PHYSICAL REVIEW E VOLUME 54, NUMBER 6 DECEMBER 1996

Application of a new renormalization group to the equation of state of a hard-sphere fluid

Andrzej R. Altenberger and John S. Dahler
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

(Received 16 February 1996; revised manuscript received 11 July 1996)

A new renormalization group method is developed and applied to the task of resumming the virial series for the compressibility factor of a hard-sphere fluid. Results are compared with the predictions of earlier equations of state and with the outputs of computer simulations. [S1063-651X(96)12312-6]

PACS number(s): 05.70.Ce, 64.60.Ak

I. INTRODUCTION

The equation of state for an imperfect gas may be written in the form

$$p = k_B T n \phi(n,T), \tag{1.1}$$

with n the number density, T the absolute temperature, and ϕ the compressibility factor. The coefficients B_j occurring in the virial expansion

$$\phi(n,T) = 1 + \sum_{j=1}^{\infty} B_{j+1}(T) n^j \tag{1.2}$$

are functions of temperature and functionals of the particle interactions. When these interactions are central and pair additive, the associated interparticle potential function is commonly expressed in terms of a characteristic range σ, a characteristic energy ϵ, and a number of additional, dimensionless parameters, ξ, viz., $u(r) = \epsilon v(r/\sigma, \xi)$. The compressibility factor of Eq. (1.2) then can be written in the alternative form

$$\phi(n,T) = 1 + \sum_{j=1}^{\infty} \tilde{B}_{j+1}(\tilde{T},\xi)\eta^j, \tag{1.3}$$

with the symbol

$$\eta = \frac{\pi\sigma^3}{6} n, \tag{1.4}$$

denoting a dimensionless volume fraction and where

$$\tilde{B}_j(\tilde{T},\xi) = B_j(T) \bigg/ \left(\frac{\pi\sigma^3}{6}\right)^{j-1} \tag{1.5}$$

is a function of the "reduced temperature" $\tilde{T} = k_B T/\epsilon$ and of the parameters ξ.

The evaluation of B_j (or $\tilde{B}_j$) involves integration over the coordinates of j interacting particles [1]. The difficulty and expense of performing this calculation rise rapidly with the value of the index j. The first five virial coefficients have been evaluated for the Lennard-Jones 6-12 potential [2]. Much less is known about the virial coefficients for other, continuous two-parameter potentials [2]. The second virial coefficient can be easily evaluated for the more realistic multiparameter potentials, but few if any higher order coefficients appear to have been examined for these potentials.

The system about which the most is known is a dense gas of rigid spheres. Due to the singularity of the hard-sphere potential the virial coefficients for this case are independent of temperature. Eight have been evaluated [2,3]. The corresponding virial expansion of the compressibility factor is

$$\phi(\eta) = 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.24\eta^4 + 39.5\eta^5 + 56.5\eta^6 + 70.779\eta^7 + \cdots . \tag{1.6}$$

As illustrated in Fig. 1, computations based on this truncated, eight-term virial series are in excellent agreement with the results of computer simulations, over the entire range of existence of the hard-sphere disordered fluid phase, $0 \leqslant \eta \lesssim 0.6$. We are fortunate in this case to have available so many virial coefficients. However, as noted in the preceding paragraph, much less information usually is available. This, in turn, severely limits our ability to produce reliable estimates of the compressibility factor. For example, it is evident from Fig. 1 that the more severely truncated 3-virial coefficient approximation fails to produce accurate estimates of $\phi(\eta)$ for volume fractions as small as 0.20. It is therefore natural to search for means by which a knowledge of only a very few virial coefficients can be used to generate reliable estimates of $\phi(\eta)$ for all values of the volume fraction.

In this paper we propose a new method for achieving this goal. Our procedure is based on renormalization group theory [4,5]. It is restricted to stable gas phases for which the pressure is a positive definite quantity. The hard-sphere disordered fluid phase therefore serves as an excellent test case for the method. Furthermore, because the compressibility factor for this phase is so well described by the truncated virial series (1.6), we adopt this polynomial approximation for $\phi(\eta)$ as a (nearly exact) standard to which all other estimates will be compared.

In the next section the basic principles of the new renormalization group method are outlined. Section III is devoted to the renormalization group (RG) calculation of the hard-sphere compressibility factor and to the comparison of this result with estimates of $\phi(\eta)$ obtained by other methods. In this context it should be emphasized that the purpose of this study has not been to produce a new and/or better equation of state for rigid spheres but to test our RG theory and thereby illustrate its capability (or lack thereof) of treating a specific and familiar problem of statistical physics. The final section includes a discussion of results and of other possible

1063-651X/96/54(6)/6242(11)/$10.00

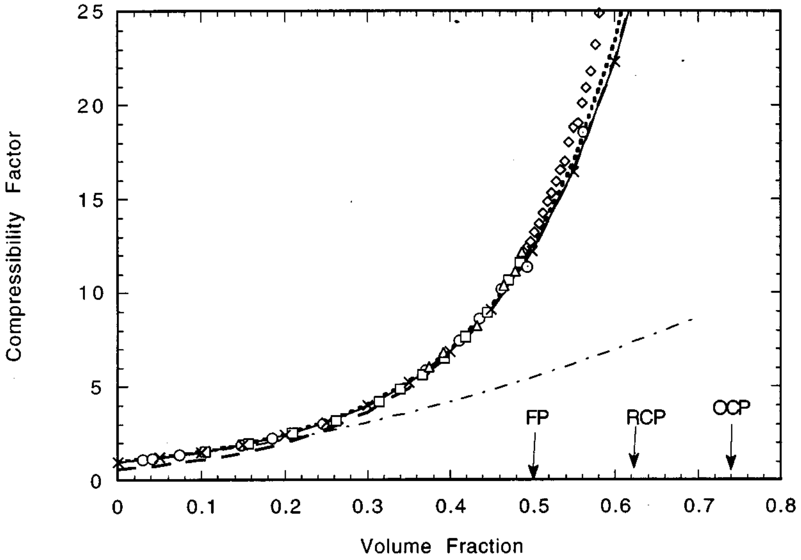

FIG. 1. Compressibility factors generated by various theories and computer simulations. The lower (dot-dashed) curve was obtained using only the second and third virial coefficients. The upper, solid curve is the eight-term virial polynomial of Eq. (1.6); it is indistinguishable on the scale of this graph from the PFRG equation of state, indicated by ×. The heavy dashed curve (––) is obtained from the asymptotic formula, Eq. (3.18), and the dotted curve (---) indicates results produced by the iteration based on the PFRG relationship of Eq. (3.9). The squares (□), circles with dots (⊙), triangles (△), circles (○), and diamonds (◇) are results of the computer simulations reported in Refs. [15–19], respectively. RCP and OCP indicate volume fractions appropriate to random close packing and ordered closest packing, respectively. FP is the ''freezing point'' density of Ref. [20].

applications of the method. Supplementary mathematical results are contained in three Appendixes.

II. THE RENORMALIZATION GROUP METHOD

Most of the many-body systems encountered in statistical physics can be characterized by two dimensionless parameters. One, which we denote by g, gauges the strength of the particle interactions. Systems for which $g=0$ are ''ideal'' and their properties are known exactly. The second parameter, t, usually (but not always) is related to the size of the system through some variable such as the particle density. Any physical quantity then can be represented by a function $f(t,g)$ of these two parameters. The standard thermodynamic perturbation procedure invariably amounts to a simple Maclaurin expansion of the function $f(t,g)$ in powers of the ''bare coupling variable'' g:

$$f(t,g)=1+f_1(t)g+\tfrac{1}{2}f_2(t)g^2+\cdots\ . \tag{2.1}$$

Here we have assumed (without loss of generality) that the function $f(t,g)$ is so defined that $f(t,0)=1$.

