

STATISTICAL MECHANICS OF SIMPLE DENSE FLUIDS USING FUNCTIONAL INTEGRATION*

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Summary

The use of functional integration in developing approximate equations of state for simple dense fluids is outlined. The repulsive (short range) and attractive parts of the potential are treated separately and the grand partition function is expressed in terms of a functional integral which involves knowledge of the thermodynamic properties of the "short-range system". Two separate procedures are outlined to obtain approximate equations of state for dense fluids from this exact functional integral.

I. INTRODUCTION

The idea of using functional integrals to solve problems in classical statistical mechanics was first introduced by Edwards (1959). The method has been used for lattice gases and spin systems by several workers (Baker 1962; Siegert 1962; Muhlschlegel and Zittartz 1963; Thompson 1965; Thompson and Lavis 1967), however it does not seem that the method has been fully developed with regard to the properties of continuum fluids. It is the purpose of this paper to show how the exact expressions (in terms of functional integrals) can be approximated by well-defined procedures to give approximate equations of state for simple fluids for a wide range of densities.

We consider fluids where the intermolecular potential consists of the sum of a short-range potential $U_{ij} = U(r_{ij})$ which is repulsive at the origin and a potential $V_{ij} = V(r_{ij})$ which is restricted in that it has a well-defined Fourier transform

$$v(k) = \int d\mathbf{r} V(r) \exp(-i \mathbf{k} \cdot \mathbf{r})$$

that satisfies $v(k) < 0$ for all k . These conditions are not too restrictive and most potentials that are in common use can be divided in this way. One notices, however, that the division is not unique for a potential which can be regarded as having a hard core of radius d , for then the potential $V(r)$ can be chosen with a great deal of freedom for $r < d$; it being subject only in the condition $v(k) < 0$. This fact can be exploited in developing the variational principle and so we will restrict our consideration to potentials of this type.

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II. FORMULATION

The thermodynamic properties of a system of particles can be found from a knowledge of the grand partition function Z_G as a function of the temperature T and chemical potential μ . Thus we look for

$$Z_G = \sum_{N=0}^{\infty} (N! \lambda^{3N})^{-1} \int \dots \int \exp\left(\beta N \mu - \frac{1}{2} \beta \sum'_{ij} U_{ij} - \frac{1}{2} \beta \sum'_{ij} V_{ij}\right) d\Omega_N, \quad (1)$$

where $\beta = 1/kT$ and $d\Omega_N$ represents an element of the configuration spaces of N particles each of which is in a volume V . As shown by Edwards (1959), if we use the functional analogue of

$$\begin{aligned} \int \dots \int \prod_{a=1}^N d\xi_a \exp\left(-\frac{1}{2} \beta \sum_{a,b} \xi_a A_{ab}^{-1} \xi_b + \beta \sum_a \xi_a \eta_a\right) \\ = \exp\left\{\frac{1}{2} N \ln\left(\frac{2\pi}{\beta}\right) + \frac{1}{2} \text{Tr}(\ln A) + \frac{1}{2} \beta \sum_{a,b} \eta_a A_{ab} \eta_b\right\} \end{aligned} \quad (2)$$

then Z_G can be written as

$$\begin{aligned} Z_G = C \int \delta\Phi \sum_{N=0}^{\infty} (N! \lambda^{3N})^{-1} \int d\Omega_N \exp\left(\beta N(\mu + \frac{1}{2} V_0) - \frac{1}{2} \beta \sum'_{ij} U_{ij} \right. \\ \left. + \beta \sum_i \Phi(\mathbf{x}_i) + \frac{1}{2} V (2\pi)^{-3} \int \ln\{t(k)\} dk - \frac{1}{2} \beta \iint \Phi(\mathbf{x}) T(\mathbf{x}-\mathbf{y}) \Phi(\mathbf{y}) d\mathbf{x} d\mathbf{y}\right), \end{aligned} \quad (3)$$

where C is a normalization constant, $V_0 = V(\mathbf{r})|_{r=0}$, and the operator $T(\mathbf{x}-\mathbf{y})$ satisfies

$$\int T(\mathbf{x}-\mathbf{y}) V(\mathbf{y}-\mathbf{z}) d\mathbf{y} = -\delta(\mathbf{x}-\mathbf{z}), \quad (4)$$

that is,

$$t(k) = -1/v(k) \quad (5)$$

if $t(k)$ is the Fourier transform of $T(x)$. Note that if $U(r)$ contains a hard core of radius d then Z_G is independent of the values of $V(r)$ for $r < d$ and hence is independent of V_0 .

