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Integral Equations and Inequalities in the Theory of Fluids*

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Using the method of functional Taylor expansion developed previously, an extensive set of equations is obtained for the distribution functions and Ursell functions in a classical fluid. These include in a systematic way many previously derived relations, e.g., Mayer–Montroll and Kirkwood–Salsburg equations. By terminating the Taylor expansion after a finite number of terms and retaining the remainder, we also obtain inequalities for the distribution functions and thermodynamic parameters of the fluid. For the case of positive interparticle potentials, we recover the inequalities first found by Lieb. For nonpositive potentials, new inequalities (some also obtained by Penrose) are derived. These inequalities are applied to the case of a hard-sphere fluid in three dimensions where they are compared with the results of machine computations and approximate theories. Different inequalities, not obtainable from the above considerations, and some properties of the fugacity expansions, are also derived.

I. INTRODUCTION

RECENTLY, several authors have derived a number of exact results for classical equilibrium systems. Lieb[1] found a series of inequalities for the thermodynamic parameters and distribution functions when the pair potential $\phi(r) \geq 0$, and indicated how these may be extended, partially at least, to more general potentials. Independently of this, Groeneveld,[2] Penrose,[3] and Ruelle[4] obtained rigorous bounds for the radius of convergence of the Mayer series, in powers of the fugacity, for the pressure and distribution functions. The latter two authors used as their starting points the Mayer–Montroll and the Kirkwood–Salsburg[5] sets of equations for the distribution functions. In the present paper, we develop a wide class of new integral equations for the various correlation functions of interest in fluids. One set of these equations is equivalent to those obtained by Mayer[6] of which the Mayer–Montroll and Kirkwood–Salsburg are special cases. Another set of equations includes as a special case two equations recently derived by Green.[7] The same equations also yield in a very natural way the inequalities found by Lieb[1] and Penrose as well as some new inequalities.

The technique used in this paper is an extension of our previous work on the correlation functions and thermodynamic parameters of nonuniform classical fluids.[8] We consider a system represented by a grand canonical ensemble with a chemical potential μ and reciprocal temperature β. Each particle is subject to an external potential $U(\mathbf{r})$, so that the system is characterized by a point function

$$\begin{aligned}\gamma(\mathbf{r}) &= \tfrac{3}{2}\ln(2\pi m/\beta h^2) + \beta\mu - \beta U(\mathbf{r}) \\ &= \ln z - \beta U(\mathbf{r}),\end{aligned} \tag{1.1}$$

where z is the fugacity. Any function of interest in this ensemble ψ may be expanded (formally at least) in a functional Taylor series (with or without remainder) in the deviation of $\gamma(\mathbf{r})$ from some reference value $\gamma_0(\mathbf{r})$. Any other function $\omega(\mathbf{r})$ which is uniquely related to $\gamma(\mathbf{r})$ can equally well serve to characterize the system, and expansions can be made in the deviation of $\omega(\mathbf{r})$ from its corresponding reference value $\omega_0(\mathbf{r})$. In particular, in I and II,[8] we were concerned principally with expansions in $\gamma(\mathbf{r})$ or in the density $n(\mathbf{r})$.

Once we have decided on an appropriate "independent variable" $\omega(\mathbf{r})$ to expand in, it is convenient to introduce a parameter α such that

$$\begin{aligned}\omega(\mathbf{r}, \alpha) &= \omega_0(\mathbf{r}) + \alpha[\omega(\mathbf{r}) - \omega_0(\mathbf{r})], \\ &= \omega_0(\mathbf{r}) + \alpha\Delta\omega(\mathbf{r}).\end{aligned} \tag{1.2}$$

The function to be expanded, ψ, which is a functional of $\omega(\mathbf{r})$, $\psi[\omega(\mathbf{r})]$, may now be considered to be simply a function of α, $\psi(\alpha)$. The expansion is then

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[6] J. E. Mayer, J. Chem. Phys. 15, 187 (1947).
[7] H. S. Green, Nucl. Fusion 1, 69 (1961).
[8] J. L. Lebowitz and J. K. Percus, J. Math. Phys. 4, 116, 248 (1963) (hereafter referred to as I and II, respectively).