At this point we briefly interject a few comments intended to demonstrate the connection between these general remarks and the previously described hard-sphere compressibility factor problem. In the case of the hard-sphere fluid we identify the ''bare'' interaction parameter with a volume fraction η_0 so small that some low-order, polynomial truncation of the virial series (1.3) produces an accurate estimate of the compressibility factor. The parameter t is taken equal to the ratio of the actual volume fraction to that of the reference state. The pair of variables

$$\begin{aligned} g&=\eta_0,\\ t=\eta/\eta_0&=\begin{cases} n/n_0, & \text{if } \sigma_0 \text{ is constant}\\ (\sigma/\sigma_0)^3, & \text{if } n \text{ is constant}\end{cases}\end{aligned} \tag{2.2}$$

is capable of describing two distinct scenarios. In the first, we increase the number density of particles while maintaining a constant ''excluded volume'' range parameter σ_0. In the second, the system is crowded by increasing the range parameter without altering the particle number density. Using the variables defined by Eq. (2.2), we rewrite the virial expansion (1.3) in the form

$$\phi(tg)\equiv\phi(t,g)=1+\sum_{j=1}^{\infty}\frac{1}{j!}\,\phi_j(t)g^j, \tag{2.3}$$

with

$$\phi_j(t)=j!\,\widetilde{B}_{j+1}(\widetilde{T})t^j. \tag{2.4}$$

The compressibility factor function $\phi(t,g)$ defined by Eqs. (2.3) and (2.4) is an example of the function $f(t,g)$ introduced in the preceding paragraph.

Truncated, polynomial approximations to the Maclaurin series (2.1) generally cannot be expected to produce accurate estimates of the function $f(t,g)$ for large values of the variable t. The most fundamental idea of the renormalization group method is that instead of using the perturbation series one constructs an equation of evolution for $f(t,g)$, wherein (for historical reasons) the parameter t is interpreted as a ''generalized time.'' In group theoretical jargon we assume that the function $f(t,g)$ is a representation of a continuous one-parameter group (or semigroup), with the variable $t\geqslant 1$

playing the role of the group parameter. Once the equation of evolution (Lie equation) for this function has been established we can calculate $f(t,g)$ for a whole range of values of the group parameter t, including those for which the initial perturbation series may have been unreliable or even divergent. The crucial step in applying the renormalization group method is that of deciding for which group the given function f is a representation. In other words, what is the functional equation of the group operation satisfied by the function f? The form of the group operation determines the form of the (Lie) equation of evolution. This in turn fixes the behavior of the function $f(t,g)$ at values of t greater than those for which the original perturbation series was valid. So far as we have been able to determine, nothing can be inferred about the form of this functional equation unless restrictions are imposed upon the physical quantity $f(t,g)$. Here we assume this function to be positive definite, $f(t,g) > 0$, over the entire range of the group parameter t.

The next step is to introduce the ''transfer function'' $\tilde{f}(t,g)$, defined in terms of the original function $f(t,g)$ by the formula

$$\tilde{f}(t,g)=f(t,g)/f(1,g). \tag{2.5}$$

This function also can be called the ''normalized'' form of $f(t,g)$, since it exhibits the property $\tilde{f}(1,g)=1$. Evidently, the transfer function is an elementary solution of the equation of evolution for $f(t,g)$.

To derive the functional equation satisfied by the transfer function we observe that every positive definite function $\tilde{f}(t,g)$ can be written in the form

$$\tilde{f}(t,g)=\exp\left\{\int_1^t dx\,\mathcal{L}(x,g)\right\}, \tag{2.6}$$

with

$$\mathcal{L}(x,g)=\frac{\partial}{\partial x}\ln \tilde{f}(x,g). \tag{2.7}$$

By applying Eq. (2.6) to two different values of the parameter t we find that

$$\tilde{f}(x,g)=\tilde{f}(z,g)\left[\exp\left\{\int_1^{x/z} dt\,\mathcal{L}(tz,g)\right\}\right]^z. \tag{2.8}$$

This formula can be identified as the functional equation for the group operation provided that there exists a function $\overline{g}(z,g)$, known as the ''effective'' or ''running'' coupling function, which allows the integrand factor $\mathcal{L}(tz,g)$ to be written as

$$\mathcal{L}(tz,g)=\mathcal{L}(t,\overline{g}(z,g)). \tag{2.9}$$

This effective coupling function is required to satisfy the initial condition $\overline{g}(1,g)=g$. We then can rewrite Eq. (2.8) as the functional equation

$$\tilde{f}(tz,g)=\tilde{f}(z,g)[\tilde{f}(t,\overline{g}(z,g))]^z, \tag{2.10}$$

defining the group operation. Equation (2.10) may be written in the alternative form

$$\tilde{f}(x,g)/\tilde{f}(z,g)=[\tilde{f}(x/z,\overline{g}(z,g))]^z. \tag{2.11}$$

The left-hand side of this last equation can be identified as the ''renormalized'' form of the initial function $f(t,g)$; the ratio $\tilde{f}(x,g)/\tilde{f}(z,g)$ is equal to unity for the group parameter value $x=z$, whereas $\tilde{f}(x,g)\equiv f(x,g)/f(1,g)$ equals unity for $x=1$.

The functional equation satisfied by the effective coupling function $\overline{g}(t,g)$ is obtained by noting that the value of the transfer function appearing on the left-hand side of Eq. (2.10) remains the same when the order of the group parameters is interchanged in the product tz. The right-hand side of Eq. (2.10) will exhibit this same invariance only if (see Appendix A) the effective coupling function satisfies the familiar functional equation [5]

$$\overline{g}(x,g)=\overline{g}(x/z,\overline{g}(z,g)). \tag{2.12}$$

The Lie equations of evolution are obtained from Eqs. (2.11) and (2.12) by differentiating with respect to the group parameter x and then equating x to z. This operation produces the following equations for the ''renormalized flow'' of our new renormalization group for positive definite functions (PFRG):

$$\frac{\partial \ln \tilde{f}(x,g)}{\partial x}=\gamma[\overline{g}(x,g)], \tag{2.13}$$

$$\frac{\partial \overline{g}(x,g)}{\partial \ln x}=\beta[\overline{g}(x,g)]. \tag{2.14}$$

The functions $\gamma(g)$ and $\beta(g)$ are the so-called ''infinitesimal generators'' of the PFRG transformation. They can be identified as functionals of the transfer function, viz.,

$$\gamma(g)=\left.\frac{\partial \tilde{f}(x,g)}{\partial x}\right|_{x=1}=f'(1,g)/f(1,g), \tag{2.15}$$

$$\beta(g)=\left.\frac{\partial \overline{g}(x,g)}{\partial x}\right|_{x=1}=\frac{f''(1,g)/f(1,g)-\gamma^2(g)}{(\partial\gamma/\partial g)}. \tag{2.16}$$

Here $f'(1,g)=\partial f(x,g)/\partial x|_{x=1}$ and $f''(1,g)=\partial^2 f(x,g)/\partial x^2|_{x=1}$. It is established in Appendix B that the Eqs. (2.13) and (2.14) are unique, provided that the infinitesimal generator $\gamma(g)$ is a single valued function of the ''bare'' coupling constant g. An alternative pair of evolution equations is derived in Appendix C.