We now assume that we can solve the complete statistical mechanical problem for a system of particles interacting via the short-range potential $U(r)$ only and moving in a random external field $-\Phi(\mathbf{x})$, i.e. that we can find the local pressure $p_s(\mathbf{x}; \{\mu + \Phi(\mathbf{x})\})$ for such a system. This local pressure is a function of position which depends on the form of the external potential over all space, i.e. it is a functional of $\Phi(\mathbf{x})$. The functional $p_s(\mathbf{x}; \{\mu + \Phi(\mathbf{x})\})$ satisfies

$$\begin{aligned} Z_G^s &= \exp\left(\beta \int d\mathbf{x} p_s(\mathbf{x}; \{\mu + \Phi(\mathbf{x})\})\right) \\ &= \sum_{N=0}^{\infty} (N! \lambda^{3N})^{-1} \int d\Omega_N \exp\left(\beta N \mu - \frac{1}{2} \beta \sum'_{ij} U_{ij} + \beta \sum_i \Phi(\mathbf{x}_i)\right). \end{aligned} \quad (6)$$

Hence equation (3) becomes

$$Z_G = C \int \delta\Phi \exp\left(\frac{1}{2}V(2\pi)^{-3} \int d\mathbf{k} \ln\{t(k)\} + \beta \int d\mathbf{x} p_s(\mathbf{x}; \{\mu + \Phi(\mathbf{x}) + \frac{1}{2}V_0\}) - \frac{1}{2}\beta \iint \Phi(\mathbf{x}) T(\mathbf{x}-\mathbf{y}) \Phi(\mathbf{y}) d\mathbf{x} d\mathbf{y}\right). \quad (7)$$

We have thus reduced the problem to one of evaluating a functional integral over the random field $\Phi(\mathbf{x})$. This is an exact, although formal, expression and it may be that methods other than those outlined here will be developed to evaluate functional integrals of this type.

The first approximation we present is obtained by expanding the functional $\ln Z_G^s$ about a constant function by using the functional Taylor expansion discussed, for example, by Lebowitz and Percus (1963) and Lebowitz (1964). They showed that

$$\left. \frac{\delta(\ln Z_G^s)}{\delta\Phi(\mathbf{x})} \right|_{\Phi=\phi} = \beta n_s(\mu + \phi) \quad (8)$$

and

$$\left. \frac{\delta^2(\ln Z_G^s)}{\delta\Phi(\mathbf{x}) \delta\Phi(\mathbf{y})} \right|_{\Phi=\phi} = \beta^2 n_s^2(\mu + \phi) h_s(|\mathbf{x}-\mathbf{y}|; \mu + \phi) + \beta^2 n_s(\mu + \phi) \delta(\mathbf{x}-\mathbf{y}), \quad (9)$$

where $n_s(\mu)$ and $h_s(r, \mu) = g_s(r, \mu) - 1$ are the number density and correlation function of the "short-ranged system" when it has a chemical potential μ . Thus, including terms to second order in Φ , we have

$$\begin{aligned} \beta \int d\mathbf{x} p_s(\mathbf{x}; \{\mu + \Phi(\mathbf{x})\}) &= \beta V p_s(\mu + \phi) + \beta n_s(\mu + \phi) \int \{\Phi(\mathbf{x}) - \phi\} d\mathbf{x} \\ &\quad + \frac{1}{2}\beta^2 \iint \{\Phi(\mathbf{x}) - \phi\} \{n_s^2 h_s(|\mathbf{x}-\mathbf{y}|) \\ &\quad + n_s \delta(\mathbf{x}-\mathbf{y})\} \{\Phi(\mathbf{y}) - \phi\} d\mathbf{x} d\mathbf{y}, \end{aligned} \quad (10)$$

where $p_s(\mu)$ is the pressure of the short-ranged system in the absence of an external field. If we use this approximation in equation (7) then

$$\begin{aligned} Z_G \approx C \int \delta\Psi \exp\left(\frac{1}{2}V(2\pi)^{-3} \int d\mathbf{k} \ln t(k) + \beta V p_s(\mu + \nu) \right. \\ \left. + \frac{1}{2}\beta V (\frac{1}{2}V_0 - \nu)^2 v(0) + \{\beta n_s(\mu + \nu) - \beta (\frac{1}{2}V_0 - \nu)/v(0)\} \int \Psi(\mathbf{x}) d\mathbf{x} \right. \\ \left. + \frac{1}{2}\beta \iint \Psi(\mathbf{x}) \{\beta n_s^2 h_s(|\mathbf{x}-\mathbf{y}|) + \beta n_s \delta(\mathbf{x}-\mathbf{y}) - T(\mathbf{x}-\mathbf{y})\} \Psi(\mathbf{y}) d\mathbf{x} d\mathbf{y}\right), \end{aligned} \quad (11)$$