a simple Taylor series in α,

$$\psi(\alpha = 1) = \sum_{i=0}^{\ell} \frac{1}{\ell!} \frac{d^i\psi(\alpha)}{d\alpha^i}\bigg|_{\alpha=0} + \frac{1}{\ell!}\int_0^1 (1-\alpha)^\ell \frac{d^{\ell+1}\psi(\alpha)}{d\alpha^\ell}\, d\alpha,$$

$$= \psi[\omega_0] + \int \frac{\delta\psi[\omega]}{\delta\omega(\mathbf{r}_1)}\bigg|_0 \Delta\omega(\mathbf{r}_1)\, d\mathbf{r}_1 + \frac{1}{2!}\iint \frac{\delta^2\psi[\omega]}{\delta\omega(\mathbf{r}_1)\,\delta\omega(\mathbf{r}_2)}\bigg|_0 \Delta\omega(\mathbf{r}_1)\Delta\omega(\mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2 + \cdots + \frac{1}{\ell!}\int_0^1 \int \cdots \int (1-\alpha)^\ell \frac{\delta^{\ell+1}\psi[\omega]}{\delta\omega(\mathbf{r}_1, \alpha) \cdots \delta\omega(\mathbf{r}_\ell, \alpha)} \times \Delta\omega(\mathbf{r}_1) \cdots \Delta\omega(\mathbf{r}_\ell)\, d\mathbf{r}_1 \cdots d\mathbf{r}_\ell\, d\alpha, \tag{1.3}$$

and the burden of the physics lies in suitable choice of ψ, ω, and ω_0.

II. DISTRIBUTION FUNCTIONS

Let us denote the N-body coordinate-space Boltzmann factor by $e_N(\mathbf{r}_1, \cdots, \mathbf{r}_N) \equiv e_N(\mathbf{r}^N)$. Thus,

$$e_N(\mathbf{r}^N) = \exp\,[-\beta \sum_{i<j\le N} \phi(\mathbf{r}_{ij})], \tag{2.1}$$

for particles interacting via the pair potential $\phi(\mathbf{r}_{ij})$. The grand partition function has the form[9]

$$\Xi[\gamma] = \sum_{N=0}^{\infty} \frac{1}{N!}\int e_N(\mathbf{r}^N) \prod_{i=1}^{N} e^{\gamma(\mathbf{r}_i)}\, d\mathbf{r}^N, \tag{2.2}$$

and the ensemble weight factor of (2.2) determines all expectation values. Hence, if

$$F_s^N(\mathbf{y}^N) = \sum_{i_1<i_2\cdots i_s\le N} F_s(\mathbf{y}_{i_1}, \mathbf{y}_{i_2}, \cdots, \mathbf{y}_{i_s}), \tag{2.3}$$

then

$$\langle F_s^N(\mathbf{y}^N)\rangle = \Xi[\gamma]^{-1} \sum_s^{\infty} \frac{1}{N!} \times \int F_s^N(\mathbf{r}^N) e_N(\mathbf{r}^N) \prod_1^N e^{\gamma(\mathbf{r}_i)}\, d\mathbf{r}^N. \tag{2.4}$$

Since the distribution functions $n_s(\mathbf{y}^s, [\gamma])$ are defined by

$$\langle F_s^N(\mathbf{y}^N)\rangle = \frac{1}{s!}\int F_s(\mathbf{y}^s) n_s(\mathbf{y}^s, [\gamma])\, d\mathbf{y}^s, \tag{2.5}$$

it readily follows from (2.4) [on counting the terms in (2.3)] that

$$n_s(\mathbf{y}^s, [\gamma]) = \Xi[\gamma]^{-1} \prod_{i=1}^{s} e^{\gamma(\mathbf{y}_i)} \sum_0^{\infty} \frac{1}{N!} \times \int e_{N+s}(\mathbf{y}^s, \mathbf{r}^N) \prod_1^N e^{\gamma(\mathbf{r}_i)}\, d\mathbf{r}^N. \tag{2.6}$$