The flow equations (2.13) and (2.14) could be solved for $\tilde{f}(t,g)$ and $\overline{g}(x,g)$ if the infinitesimal generators β and γ were known. However, β and γ are themselves functionals of $f(t,g)$. Some approximation must be introduced in order to produce estimates of the infinitesimal generators. For this purpose we use the initial polynomial approximation to the function $\tilde{f}(x,g)$. Since this approximation works well for $x\approx 1$, the procedure should produce reasonable estimates for $\beta(g)$ and $\gamma(g)$; the derivatives occurring in Eqs. (2.15) and (2.16) are to be evaluated at $x=1$.

The behavior of the transfer function at large values of the group parameter is controlled by the asymptotic properties of the effective coupling function $\overline{g}(x,g)$. According to Eqs.

(2.13) and (2.14), this function determines the behavior of the infinitesimal generators of the renormalization flow. The properties of $\overline{g(x,g)}$ for large values of x are determined by the stable fixed points of the renormalization group transformation. These fixed points are solutions of the equation

$$\beta(g^*)=0. \tag{2.17}$$

According to the Lie equations (2.13) and (2.14), the behavior of $f(t,g)$ at large values of the group parameter ($x\rightarrow\infty$) depends on the asymptotic limit of the effective coupling function $\overline{g(x,g)}$, if such a limit does indeed exist.

In the neighborhood of the fixed point $g^*>0$ we can write the effective coupling function in the form

$$\overline{g(x,g)}=g^*+\delta\overline{g(x,g)} \tag{2.18}$$

and determine the deviation $\delta\overline{g(x,g)}$ from the linearized equation

$$\frac{\partial}{\partial \ln x}\,\delta\overline{g}=\beta_1^*\,\delta\overline{g(x,g)}, \tag{2.19}$$

where

$$\beta_1^*=\partial\beta(g)/\partial g|_{g=g^*}. \tag{2.20}$$

The solution of Eq. (2.19) is

$$\delta\overline{g(x,g)}=(g-g^*)x^{\beta_1^*}. \tag{2.21}$$

The fixed point g^* is stable if $\beta_1^*<0$, since only then does the perturbation given by Eq. (2.21) vanish in the large x limit.

The asymptotic behavior of the function $\tilde{f}(t,g)$ can be obtained by solving the (linearized) equation

$$\frac{\partial \ln \tilde{f}(x,g)}{\partial x}=\gamma(g^*)+\gamma_1(g^*)(g-g^*)x^{\beta_1^*}, \tag{2.22}$$

wherein

$$\gamma_1(g)=\partial\gamma/\partial g. \tag{2.23}$$

In the special case of $\beta_1^*=-1$, the solution of Eq. (2.22) is

$$f(x,g)\underset{x\rightarrow\infty}{\sim} f(x_0,g)e^{\gamma(g^*)(x-x_0)}\left(\frac{x}{x_0}\right)^{\gamma_1(g^*)(g-g^*)}. \tag{2.24}$$

For $\beta_1^*\neq-1$ (but $\beta_1^*<0$) the solution is given by

$$f(x,g)\underset{x\rightarrow\infty}{\sim} f(x_0,g)e^{\gamma(g^*)(x-x_0)} \times e^{\gamma_1(g^*)(g-g^*)(x^{\beta_1^*+1}-x_0^{\beta_1^*+1})/(\beta_1^*+1)}. \tag{2.25}$$

The system is ‘‘asymptotically free’’ if $g^*=0$, in which case the asymptotic form of $f(t,g)$ is given either by

$$f(x,g)\underset{x\rightarrow\infty}{\sim} f(x_0,g)\left(\frac{x}{x_0}\right)^{\gamma_1(0)g}, \quad \beta_1^*=-1, \tag{2.24$'$}$$

or by

$$f(x,g)\underset{x\rightarrow\infty}{\sim} f(x_0,g)e^{\gamma_1(0)g(x^{\beta_1^*+1}-x_0^{\beta_1^*+1})/(\beta_1^*+1)}, \quad \beta_1^*\neq-1. \tag{2.25$'$}$$

III. EQUATION OF STATE OF THE HARD-SPHERE GAS

The general method developed in the preceding section now will be applied to the ‘‘resummation’’ of the compressibility factor virial series. In doing this we shall assume that the initially available truncated virial series is the *second order* polynomial,

$$\phi(t,g)=1+\phi_1(t)g+\tfrac{1}{2}\phi_2(t)g^2, \tag{3.1}$$

with [cf. Eqs. (2.3) and (2.4)]

$$\phi_1(t)=\tilde{B}_2(\tilde{T})t$$

and

$$\phi_2(t)=2\tilde{B}_3(\tilde{T})t^2. \tag{3.2}$$

The transfer function $\tilde{\phi}(t,g)$ is then given by the series

$$\tilde{\phi}(t,g)=1+\tilde{\phi}_1(t)g+\tfrac{1}{2}\tilde{\phi}_2(t)g^2+\cdots, \tag{3.3}$$

with

$$\begin{aligned}\tilde{\phi}_1(t)&=\tilde{B}_2(t-1),\\ \tilde{\phi}_2(t)&=2\tilde{B}_3t^2-2\tilde{B}_2^2t-2\tilde{B}_3+2\tilde{B}_2^2.\end{aligned} \tag{3.4}$$

From these we obtain the following second-order approximations to the infinitesimal generators of the PFRG transformation.

$$\begin{aligned}\gamma(g)&=\tilde{B}_{2g}+(2\tilde{B}_3-\tilde{B}_2^2)g^2,\\ \beta(g)&=\frac{2\tilde{B}_3-\tilde{B}_2^2}{\tilde{B}_2}\,g^2.\end{aligned} \tag{3.5}$$

They in turn lead to the formulas

$$\overline{g(x,g)}=\frac{g}{1-\dfrac{2\tilde{B}_3-\tilde{B}_2^2}{\tilde{B}_2}\,g\ln x}, \tag{3.6}$$

and

$$\phi(\eta)=\phi(\eta_0)\exp\left\{\tilde{B}_2\int_1^{\eta/\eta_0}dx\left[\overline{g(x,\eta_0)}+\frac{2\tilde{B}_3-\tilde{B}_2^2}{\tilde{B}_2}\,\overline{g^2(x,\eta_0)}\right]\right\}, \tag{3.7}$$

respectively, for the effective coupling function and the compressibility factor. Here, $\phi(\eta_0)$ denotes the compressibility factor of the reference state which either is known or can be calculated from the initial second order polynomial approxi-