where we have written $\Psi(\mathbf{x}) = \Phi(\mathbf{x}) + \frac{1}{2}V_0 - \nu$. In this expression the value of V_0 is arbitrary and it is appropriate to choose the value which eliminates the term linear in Ψ in the integrand, i.e. we require

$$\frac{1}{2}V_0 - \nu = v(0) n_s(\mu + \nu). \quad (12)$$

The functional integral can then be evaluated to give the approximation

$$V^{-1} \ln Z_G = \beta p(\mu) = \beta p_s(\mu + \nu) + \frac{1}{2} \beta v(0) \{n_s(\mu + \nu)\}^2 - \frac{1}{2} (2\pi)^{-3} \int d\mathbf{k} \ln[1 + v(k) \{n_s + n_s^2 h_s(k)\}], \quad (13)$$

where

$$h_s(k) = \int d\mathbf{x} \exp(i\mathbf{k} \cdot \mathbf{x}) h_s(r).$$

Since ν is an arbitrary parameter in this expression one should choose ν so that $p(\mu)$ is independent (at least to first order) of small changes in ν , that is, we require $\partial p / \partial \nu = 0$. Thus ν should be chosen so that

$$\frac{\partial}{\partial n_s} \left(\int d\mathbf{k} \ln[1 + \beta v(k) \{n_s(\mu + \nu) + n_s^2 h_s(k)\}] \right) = 0. \quad (14)$$

This requirement simplifies the equation of state since then the equation determining the number density becomes

$$n(\mu) = dp/d\mu = n_s(\mu + \nu), \quad (15)$$

so that the equation of state, in this approximation, is

$$\beta p(n) = \beta p_s(n) + \frac{1}{2} \beta v(0) n^2 - \frac{1}{2} (2\pi)^{-3} \int d\mathbf{k} \ln[1 + \beta v(k) \{n + n^2 h_s(k)\}] \quad (16)$$

with $v(k)$ and ν chosen to satisfy equations (12) and (14).

If we regard $\beta v(k)$ as a small quantity and retain from equation (13) only the first-order terms then we have to vary the expression

$$p(\mu) \approx p_s(\mu + \nu) - \nu n_s(\mu + \nu) - \frac{1}{2} n_s^2 \int g_s(r) V(r) d\mathbf{x}$$

with respect to ν . Using the first-order form of equation (14) and equation (12), this implies the choice

$$\nu = - \frac{\partial}{\partial n_s} \left(\frac{1}{2} n_s^2 (\mu + \nu) \int g_s(r) V(r) d\mathbf{x} \right)$$

and so, since we can now replace $n_s(\mu + \nu)$ by $n(\mu)$ (equation (15)), the equation of state is

$$p(n) \approx p_s(n) + \frac{1}{2} n^2 \frac{\partial}{\partial n} \left(n \int g_s(r) V(r) d\mathbf{x} \right),$$

which is the result Zwanzig (1954) obtained from a simple inverse temperature expansion (see also Storer 1969). One would hope that the full approximation would give an even better result.

III. VARIATIONAL APPROXIMATION

An alternative approximation to the exact equation of state can be obtained by following the variational procedure introduced by Feynman (1955) and used in this context by Edwards (1959). If

$$Z_G = \int \delta\Phi \exp(-G) \quad (17)$$

then

$$Z_G > Z_G^0 = \int \delta\Phi \exp(-G_0 - \langle G - G_0 \rangle), \quad (18)$$

where

$$\langle G - G_0 \rangle = \int \delta\Phi \exp(-G_0) (G - G_0) / \int \delta\Phi \exp(-G_0). \quad (19)$$