We also have from (2.3) and (2.5) the alternative definition

$$n_s(\mathbf{y}^s, [\gamma]) = \langle \sum_{i_1\ne i_2\cdots\ne i_s} \delta(\mathbf{y}_1 - \mathbf{r}_{i_1}) \cdots \delta(\mathbf{y}_s - \mathbf{r}_{i_s})\rangle, \tag{2.7}$$

precisely the distribution of s distinct particles. It is often of value to introduce as well the distributions $\hat{n}_s$ in which[8] the arguments are allowed to refer to identical particles:

$$\hat{n}_s(\mathbf{y}^s, [\gamma]) = \langle (\sum_i \delta(\mathbf{y}_1 - \mathbf{r}_i)) \cdots (\sum_i \delta(\mathbf{y}_s - \mathbf{r}_i))\rangle. \tag{2.8}$$

It is a simple matter to derive the relations

$$\hat{n}_1(\mathbf{y}) = n_1(\mathbf{y}),$$
$$\hat{n}_2(\mathbf{y}_1, \mathbf{y}_2) = n_2(\mathbf{y}_1, \mathbf{y}_2) + n_1(\mathbf{y}_1)\delta(\mathbf{y}_1 - \mathbf{y}_2), \cdots. \tag{2.9}$$

Both sequences of distributions possess generating functions. If $\lambda(\mathbf{y})$ is a suitably well-behaved test function, then according to (2.8) and (2.2),

$$\int \hat{n}_s(\mathbf{y}^s, [\gamma]) \prod_1^s \lambda(\mathbf{y}_i)\, d\mathbf{y}^s = \Xi[\gamma]^{-1} \sum_0^{\infty} \frac{1}{N!} \times \int e_N(\mathbf{r}^N) \prod_{i=1}^N e^{\gamma(\mathbf{r}_i)} (\sum_1^N \lambda(\mathbf{r}_i))^s\, d\mathbf{r}^N, \tag{2.10}$$

leading at once to the relation

$$\sum_0^{\infty} \frac{1}{s!}\int \hat{n}_s(\mathbf{y}^s, [\gamma]) \prod_1^s \lambda(\mathbf{y}_i)\, d\mathbf{y}^s = \Xi[\gamma + \lambda]/\Xi[\gamma]. \tag{2.11}$$

Since (2.11) is itself a functional power series in λ, we have by direct comparison with (1.3),

$$\hat{n}_s(\mathbf{y}^s, [\gamma]) = \Xi[\gamma]^{-1} \frac{\delta^s \Xi[\gamma]}{\delta\gamma(\mathbf{y}_1) \cdots \delta\gamma(\mathbf{y}_s)}. \tag{2.12}$$

On the other hand, from (2.1) and (2.2), using a test function denoted by $\Delta e^{\gamma(\mathbf{y})}$,

$$\int n_s(\mathbf{y}^s, [\gamma]) \prod_1^s \Delta e^{\gamma(\mathbf{y}_i)}\, d\mathbf{y}^s = \Xi[\gamma]^{-1} \sum_0^{\infty} \frac{1}{N!}\int e_N(\mathbf{r}^N) \prod_1^N e^{\gamma(\mathbf{r}_i)} \times \sum_{i_1\ne i_2\cdots\ne i_s\le N} \Delta e^{\gamma(\mathbf{r}_{i_1})} \cdots \Delta e^{\gamma(\mathbf{r}_{i_s})}\, d\mathbf{r}^N. \tag{2.13}$$

Hence, if $\Delta e^{\gamma} \equiv e^{\gamma+\Delta\gamma} - e^{\gamma}$,

$$\sum_0^{\infty} \frac{1}{s!}\int n_s(\mathbf{y}^s, [\gamma]) \prod_1^s \Delta e^{\gamma(\mathbf{y}_i)}\, d\mathbf{y}^s = \Xi[\gamma + \Delta\gamma]/\Xi[\gamma], \tag{2.14}$$

from which, noting that $\Delta e^{\gamma} = e^{\gamma}(e^{\Delta\gamma} - 1)$,

$$n_s(\mathbf{y}^s, [\gamma]) = \Xi[\gamma]^{-1} \prod_1^s e^{\gamma(\mathbf{y}_i)} \frac{\delta^s \Xi[\gamma]}{\delta e^{\gamma(\mathbf{y}_1)} \cdots \delta e^{\gamma(\mathbf{y}_s)}}. \tag{2.15}$$

[9] See, for example, T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), p. 233.