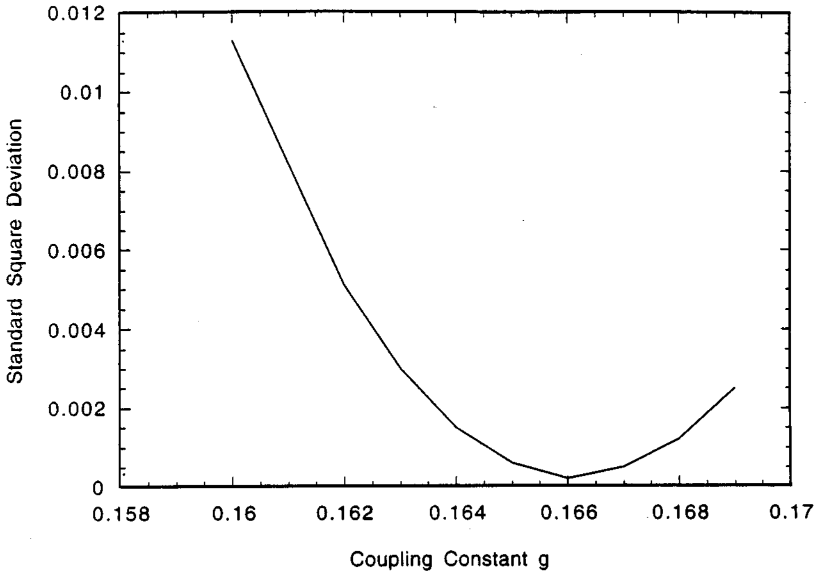

FIG. 2. Mean squared deviation $\sigma^2(\eta_0)$, as defined by Eq. (3.8), plotted versus the ''bare'' coupling constant η_0.

mation (3.1). It is also possible to treat the reference state concentration η_0 and the corresponding compressibility factor $\phi(\eta_0)$ as adjustable parameters with values selected so as to produce the best possible agreement with the ''correct'' compressibility factor $\phi(\eta)$ data obtained either from the available, eight-term virial series (1.6), such as we have elected to do, or from information generated by computer simulations. [The formula (3.6) is the precise analogue of the ''single-loop'' estimate for the invariant charge constructed in Appendix IX of Ref. [5].]

The accuracy with which the PFRG formula (3.7) approximates the eight-term virial series (1.6) (treated here as ''correct'' or ''exact'') depends upon the choice of the ''bare'' coupling constant $g=\eta_0$ and the value of the corresponding compressibility factor $\phi(\eta_0)$. If the values of $\phi(\eta_0)$ are calculated directly from the series (1.6), it is possible to identify a value of the bare coupling constant for which the standard deviation

$$\frac{1}{N}\sum_{i=1}^{N}[\phi_{\text{VIRIAL}}(\eta_i)-\phi_{\text{PFRG}}(\eta_i)]^2=\sigma^2(\eta_0) \tag{3.8}$$

is a minimum. Here ϕ_{VIRIAL} and ϕ_{PFRG} denote the compressibility factors given by Eqs. (1.6) and (3.7), respectively. This procedure is illustrated by Fig. 2, from which it follows that the ''optimum'' choice for η_0 is 0.166; the corresponding value of $\phi(\eta_0)$ is 2.0514. With this choice for the initial point of the RG trajectory, the formula (3.7)—based only upon the second and third virial coefficients—reproduces the eight-term virial coefficient equation of state almost perfectly: the curves for the two are virtually indistinguishable in Figs. 1 and 5.

In less fortunate circumstances the only available data might be the values of the second and third virial coefficients. When this is the case, the optimization procedure just described cannot be conducted. An alternative which works begins by using the second order polynomial approximation (3.1) to compute a trial value of the compressibility factor at a very small value of the concentration. For the example illustrated in Figs. 1 and 5 we selected the value of $\eta_0=0.01$ for this initial step, used the second order polynomial (3.1) to calculate the corresponding value of $\phi(\eta_0)$, and then computed $\phi(\eta_1=0.05)$ from the PFRG equation (3.7). From this point on, the iterative relationship

$$\phi(\eta_{i+1})=\phi(\eta_i)\exp\left\{\tilde{B}_2\int_1^{\eta_{i+1}/\eta_i}dx\left[\overline{g(x,\eta_i)}+\frac{2\tilde{B}_3-\tilde{B}_2^2}{\tilde{B}_2}\overline{g^2(x,\eta_i)}\right]\right\} \tag{3.9}$$

was used to generate estimates of the compressibility factor for successively larger values of the concentration. The calculations were performed using a step size $\Delta\eta=0.05$ so that $\eta_{i+1}=\eta_i+0.05$. Results obtained in this way are included in Table I and appear in Figs. 1 and 5 as the dotted lines (---) that lie very close to the solid curves for the ''exact,'' eight-term virial series.

The compressibility factor of the hard-sphere gas can be estimated by other methods. Although it appears not to have been done previously, a simple procedure for resumming the truncated virial series (1.6) is to construct the corresponding cumulant expansion [6]

$$\ln\phi_c(\eta)=4\eta+2\eta^2-0.302\eta^3+0.780\eta^4+1.530\eta^5+3.810\eta^6-12.605\eta^7+\cdots. \tag{3.10}$$

Closely related to this is the nonperturbative equation of state

$$\phi_{\text{SH}}(\eta)=\exp\left[4\eta\left(1+\frac{1}{2}\eta\right)\right] \tag{3.11}$$

derived by Shinomoto [7]. Indeed, this equation of state is precisely the same as the second order approximation to the cumulant expansion (3.10).

At least three other hard-sphere, algebraic equations of state frequently are used. One of these, the Carnahan-Starling formula [8]

TABLE I. Compressibility factors. The entries in this table are values of the compressibility factor, $\phi(\eta)$, computed from a variety of formulas. Identifying labels and text equation numbers appear at the head of each column, viz., virial series, positive function renormalization group (PFRG), cumulant expansion, PFRG iteration, Shinomoto, Carnahan-Starling (CS), Percus-Yevick compressibility (PYC), and Percus-Yevick virial (PYV). At the bottom of each column appears the value of the mean squared deviation σ^2, defined according to Eq. (3.8) of the text. The tabular entries for the PFRG in column 2 were computed using the value $\eta_0=0.166$ identified in the text.

η	Virial series Eq. (1.6)	PFRG Eq. (3.7)	Cumul. Eq. (3.10)	PFRG (iter.) Eq. (3.9)	Shinomoto Eq. (3.11)	CS Eq. (3.12)	PYC Eq. (3.13)	PYV Eq. (3.14)
0.1	1.5216	1.5273	1.5216	1.5186	1.5220	1.5213	1.5226	1.6872
0.2	2.4093	2.4111	2.4095	2.4091	2.4109	2.4062	2.4219	2.9688
0.3	3.9773	3.9959	3.9825	3.9879	3.9749	3.9738	4.0525	5.4519
0.4	6.8502	6.8761	6.8982	6.8867	6.8210	6.9259	7.2222	10.5556
0.5	12.2308	12.2144	12.4270	12.406	12.1825	13.0000	14.0000	22.0000
0.6	22.3157	22.3148	22.1926	23.309	22.6464	27.2500	30.6250	51.2500
σ^2	0	0.0002	0.093	0.1697	0.188	4.1575	12.0532	158.1462

$$\phi_{\mathrm{CS}}(\eta)=\frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{3.12}$$

often is described as that which best agrees with the results of computer simulations. Two others [9,10],

$$\phi_{\mathrm{PY}}^{c}(\eta)=\frac{1+\eta+\eta^2}{(1-\eta)^3}, \tag{3.13}$$

$$\phi_{\mathrm{PY}}^{v}(\eta)=\frac{1+2\eta+3\eta^2}{(1-\eta)^3}, \tag{3.14}$$

originate from solutions of Percus-Yevick (PY) integral equations for the pair distribution function of a hard-sphere fluid. Although Eqs. (3.13) and (3.14) usually are identified in the literature as Percus-Yevick equations of state, Eq. (3.13) first was obtained by Reiss, Frisch, and Lebowitz [11] on the basis of the scaled particle theory.

