ_j (see Eq. (2.30)) for two (2D) and three (3D) dimensional hard-core fluids [2].

	2D		3D	
j	$\overline{B}_j$	Γ_j	$\overline{B}_j$	Γ_j
2	2	2	4	4
3	3.128	2.256	10	4
4	4.258	2.005	18.365	–0.906
5	5.337	1.764	28.224	3.061
6	6.363	1.732	39.739	9.151
7	7.351	1.820	53.539	–1.208
8	8.338	2.038	70.779	5.002

The squares, circles, triangles and diamonds of Figure 2 locate values of the hard-disc compressibility factor obtained from several computer simulations. Compressibility factor estimates based on the Shinomoto-type, second-order cumulant approximation fall below all the simulation data except for those indicated by circles [23]. Significantly better predictions are produced by the *third* order cumulant approximation, marked "2" in the figure, which utilizes only the three virial coefficients $\overline{B}_2$, $\overline{B}_3$ and $\overline{B}_4$. Indeed, curve "2" is indistinguishable from a plot of the *seventh* order virial polynomial. Even better agreement with the computer simulations is provided by the seventh order cumulant approximation of (4.3), which appears in the figure as curve "3".

It is unfortunate that the simulations of Erpenbeck and Luban [22], which appear to be the most precise presently available, are limited to densities $\eta < 0.65$. We have included these simulation data (indicated by solid squares in Fig. 2) in Table 2 so that they can be compared directly with the predictions of several approximation formulas. It is apparent from the entries in this table (see the percent deviations appearing in the last row) that, for the densities studied by Erpenbeck and Luban, the Padé Approximant equation of state agrees best with the simulation data. Second in perfor-

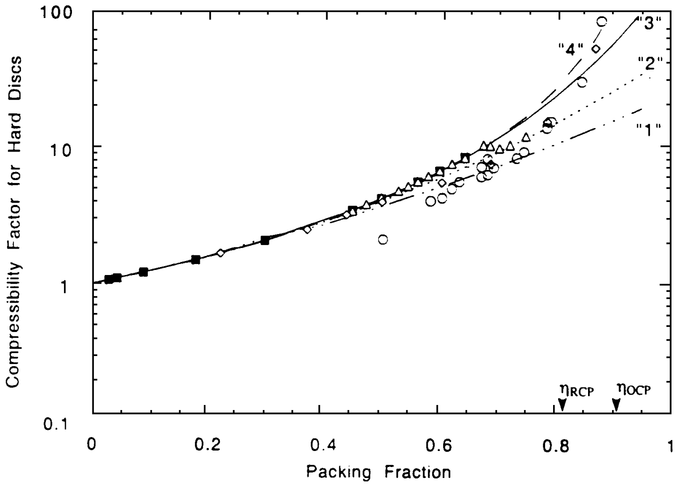

Figure 2. The compressibility factor of a two-dimensional hard-disc fluid. The solid squares, circles, triangles and diamonds indicate values of the compressibility factor obtained from the computer simulations of Erpenbeck and Luban [22], Rotenberg [23], Metropolis *et al.* [24] and from Ree and Hoover's collection of Alder data [7], respectively.

The curve labeled "1" is a plot of the Shinomoto, second-order cumulative approximation of Eq. (4.1). The third-order cumulant approximation of curve "2" is virtually identical with the seventh order virial polynomial. Curve "3" is the seventh order cumulant approximation (the highest order available). Curve "4" is a plot of the "resummed" virial series given by Eq. (1.4). Finally, η_{RCP} and η_{OCP} are the packing fractions for random (RCP) and ordered (OCP) close packing, respectively.

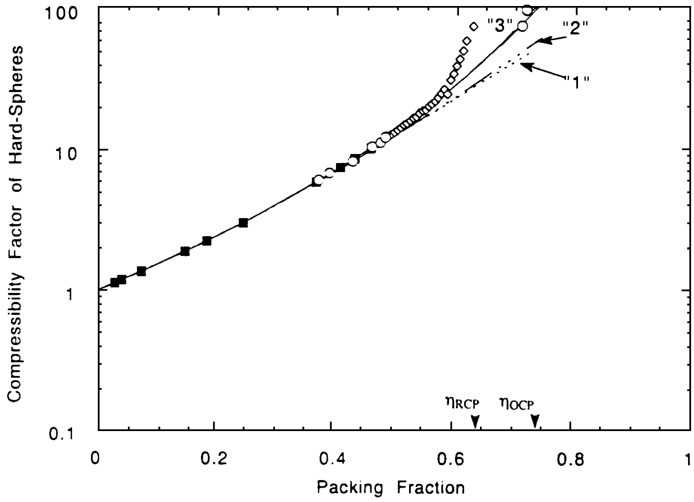

Figure 3. The compressibility factor of a hard-sphere fluid. The solid squares, circles and diamonds indicate values obtained from the computer simulations of Erpenbeck and Wood [25], Rotenberg [23] and Woodcock [26], respectively.

The curve "1" is a plot of the seventh-order virial polynomial. Curve "2" is the Shinomoto, second-order cumulant approximation of Eq. (4.2). Finally, "3" is a plot of the RG seventh-order cumulant approximation of Eq. (4.4) and of the Carnahan-Starling equation (1.3) as well, since they are indistinguishable on the scale of this figure.

mance is the RG equation of state (seventh order cumulant) and third is (1.4), which we obtained in Section I by using the Carnahan-Starling [4] trick for summing the virial series and which earlier was gotten by using the scaled-particle method [6].

Table 2. Compressibility factors for a 2D system of hard discs. Here η denotes the packing fraction and $\Delta = 1/10 \sum_{j=1}^{10} |\phi_{MC}(\eta_j) - \phi(\eta_j)|/\phi_{MC}(\eta_j)$ is the average fractional deviation from the Monte Carlo (MC), computer simulation data of Ref. [22].