Finally, we may similarly consider the Ursell[10] distributions $\mathfrak{F}_s$ and $\hat{\mathfrak{F}}_s$ associated with n_s and $\hat{n}_s$. Indeed, they are most simply defined by relating their generating functions.[11] With the above notation, one defines

$$\sum_1^\infty \frac{1}{s!}\int \hat{\mathfrak{F}}_s(\mathbf{y}^s, [\gamma]) \prod_1^s \lambda(\mathbf{y}_i)\, d\mathbf{y}^s = \ln \sum_0^\infty \frac{1}{s!}\int \hat{n}_s(\mathbf{y}^s, [\gamma]) \prod_1^s \lambda(\mathbf{y}_i)\, d\mathbf{y}^s = \ln \Xi[\gamma + \lambda] - \ln \Xi[\gamma], \tag{2.16}$$

$$\sum_1^\infty \frac{1}{s!}\int \mathfrak{F}_s(\mathbf{y}^s, [\gamma]) \prod_1^s \Delta e^{\gamma(\mathbf{y}_i)}\, d\mathbf{y}^s = \ln \sum_0^\infty \frac{1}{s!}\int n_s(\mathbf{y}^s, [\gamma]) \prod_1^s \Delta e^{\gamma(\mathbf{y}_i)}\, d\mathbf{y}^s = \ln \Xi[\gamma + \Delta\gamma] - \ln \Xi[\gamma]. \tag{2.17}$$

By expansion, the relations

$$\mathfrak{F}_1(\mathbf{y}) = n_1(\mathbf{y}),$$
$$\mathfrak{F}_2(\mathbf{y}_1, \mathbf{y}_2) = n_2(\mathbf{y}_1, \mathbf{y}_2) - n_1(\mathbf{y}_1)n_1(\mathbf{y}_2), \tag{2.18}$$
$$\mathfrak{F}_3(\mathbf{y}_1, \mathbf{y}_2, \mathbf{y}_3) = n_3(\mathbf{y}_1, \mathbf{y}_2, \mathbf{y}_3) - n_2(\mathbf{y}_1, \mathbf{y}_2)n_1(\mathbf{y}_3) - n_2(\mathbf{y}_2, \mathbf{y}_3)n_1(\mathbf{y}_1) - n_2(\mathbf{y}_3, \mathbf{y}_1)n_1(\mathbf{y}_2) + 2n_1(\mathbf{y}_1)n_1(\mathbf{y}_2)n_1(\mathbf{y}_3), \cdots$$

are obtained, and precisely the same relations hold between the $\hat{\mathfrak{F}}_s$ and $\hat{n}_s$. As a consequence of (2.16) and (2.17), we now have

$$\hat{\mathfrak{F}}_s(\mathbf{y}^s, [\gamma]) = \frac{\delta^s \ln \Xi[\gamma]}{\delta\gamma(\mathbf{y}_1) \cdots \delta\gamma(\mathbf{y}_s)},$$
$$\mathfrak{F}_s(\mathbf{y}^s, [\gamma]) = \prod_1^s e^{\gamma(\mathbf{y}_i)} \frac{\delta^s \ln \Xi[\gamma]}{\delta e^{\gamma(\mathbf{y}_1)} \cdots \delta e^{\gamma(\mathbf{y}_s)}}. \tag{2.19}$$