We therefore choose G_0 so that equation (19) can be evaluated and then vary the parameters to maximize Z_G^0 . Let us choose in this case

$$G_0 = \frac{1}{2}\beta \iint d\mathbf{x} d\mathbf{y} \{ \Phi(\mathbf{x}) - \Phi_0 \} S(\mathbf{x} - \mathbf{y}) \{ \Phi(\mathbf{y}) - \Phi_0 \} \quad (20)$$

and vary the constant Φ_0 and the function $S(\mathbf{x})$. We can also regard V_0 and $V(r)$ for $r < d$ as variational parameters, since in an exact calculation these will not affect the result. Changing variables to $\Psi(\mathbf{x}) = \Phi(\mathbf{x}) - \Phi_0$ we have

$$\begin{aligned} \int \delta\Phi \exp(-G_0) &= \int \delta\Psi(\mathbf{x}) \exp\left(-\frac{1}{2}\beta \iint \Psi(\mathbf{x}) S(\mathbf{x} - \mathbf{y}) \Psi(\mathbf{y}) d\mathbf{x} d\mathbf{y}\right) \\ &= C \exp\left(\frac{1}{2}V(2\pi)^{-3} \int \ln s(k) d\mathbf{k}\right), \end{aligned} \quad (21)$$

where $s(k)$ is the Fourier transform of $S(\mathbf{x})$. Also

$$\begin{aligned} \langle G - G_0 \rangle &= \left\langle -\beta \int d\mathbf{x} p_s(\mathbf{x}; \{\mu + \frac{1}{2}V_0 + \Phi_0 + \Psi(\mathbf{x})\}) \right\rangle \\ &\quad + \left\langle \frac{1}{2}\beta \iint d\mathbf{x} d\mathbf{y} \Psi(\mathbf{x}) \{T(\mathbf{x} - \mathbf{y}) - S(\mathbf{x} - \mathbf{y})\} \Psi(\mathbf{y}) \right\rangle \\ &\quad - \frac{1}{2}V(2\pi)^{-3} \int \ln t(k) d\mathbf{k} + \frac{1}{2}V\beta\Phi_0^2 t(0). \end{aligned} \quad (22)$$

Hence

$$\begin{aligned} \ln Z_G^0 &= \left\langle \beta \int d\mathbf{x} p_s(\mathbf{x}; \{\mu + \frac{1}{2}V_0 + \Phi_0 + \Psi(\mathbf{x})\}) \right\rangle \\ &\quad + \frac{1}{2}\beta V\Phi_0^2/v(0) - \frac{1}{2}V(2\pi)^{-3} \int d\mathbf{k} \ln\{-v(k)s(k)\} \\ &\quad + \frac{1}{2}V(2\pi)^{-3} \int d\mathbf{k} \left(1 + \frac{1}{v(k)s(k)}\right). \end{aligned} \quad (23)$$

We now make one further approximation and that is to assume that p_s is a local functional of $\Psi(\mathbf{x})$, that is,

$$p_s(\mathbf{x}; \{\Psi(\mathbf{x})\}) = p_s(\Psi(\mathbf{x})), \quad (24)$$

where $p_s(\mu)$ is the pressure of the short-ranged system as a function of the chemical potential. This is an assumption of local equilibrium which one would not expect to break down except when $\Psi(\mathbf{x})$ is a rapidly varying function of $\mathbf{x}$.

Using the functional analogue of

$$\begin{aligned} & \int \prod_{a=1}^N d\xi_a \exp\left(-\sum_{a,b} \xi_a A_{ab}^{-1} \xi_b\right) \sum_a f(\xi_a) \\ &= \exp\left\{\frac{1}{2}N \ln \pi + \frac{1}{2}\text{Tr}(\ln A)\right\} \sum_a \pi^{-\frac{1}{2}} A_{aa}^{-\frac{1}{2}} \int d\xi \exp(-\xi^2/A_{aa}), \end{aligned} \quad (25)$$

we have

$$\left\langle \beta \int d\mathbf{x} p_s(\mu + \Psi(\mathbf{x})) \right\rangle = V(\pi\sigma)^{-\frac{1}{2}} \int_{-\infty}^{\infty} d\psi \exp(-\psi^2/\sigma) \beta p_s(\mu + \psi), \quad (26)$$

where

$$\sigma = (2/\beta)(2\pi)^{-3} \int \frac{d\mathbf{k}}{s(k)}. \quad (27)$$

To simplify notation we write

$$[p_s(\mu)] = (\pi\sigma)^{-\frac{1}{2}} \int_{-\infty}^{\infty} d\psi \exp(\psi^2/\sigma) p_s(\mu + \psi), \quad (28)$$

so

$$\begin{aligned} V^{-1} \ln Z_G^0 &= [p_s(\mu + \frac{1}{2}V_0 + \Phi_0)] + \frac{1}{2}\beta\Phi_0^2/v(0) - \frac{1}{2}(2\pi)^{-3} \int d\mathbf{k} \ln\{-v(k)s(k)\} \\ &\quad + \frac{1}{2}(2\pi)^{-3} \int d\mathbf{k} \left(1 + \frac{1}{v(k)s(k)}\right). \end{aligned} \quad (29)$$

The variational principle, based on equation (18), consists of varying Φ_0 and $s(k)$ to make $\ln Z_G^0$ a maximum.