Compressibility factors calculated from this collection of formulas are presented in Table I. In each case we have computed the mean square deviation of the compressibility factor from that given by the ''exact'' seventh order virial polynomial (1.6). Because this truncated virial series has been selected as our standard, the approximate equation of state with the smallest mean square deviation may not be that which best fits the computer simulation data. Indeed, there are several semiempirical equations of state [12,13] (in addition to the well known Padé approximants) that have been constructed to produce better agreement with the available simulation data than does the eight-term virial polynomial. We have chosen the latter as our basis for comparison because virial coefficients are the input data to our PFRG calculations. The simulation data are included in Figs. 1 and 5 in order to indicate the degree by which they differ from the predictions of the virial polynomial (1.6) and our PFRG approximation. It is clear that the agreement generally is quite good between the predictions of the analytical equations of state and the computer generated ''experimental results.'' The entries in Table I indicate that the PFRG formula (3.7) with $\eta_0=0.166$ is the most successful in reproducing the seventh order virial polynomial. It should be recalled that this formula is based on the values of only two virial coefficients, $\widetilde{B}_2=4$ and $\widetilde{B}_3=10$. Next in accuracy to the PFRG formula is the cumulant series (3.10), followed by the iterative PFRG calculation based on Eq. (3.9) and the appealingly simple Shinomoto equation (3.11).

It is interesting to see how PFRG results based on the second order polynomial approximation (3.1) compare with the predictions of a renormalization group computation based on the entire seventh order polynomial (1.6). The infinitesimal generators associated with the latter are easily computed from the formulas

$$\gamma(g)=g\,\frac{\partial \ln \phi(g)}{\partial g} \tag{3.15}$$

and

$$\beta(g)=g^2\,\frac{\partial^2 \ln \phi(g)}{\partial g^2}\bigg/\left(\frac{\partial \gamma}{\partial g}\right). \tag{3.16}$$

Their graphs are shown in Figs. 3 and 4. The solution of the equation $\beta(g^*)=0$ is a single, nontrivial, stable fixed point at $g^*=0.6248$. This corresponds to a volume fraction of $\eta=0.6248$ which falls within the range 0.64 ± 0.02 that Berryman [14] recently has estimated for the random close packing (RCP) of a hard-sphere fluid. (His paper also includes an extensive bibliography pertaining to earlier estimates of η_{RCP}.) The tentative identification of the stable fixed point with the condition of random close packing seems reasonable since, according to Eq. (2.2), the PFRG transformation can be interpreted as the continuous growth of hard-sphere particles.

Using the calculated value of g^* we obtain the following asymptotic formula for the compressibility of a dense ($\eta>0.4$) hard-sphere fluid:

$$\phi(\eta)=\phi(g^*)e^{3.7915[\eta/g^*-1]}. \tag{3.17}$$

With $\phi(g^*)$ calculated from Eq. (3.7), this becomes

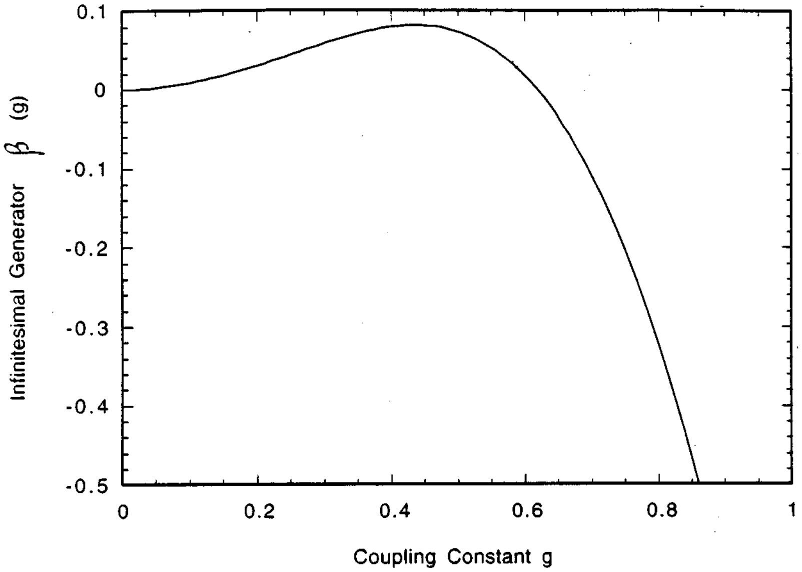

FIG. 3. The infinitesimal generator $\beta(g)$ of Eq. (3.15) computed from the eight-term virial polynomial of Eq. (1.6).

$$\phi(\eta)=0.5852e^{6.0883\eta}, \quad \eta>0.4. \tag{3.18}$$

Predictions based on the seventh order virial polynomial (1.6), the PFRG formula (3.7), and the asymptotic formula (3.18) are shown in Figs. 1 and 5. In both figures the PFRG and virial polynomial predictions are indistinguishable. Thus, the PFRG method clearly provides a remarkably efficient procedure for resumming the truncated, two-term virial polynomial of Eq. (3.1). The points appearing in these figures indicate results of computer simulations performed by Barker and Henderson [15], Wood [16], Rotenberg [17], Erpenbeck and Wood [18] and Woodcock [19]. Except for densities so low that $\eta<0.4$ and nearly as great as that at random close packing, the computer simulation results are described quite well by the exponential asymptotic law of Eq. (3.18). The fixed points of the PFRG transformation at $g=0$ and 0.6248, respectively, can be interpreted as the limits of weakly and strongly interacting systems composed of randomly distributed hard-sphere particles.

A disconcerting aspect of the PFRG results displayed in Figs. 1 and 5 is their failure to exhibit any trace whatsoever of the singular behavior that surely must occur as the density approaches that of closest packing. One could dismiss this whole issue as being peripheral to the stated objective of the present paper, namely, the determination of whether and/or to what extent the PFRG method is capable of resumming a truncated, perturbative virial series. However, since the high density behavior of the rigid-sphere system has been an intriguing and controversial issue for over 40 years, it is natural to wonder why the PFRG method, as presented above, appears to fail in this limit. Before attempting to answer this question, let us briefly examine the computer simulation data included in Figs. 1 and 5 in order to determine what the ''expected'' high-density behavior really is. (These data are representative, but by no means exhaustive, of studies made over the period extending from 1960 to the present.) Because three different measures of the density are in common use, we have prepared Table II to facilitate comparisons; $\eta=n\pi\sigma^3/6$, $n\sigma^3=(6/\pi)\eta=1.90986\eta$, and $V/V_0=(\pi\sqrt{2}/6)\eta^{-1}=0.74048\eta^{-1}$.

Woodcock's [19] compressibility factors, indicated by the diamonds (◇), being to deviate from the eight-term virial polynomial curve at the ''freezing point'' (FP) density of $\eta=0.493$ and then rise much more rapidly as η approaches a value of about 0.62, corresponding to the volume fraction 0.64 ± 0.02 [14] at random closest packing (RCP). Wood's [18] results (⊙) follow the virial polynomial curve to higher densities than Woodcock's and then rise more abruptly as the RCP density is approached. Rotenberg's [17] much earlier simulations (△) produce compressibility factors which closely follow the virial polynomial curve to about $\eta\sim0.69$ and then rise rapidly in the vicinity of $\eta\sim0.74$, corresponding to the volume fraction 0.7405 at ordered closest packing (OCP).