Packing fraction η	Simulations MC	Virial series	Scaled particle theory Eg. (1.4)	Shinomoto Eq. (4.1)	Padé approximant Eq. (1.5)	RG theory Eq. (4.3)
0.03023	1.06337(2)	1.06344	1.06332	1.06342	1.06344	1.06344
0.04534	1.09743(3)	1.09753	1.09724	1.09746	1.09753	1.09753
0.09069	1.21068(3)	1.21069	1.20972	1.21004	1.21069	1.21069
0.18138	1.4983(1)	1.49852	1.49223	1.49163	1.49844	1.49843
0.30230	2.0771(2)	2.07625	2.05429	2.02928	2.07730	2.07717
0.45345	3.4243(3)	3.39145	3.34765	3.12313	3.42425	3.42205
0.50383	4.1715(4)	4.08566	4.06199	3.64734	4.17030	4.16419
0.56681	5.4963(6)	5.23751	5.32897	4.46387	5.49079	5.46884
0.60460	6.6074(6)	6.12604	6.39627	5.06083	6.59791	6.55083
0.64779	8.306(1)	7.37348	8.06114	5.86454	8.31249	8.20012
100Δ	0	2.64	1.57	9.58	0.0388	0.290

Table 3. Compressibility factors for a 3D system of hard spheres. η denotes the packing fraction and $\Delta = 1/10 \sum_{j=1}^{10} |\phi_{MC}(\eta_j) - \phi(\eta_j)|/\phi_{MC}(\eta_j)$ is the average fractional deviation from the Monte Carlo (MC), computer simulation data of Ref. [25].

Packing fraction η	Simulations MC	Virial series	C-S Eq. (1.3)	Shinomoto Eq. (4.2)	Padé approximant Eq. (1.6)	RG theory Eq. (4.4)
0.0296	1.12777	1.12766	1.1277	1.12767	1.12766	1.12766
0.0411	1.18282	1.18265	1.1826	1.18267	1.18265	1.18265
0.0740	1.35939	1.35915	1.3590	1.35928	1.35915	1.35915
0.1481	1.88839	1.88848	1.8872	1.88941	1.88847	1.88850
0.1851	2.24356	2.24394	2.2416	2.24549	2.24394	2.24409
0.2468	3.03114	3.02952	3.0252	3.03139	3.03026	3.03129
0.3702	5.85016	5.79471	5.8305	5.78285	5.83311	5.85230
0.4114	7.43040	7.29440	7.4099	7.27250	7.39697	7.44104
0.4356	8.60034	8.37362	8.5806	8.34694	8.54838	8.61875
0.4628	10.19388	9.79982	10.1780	9.77246	10.10784	10.22531
100Δ	0	0.940	0.140	1.053	0.228	0.078

Figure 3 and Table 3 tell a somewhat similar story for 3D hard spheres, but here the seventh order cumulant approximation of the RG theory provides the most accurate representation of the Monte Carlo simulation data. The average deviation between Monte Carlo data points and our predictions is less than 0.08%. Next in accuracy is the Carnahan-Starling Eq. (1.3) which exhibits a relative deviation that is almost twice as large as that of the RG equation of state (4.4). Also of interest in this context are predictions of the compressibility factor extracted from the theory of Labik *et al.* [15,16]). Although these are not included in Figure 3 or Table 3, they are characterized by an average percent deviation of $100\Delta = 0.159$, which is slightly larger than that of the Carnahan-Starling equation of state.

V. Closing remarks

The renormalization group (RG) method used in this paper is based on the assumption that the pressure of a hard-particle fluid, at constant temperature and volume, is a self-similar function of the number of particles. The hint that this might be so is provided by the equation of state of a perfect gas of N particles, which according to (2.3) equals the sum of the partial pressures exerted by N/K similar subsystems, each at the same temperature and consisting of K particles confined to a common container of volume V. The functional equation of our RG, (2.8) or (2.9), is a logical generalization of this Dalton law to *non-ideal* fluids of hard particles.

The idea of partitioning the elements of a many-body system into subsystems, deemed to be similar to the total system, is an essential feature of many real-space RG techniques. In particular, it was used in Kadanoff's approach [27,28] to the spin-lattice problem, according to which the entire lattice was divided into blocks. It also was part of de Gennes' [29] treatment of a linear polymer chain, which he divided into a collection of "blobs".

Our version of this method stresses the intimate relationship that can be established between the object function (here the compressibility factor) and the effective coupling function, which here serves simply as a control function of the approximation. Thus, the role of this coupling function is to ensure that the basic conservation (or evolution) equation (2.8) is a mathematical identity. This formulation of RG theory closely follows the general line of reasoning of the "old RG method", as outlined by Shirkov [10] and by Bogoliubov and Shirkov [18]. The method is treated as a mathematical procedure by which one can extend the range of group parameters (N in our case) for which an initial approximation to the object function is applicable. To accomplish this one derives an equation of evolution for the quantity of interest. This last feature of the theory, as presented here, distinguishes it from other approaches used in statistical mechanics to obtain equations of state for non-ideal fluids. Thus, for example, widely known equations of state for hard-particle fluids such as those of Percus and Yevick, the HNC theory [30] and those cited in [15] and [16], are obtained by procedures designed to determine the equilibrium pair correlation function of the fluid. Once this has been found, the compressibility factor then is determined from the relationship (in 3 dimensions)

$$\phi = 1 + \frac{2\pi\sigma^3}{3}\frac{N}{V}\,g_2(\sigma) \tag{5.1}$$

with $g^2(\sigma)$ denoting the value at contact of the radial distribution function. In this respect, our method is more direct and relies only on a knowledge of a few virial coefficients.

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