Before we go into the details of this procedure let us note an interesting fact. The total interparticle potential can be separated into two parts U and V in a rather arbitrary fashion, provided that their sum is equal to the original potential. However, the approximation to $\ln Z_G^0$ given by equation (29) is not independent of this division and so we could perhaps choose the division to make $\ln Z_G^0$ a maximum. If we do this arbitrarily then one finds an exact solution to the problem is given by $V(r) = 0$, in which case

$$\ln Z_G = \beta p_s V. \quad (30)$$

This of course is not a useful solution at all because now U is equal to the total interparticle potential and we are left with the original problem. So we should choose U such that p_s can be evaluated to a good approximation and then we can vary $V(r)$ where this variation is allowed, e.g. if U has a hard core of radius d we can vary $V(r)$ for $r < d$, otherwise $V(r)$ has to be regarded as fixed.

Because the parameter σ is used in all the open-bracket expressions via equation (28) we will find that it allows more flexibility if we regard the equation (27) as a subsidiary condition and maximize $\ln Z_G^0$ with respect to σ subject to this constraint. This is done more conveniently by introducing a Lagrange multiplier λ and varying

$$V^{-1} \ln Z_G^0 = \llbracket \beta p_s(\mu + \frac{1}{2} V_0 + \Phi) \rrbracket + \frac{1}{2} \beta \Phi_0^2 / v(0) - \frac{1}{2} (2\pi)^{-3} \int d\mathbf{k} \ln \{-v(k) s(k)\} \\ + \frac{1}{2} (2\pi)^{-3} \int d\mathbf{k} \left(1 + \frac{1}{v(k) s(k)} \right) + \frac{1}{2} \lambda (2\pi)^{-3} \int \frac{d\mathbf{k}}{s(k)} - \frac{1}{2} \lambda \beta \sigma \quad (31)$$

with respect to Φ_0 , $s(k)$, and σ and then using equation (27). In addition one can maximize $\ln Z_G^0$ with respect to $V(r)$ for $r < d$. Complete variation of $V(r)$ for $r < d$ leads to an awkward nonlinear integral equation so we simplify this to some extent by choosing a function $H(r)$ which satisfies the conditions

$$H(r) = 0 \quad \text{for} \quad r > d, \quad (32a)$$

$$H(r) = 1 \quad \text{for} \quad r < d, \quad (32b)$$

and writing

$$V(r) = W(r) + V_0 H(r). \quad (33)$$

We can then maximize $\ln Z_G^0$ with respect to V_0 . (Note that $V_0 = V(0)$ so $W(0) = 0$.)

Let us then differentiate $\ln Z_G^0$ with respect to the variational parameters and set these derivatives equal to zero. Thus

$$\partial(\ln Z_G^0) / \partial \Phi_0 = 0 \quad (34)$$

implies

$$-\Phi_0 = v(0) \llbracket n_s(\mu + \frac{1}{2} V_0 + \Phi_0) \rrbracket, \quad (35)$$

where

$$n_s(\mu) = \partial p_s(\mu) / \partial \mu \quad (36)$$

is the number density of the short-ranged system as a function of the chemical potential. However, we know that the number density $n(\mu)$ of our system can be approximated by

$$n(\mu) \approx (V\beta)^{-1} \partial(\ln Z_G^0) / \partial \mu = \llbracket n_s(\mu + \frac{1}{2} V_0 + \Phi_0) \rrbracket, \quad (37)$$

where all the variational parameters are given a value which makes $\ln Z_G^0$ a maximum. Thus the value of Φ_0 and $v(0)$ will define $n(\mu)$ via

$$\Phi_0 = -n(\mu) v(0). \quad (38)$$

The condition

$$\partial(\ln Z_G^0) / \partial \sigma = 0 \quad (39)$$

implies

$$\lambda = 4\partial \llbracket p_s(\mu + \frac{1}{2} V_0 + \Phi_0) \rrbracket / \partial \sigma. \quad (40)$$