With this information in mind, we now return to the question of why the PFRG method has failed to produce a compressibility factor that grows rapidly as the fluid density approaches either $\eta_{\mathrm{RCP}}=0.64$ or $\eta_{\mathrm{OCP}}=0.74$. The short answer is that the PFRG method will produce a behavior that might possibly be interpreted as the occurrence of a high-density phase transition [or simply a singularity of $\phi(\eta)$] only if there is a violation of the requirement (cf. Appendix B) that the infinitesimal generator $\gamma(g)$ be a single-valued function of its argument. The approximate infinitesimal generators [cf. Eq. (3.5) and Fig. 4] used to calculate the curves of Figs. 1 and 5 are monotonically increasing functions of g, thus explaining why the corresponding compressibility factors behave as they do. It could be that, although these generators

TABLE II. Different measures of density.

η	$n\sigma^3$	V/V_0	Comment
0.494	0.943	1.500	Freezing point (Ref. [20])
0.540	1.031	1.371	Melting point (Ref. [20])
0.560	1.070	1.322	{Density of sudden crystallization
0.566	1.080	1.309	(Ref. [19])}
0.640	1.222	1.157	Random closest packing 0.64±0.02, (Ref. [14])
0.740	1.414	1.000	Ordered closest packing (fcc and hcp)

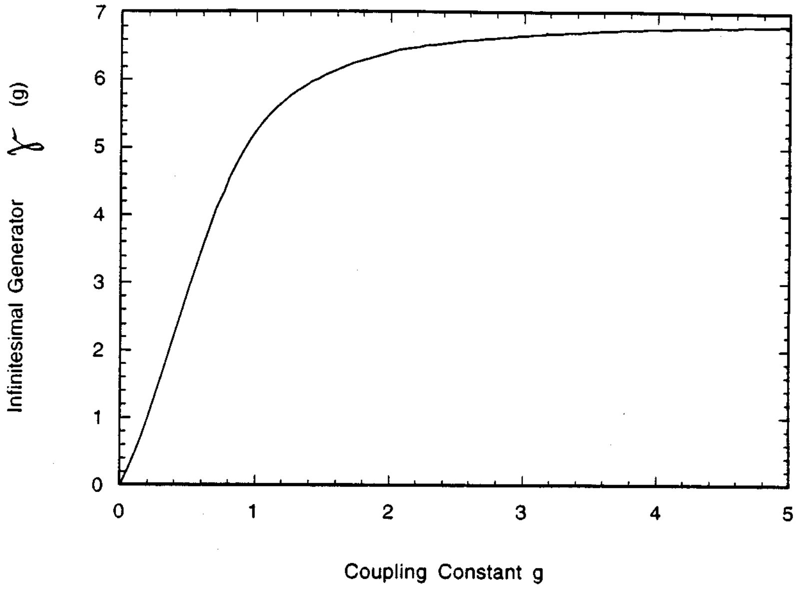

FIG. 4. The infinitesimal generator $\gamma(g)$ of Eq. (3.16) computed from the eight-term virial polynomial of Eq. (1.6).

are capable of predicting very accurate ''liquidlike'' compressibility factors, they lack something essential to the description of this liquid as its density approaches that of closest packing. To test this conjecture we have calculated $\gamma(b)$ and $\beta(b)$ using Eqs. (3.15) and (3.16) and the cumulant expansion (3.10), which presumably is more accurate than the corresponding seventh order virial polynomial (1.6). This produces an asymptotic value of $g^* = 0.4982$ for the effective coupling coefficient, cf. Fig. 6 [The occurrence of this stable fixed point at $g^* = 0.4982$ depends in an essential way on the eighth virial coefficient of Eq. (1.6). When this coefficient is omitted, the corresponding cumulant expansion produces an infinitesimal generator $\beta(g)$, which fails to exhibit a fixed point for $\eta > 0$.]

In the neighborhood of the fixed point the compressibility factor is given by the expression

$$\phi(\eta) \doteq \phi(0.4982)\exp\left[2.9779\left(\frac{\eta}{0.4982} - 1\right)\right]$$

$$= 0.6159 e^{5.9773\eta}. \tag{3.19}$$

On the scales of Figs. 1 and 5, this is virtually indistinguishable from our previous result (3.18). In the immediate vicinity of the fixed point the asymptotic equation of state (3.19) can be replaced with the scaling relation

$$\phi(\eta) \underset{\eta \to \eta^*}{\approx} \phi(0.4982)\left(\frac{\eta}{0.4982}\right)^{2.9779}. \tag{3.20}$$

The fixed point density $\eta^* = 0.4982$ is very nearly equal to the freezing point density $\eta_{\mathrm{FP}} = 0.494$ estimated by Ree and Hoover [20].

The infinitesimal generator $\beta(g)$ associated with the cumulant expansion (3.10) is discontinuous at the value $g^\# = 0.5798$ for which $\partial\gamma/\partial g$ is equal to zero; cf. Fig. 7. This value lies near the melting-point density $\eta_{\mathrm{MP}} = 0.54$ estimated by Ree and Hoover on the basis of their simulation data.

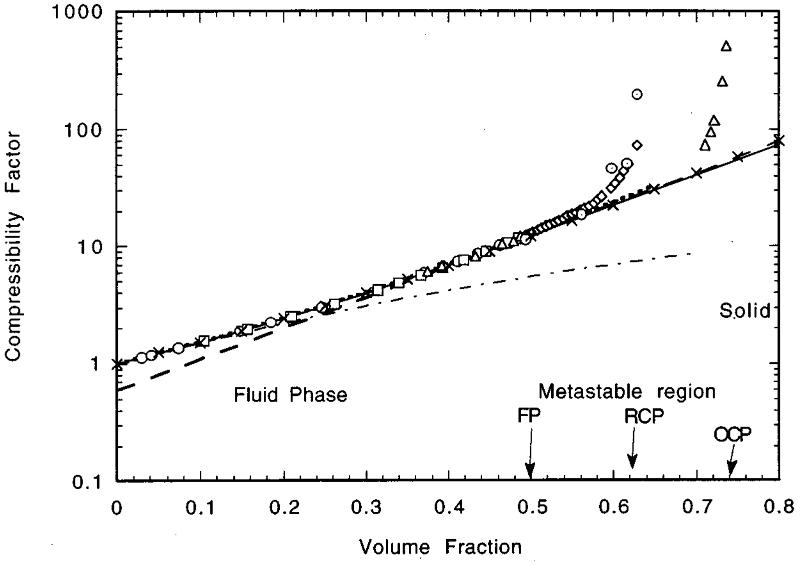

FIG. 5. Estimates of the compressibility factor using scales and ranges different from those of Fig. 1. The labels used to identify different formulas and simulations are the same as those identified in the caption of Fig. 1. It is interesting to note that the rapid increase of $\phi(\eta)$ that occurs at high densities shifts to higher densities as the number of particles used in the simulation increases from 32 and 256 in Wood's Monte Carlo computations (and 512 in those of Woodcock) to 864 in those of Rotenberg.

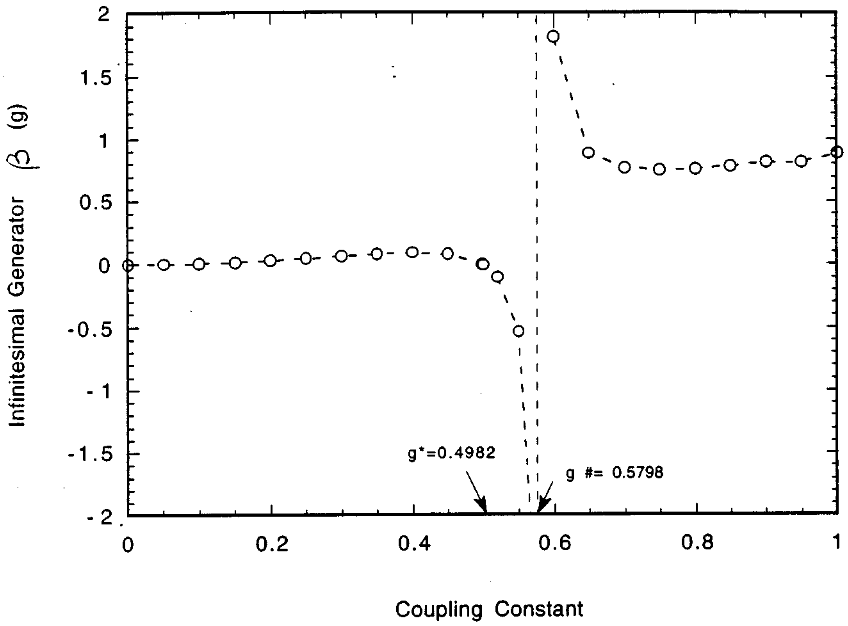

FIG. 6. The infinitesimal generator $\beta(g)$ computed using the cumulant expansion (3.10).

Although the quantitative aspects of these last few results must be viewed with caution, it does appear that the PFRG theory may be capable of accounting for some sort of a high-density phase transition in a hard-sphere fluid. And, indeed, it is plausible to conclude that the hard-sphere system described by the PFRG theory is a fluid, the stability limit of which is the density $g^{\#}$ at which $d\gamma/dg=0$. For densities in excess of $g^{\#}$ the equilibrium state of the system is then a two-phase dispersion of solid crystallites imbedded in a fluid of density g^*. The evidence presented here does not establish the validity of these conjectures nor have our calculations proved that the PFRG method actually is capable of describing such a phase transition, but the possibilities do exist. Truly convincing demonstrations would require a more ambitious investigation than that presented here.

The specific application of the PFRG approach presented in this paper is different both in intent and methodology from most previously reported methods (e.g., Padé approximants, semiempirical equations of state), which are designed to extend the range of applicability of the virial series by invoking assumptions about the functional form of the relationship $\phi=\phi(\eta)$ and/or by introducing adjustable parameters to ensure agreement with simulation data. In contrast to this, the PFRG method, as used here, has relied upon only two aspects of a hard-sphere fluid: (1) that the compressibility factor $\phi(\eta)$ is a positive valued, continuous function of η and (2) that one possesses (or can generate) a truncated power series approximation to this function which is accurate for small values of η.

IV. DISCUSSION

The hard-sphere compressibility factor problem has provided an excellent illustrative example of the positive func-

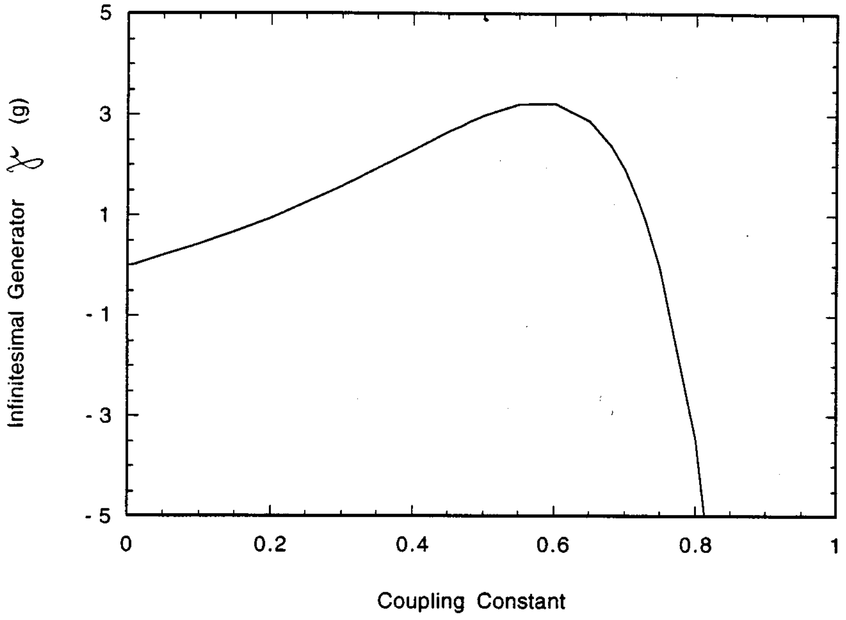

FIG. 7. The infinitesimal generator $\gamma(g)$ computed using the cumulant expansion (3.10).

tion renormalization group (PFRG) technique outlined in Sec. II of this paper. Indeed, we have found (rather to our surprise) that the method almost perfectly reproduces the seventh order virial polynomial over the entire range of volume fractions, except in the immediate vicinity of random close packing.

Our formulation of the PFRG method has been closely patterned after the ideas advanced by Shirkov [4]. However, in implementing these ideas we have fashioned a theory which differs in several significant ways from most previous adaptations of the RG method to problems in statistical physics. In particular, we strongly support the emphasis that Shirkov places on the importance of determining the functional equation satisfied by the physical property $f(x,g)$. It is essential to the method that this functional equation be established at the *beginning* of the investigation, since it defines the group operation for the class of functions to which $f(x,g)$ belongs. In the case considered here, the class of functions $f(t,g)$ representative of the nonlinear PFRG satisfy two conditions: (1) $f(x,g)\geqslant 0$, $x\geqslant 1$ (positive definiteness), and (2) $\partial f(x,g)/\partial x|_{x=1}$ is a single-valued (invertible) function of the coupling parameter g. Once the functional group operation equation (2.10) has been established, the appropriate Lie equations of evolution can be constructed, along with defining expressions for the associated infinitesimal generators $\beta(g)$ and $\gamma(g)$ of the PFRG. [Approximations for the latter can be constructed from an initial ''perturbative'' series for $f(x,g)$.] Our procedure differs in these respects from many other RG techniques and, in particular, from the so-called ''direct'' renormalization group method, users of which [21,22] tend to take a much more relaxed view than we do about the relationship between the object function $f(x,g)$ and the effective coupling function $\overline{g}(x,g)$.

We also are of the opinion that the asymptotic properties of the function $f(x,g)$ are fixed by the equation for the functional group operation (and/or by the corresponding Lie equations) and therefore are specific to the class of functions under consideration. This leads us to doubt the objectivity of formulations of the RG technique which produce some preassigned asymptotic behavior such as, for example, a ''universal'' power law dependence on the group parameter x.

In a separate paper we shall present a more detailed comparison of various approaches to the RG method. Here we only mention the fact that different equations of evolution can be used to describe various parts of the RG trajectory $f(x,g=\text{const})$. However, in order to establish the ''true'' asymptotic behavior of the function it is necessary to identify the functional group operation equation for which $f(x,g)$ is representative.

Perturbation series of the form (2.1) are encountered in many applications of statistical mechanics. Well known examples include high-temperature expansions for properties of magnetic systems and virial series for macroparticle diffusion coefficients and for the viscosity of suspensions. We shall examine some of these in future tests of the PFRG method.