This equation can be simplified by using the identity

$$\partial \llbracket p_s(\mu) \rrbracket / \partial \sigma = \frac{1}{4} \partial^2 \llbracket p_s(\mu) \rrbracket / \partial \mu^2, \quad (41)$$

which is obtained from equation (28) by integration by parts. Thus we have

$$\lambda = [\partial^2 p_s(\mu + \frac{1}{2}V_0 + \Phi_0)/\partial \mu^2]. \quad (42)$$

The third equation, obtained from

$$\delta(\ln Z_G^0)/\delta s(k) = 0, \quad (43)$$

is

$$s(k) = -1/v(k) - \lambda, \quad (44)$$

or

$$-s(k)v(k) = 1 + \lambda v(k). \quad (45)$$

Finally, the requirement

$$\partial(\ln Z_G^0)/\partial V_0 = 0 \quad (46)$$

gives, in conjunction with equations (38) and (45),

$$\beta n(\mu) - \beta n^2(\mu)h(0) = (2\pi)^{-3} \int d\mathbf{k} \frac{h(k)}{1 + \lambda v(k)}, \quad (47)$$

where $h(k)$ is the Fourier transform of the function $H(r)$ defined in equation (33). Equations (35), (42), and (47), in conjunction with equation (27), which becomes

$$\sigma = -\{2(2\pi)^{-3}/\beta\} \int d\mathbf{k} \frac{v(k)}{1 + \lambda v(k)}, \quad (48)$$

are then sufficient to determine the values of Φ_0 , V_0 , σ , and λ which make $\ln Z_G^0$ a maximum. These values can then be used in equations (31) and (38) to give the approximate equation of state, thus

$$\begin{aligned} \beta p(\mu) &= (V^{-1} \ln Z_G^0)_{\max} \\ &= [\beta p_s(\mu + \frac{1}{2}V_0 + \Phi_0)] + \frac{1}{2}\beta v(0)n^2(\mu) - \frac{1}{4}\beta \lambda \sigma - \frac{1}{2}(2\pi)^{-3} \int d\mathbf{k} \ln\{1 + \lambda v(k)\}, \end{aligned} \quad (49)$$

$$n(\mu) = -\Phi_0/v(0). \quad (50)$$

The main drawback with the procedure as outlined is that we have a set of four inter-related nonlinear equations to solve. Since the place of σ in these equations is particularly complicated we could improve this aspect somewhat by performing a limited variation of parameters and restricting σ to be zero. This will allow us to remove the open brackets and obtain the equations

$$-\Phi_0 = v(0)n_s(\mu + \frac{1}{2}V_0 + \Phi_0), \quad (51)$$

$$\beta n(\mu) - \beta n^2(\mu)h(0) = (2\pi)^{-3} \int d\mathbf{k} \ln\{1 + \lambda v(k)\}, \quad (52)$$

and

$$0 = \int d\mathbf{k} \frac{v(k)}{1 + \lambda v(k)} \quad (53)$$

to determine the parameters Φ_0 , V_0 , and λ . For this situation

$$\beta p(\mu) = \beta p_s(\mu + \frac{1}{2}V_0 + \Phi_0) + \frac{1}{2}\beta v(0)n^2(\mu) - \frac{1}{2}(2\pi)^{-3} \int d\mathbf{k} \ln\{1 + \lambda v(\mathbf{k})\} \quad (54)$$

and

$$n(\mu) = -\Phi_0/v(0) \quad (55)$$

give the approximate equation of state. In both these approximations it must be remembered that $v(k) = w(k) + V_0 \hbar(k) > 0$ and so we are not allowed an unrestricted choice for V_0 .

A further simplification which still retains many of the features of the more general approximation is obtained by further restricting the variation by requiring $V(r)$ to be fixed. This leaves two parameters Φ_0 and λ which are determined by equations (51) and (53).

IV. DISCUSSION

We have assumed that we know the equation of state for a system of particles interacting only via the short-range potential $U(r)$. For hard spheres this information could be obtained from the extensive Monte Carlo calculations (Wainwright and Alder 1958; Wood, Parker, and Jacobson 1958) or more conveniently from the exact solution of the Percus-Yevick equation (Thiele 1963, Wertheim 1963); however, the most accurate analytic representation is a Padé approximation of Ree and Hoover (1964). The "effective diameter" approximation of Rowlinson (1964) (see also Barker and Henderson 1967) gives a useful extension of these results for steep intermolecular potentials. Calculations are proceeding to compare the two approximations outlined with each other, with experiments, and with Monte Carlo results.

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