ACKNOWLEDGMENT

This research has been supported by a grant from the Theoretical and Computational Chemistry Program of the National Science Foundation.

APPENDIX A

Equation (2.12) for the effective coupling function is a direct consequence of the commutivity condition, according to which

$$\tilde{f}(tz,g)\equiv\tilde{f}(zt,g). \tag{A1}$$

From this identity and Eq. (2.10) we obtain a relationship

$$\tilde{f}(z,g)[\tilde{f}(t,\overline{g}(z,g))]^{z}\equiv\tilde{f}(t,g)[\tilde{f}(z,\overline{g}(t,g))]^{t}, \tag{A2}$$

which can be satisfied only for a very special choice of the function $\overline{g}(t,g)$. To find the functional equation satisfied by this effective coupling function we rewrite Eq. (A2) in the form

$$[\tilde{f}(t,\overline{g}(z,g))]^{z}\equiv\frac{\tilde{f}(t,g)}{\tilde{f}(z,g)}[\tilde{f}(z,\overline{g}(t,g))]^{t}. \tag{A3}$$

Then, using Eq. (2.11) to replace the factor $\tilde{f}(t,g)/\tilde{f}(z,g)$ with $[\tilde{f}(t/z,\overline{g}(z,g))]^{z}$, we rewrite (A3) as

$$\left[\frac{\tilde{f}(t,\overline{g}(z,g))}{\tilde{f}\left(\frac{t}{z},\overline{g}(z,g)\right)}\right]^{z}\equiv[\tilde{f}(z,\overline{g}(t,g))]^{t}. \tag{A4}$$

The result of applying Eq. (2.11) to the ratio of transfer functions appearing on the left-hand side of Eq. (A4) is the equation

$$\left[\tilde{f}\left(\frac{t}{t/z},\overline{g}\left(\frac{t}{z},\overline{g}(z,g)\right)\right)\right]^{(t/z)z}\equiv[\tilde{f}(z,\overline{g}(t,g))]^{t}, \tag{A5}$$

or, equivalently,

$$\left[\tilde{f}\left(z,\overline{g}\left(\frac{t}{z},\overline{g}(z,g)\right)\right)\right]\equiv[\tilde{f}(z,\overline{g}(t,g))]. \tag{A6}$$

This equality holds if and only if the function $\overline{g}(t,g)$ satisfies the functional equation

$$\overline{g}\left(\frac{t}{z},\overline{g}(z,g)\right)=\overline{g}(t,g), \tag{A7}$$

which is identical to Eq. (2.12) of the text.

APPENDIX B

The effective coupling function $\overline{g}(t,g)$ must be selected in such a way that the Lie equation (2.13) for $\tilde{f}(t,g)$ is a mathematical identity. This is possible only if the infinitesimal generator $\gamma(g)$ is a single-valued function of the bare coupling constant g. More specifically, let us assume there to be a one-to-one correspondence

$$z=\gamma(g) \tag{B1}$$

between the variables z and g. There consequently exists an inverse function γ^{-1} such that

$$g=\gamma^{-1}(z). \tag{B2}$$

We then conclude, with reference to Eq. (2.13), that

$$\overline{g(t,g)} = \gamma^{-1}\left(\frac{\partial \ln \tilde{f}(t,g)}{\partial t}\right). \tag{B3}$$

This means that there is to each function $\tilde{f}(t,g)$ a corresponding function $\overline{g(t,g)}$ which, in turn, is determined by the Lie equation (2.14) in which appears the infinitesimal generator

$$\beta(g) = \lim_{x\to 1}\frac{\partial}{\partial x}\,\gamma^{-1}\left(\frac{\partial \ln \tilde{f}(x,g)}{\partial x}\right). \tag{B4}$$

In other words, our PFRG method can be used to determine functions $\tilde{f}(x,g)$ that are (1) positive definite and (2) for which $\partial\tilde{f}(x,g)/\partial x|_{x=1} = \gamma(g)$ is a single-valued function.

APPENDIX C

An alternative set of evolution equations for the PFRG can be obtained by differentiating the functional equations (2.11) and (2.12) with respect to the ''dilation factor'' z and then setting z equal to unity. The results of these manipulations are two linear, first order differential equations,

$$0 = \gamma(g) + \ln \tilde{f}(x,g) - x\,\frac{\partial \ln \tilde{f}(x,g)}{\partial x} + \beta(g)\,\frac{\partial \ln \tilde{f}(x,g)}{\partial g} \tag{C1}$$

and

$$0 = \beta(g)\,\frac{\partial \overline{g}(x,g)}{\partial g} - x\,\frac{\partial \overline{g}(x,g)}{\partial x}. \tag{C2}$$

These are analogous to the Callan-Symanzik equations of the standard RG theory.

[1] R. Balescu, *Equilibrium and Non-Equilibrium Statistical Mechanics* (Wiley, New York, 1975), Chap. 6.

[2] E. A. Mason and T. H. Spurling, in *The International Encyclopedia of Physical Chemistry and Chemical Physics*, Vol. 2, edited by D. D. Eley and J. E. Mayer (Pergamon, Oxford, 1965).

[3] E. J. Janse van Rensburg, J. Phys. A **26**, 4805 (1993).

[4] D. V. Shirkov, Int. J. Mod. Phys. A **3**, 1321 (1988); Theor. Math. Phys. **60**, 218 (1984); Dokl. Acad. Nauk SSSR **263**, 64 (1981) [Sov. Phys. Dokl. **27**, 197 (1982)].

[5] N. N. Bogoliubov and D. V. Shirkov, *Quantum Fields* (Benjamin/Cummins, London, 1983), Appendix 9.

[6] M. G. Kendall, *Advanced Theory of Statistics* (Griffin, London, 1952), Vol. 1.

[7] S. Shinomoto, J. Stat. Phys. **32**, 105 (1983).

[8] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).

[9] J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1958).

[10] *Equilibrium and Non-Equilibrium Statistical Mechanics* (Ref. [1]), Chap. 8.4.

[11] H. Reiss, H. L. Frisch, and J. L. Lebowitz, J. Chem. Phys. **31**, 369 (1959).

[12] Y. Song, R. M. Stratt, and E. M. Mason, J. Chem. Phys. **88**, 1126 (1988).

[13] J. Tobochnik and P. M. Chapin, J. Chem. Phys. **88**, 5824 (1988).

[14] J. G. Berryman, Phys. Rev. A **27**, 1053 (1985).

[15] J. A. Barker and D. Henderson, Mol. Phys. **21**, 187 (1971).

[16] W. W. Wood, in *Physics of Simple Liquids*, edited by H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke (Wiley, New York, 1968).

[17] A. Rotenberg, J. Chem. Phys. **42**, 1126 (1965).

[18] J. J. Erpenbeck and W. W. Wood, J. Stat. Phys. **35**, 321 (1984).

[19] L. V. Woodcock, Ann. N.Y. Acad. Sci. **371**, 274 (1981).

[20] F. H. Ree and W. G. Hoover, J. Chem. Phys. **46**, 4181 (1967).

[21] J. des Cloizeaux, J. Phys. (Paris) Lett. **41**, L101 (1980); **42**, 635 (1981).

[22] K. F. Freed, *Renormalization Group Theory of Macromolecules* (Wiley, New York, 1987).