The characteristic property of the Ursell distributions is that they vanish whenever their arguments decompose into two independent sets. To see this, suppose that the total volume Ω is divided into two volumes $\Omega = \Omega_1 + \Omega_2$ such that

$$\hat{n}_{a+b}(\mathbf{y}_1, \cdots \mathbf{y}_a, \mathbf{y}_{a+1}, \cdots \mathbf{y}_{a+b}) = \hat{n}_a(\mathbf{y}_1, \cdots \mathbf{y}_a)\hat{n}_b(\mathbf{y}_{a+1}, \cdots \mathbf{y}_b),$$

when $\mathbf{y}_1, \cdots \mathbf{y}_a$ are in Ω_1, $\mathbf{y}_{a+1}, \cdots \mathbf{y}_b$ in Ω_2 (and similarly under permutations of $\hat{n}_{a+b}$). Then since

$$\int \hat{n}_s(\mathbf{y}^s)\lambda(\mathbf{y}_1) \cdots \lambda(\mathbf{y}_s)\, d\tau(\mathbf{y}_1) \cdots d\tau(\mathbf{y}_s) = \sum_a \binom{s}{a} \times \int \hat{n}_a(\mathbf{y}^a)\lambda(\mathbf{y}_1) \cdots \lambda(\mathbf{y}_a)\, d\tau_1(\mathbf{y}_1) \cdots d\tau_1(\mathbf{y}_a) \times \int \hat{n}_{s-a}(\mathbf{y}_{a+1}, \cdots, \mathbf{y}_s) \times \lambda(\mathbf{y}_{a+1}) \cdots \lambda(\mathbf{y}_s)\, d\tau_2(\mathbf{y}_{a+1}) \cdots d\tau_2(\mathbf{y}_s), \tag{2.20}$$

it follows that

$$\ln \Xi[\gamma + \lambda] - \ln \Xi[\gamma] = \ln \sum \frac{1}{a!} \times \int \hat{n}_a(\mathbf{y}^a)\lambda(\mathbf{y}_1) \cdots \lambda(\mathbf{y}_a)\, d\tau_1(\mathbf{y}_1) \cdots d\tau_1(\mathbf{y}_a) + \ln \sum \frac{1}{b!}\int \hat{n}_b(\mathbf{y}^b) \times \lambda(\mathbf{y}_1) \cdots \lambda(\mathbf{y}_b)\, d\tau_2(\mathbf{y}_1) \cdots d\tau_2(\mathbf{y}_b) \tag{2.21}$$

has no component $\hat{\mathfrak{F}}_s(\mathbf{y}^s)$ in which some particles are in Ω_1 and the others in Ω_2. The same of course holds for $\mathfrak{F}_s(\mathbf{y}^s)$.

III. BASIC INTEGRAL EQUATIONS

If one holds s particles fixed, the k-particle distribution becomes a conditional $(k + s)$-particle distribution. In a classical grand ensemble, particles may be fixed by placing their force fields at fixed points. Thus, the higher-order distributions are related to lower-order distributions with external potentials, a relation upon which many developments in classical statistical mechanics are predicated.

To be explicit, and somewhat pedantic, we have from (2.6),

$$n_s(\mathbf{y}^s, [\gamma]) = \Xi[\gamma]^{-1} \prod e^{\gamma(\mathbf{y}_i)} \times \sum \frac{1}{N!}\int e_N(\mathbf{r}^N) \prod e^{\gamma(\mathbf{r}_j)} \frac{e_{N+s}(\mathbf{r}^N\mathbf{y}^s)}{e_N(\mathbf{r}^N)}\, d\mathbf{r}^N, \tag{3.1}$$

but for two-body forces,

$$e_{N+s}(\mathbf{r}^N\mathbf{y}^s)/e_N(\mathbf{r}^N) = e_s(\mathbf{y}^s) \exp\left[-\beta \sum \phi(\mathbf{r}_i, \mathbf{y}_j)\right].$$

Hence,

$$n_s(\mathbf{y}^s, [\gamma]) = e_s(\mathbf{y}^s) \prod_1^s e^{\gamma(\mathbf{y}_i)} \Xi\left[\gamma - \beta \sum_1^s \phi_{\mathbf{y}_i}\right] \Big/ \Xi[\gamma], \tag{3.2}$$

where

$$\phi_{\mathbf{y}}(\mathbf{r}) \equiv \phi(\mathbf{r}, \mathbf{y}).$$

By virtue of (2.15), Eq. (3.2) yields the functional differential equation

$$\delta^s \Xi[\gamma]/\delta e^{\gamma(\mathbf{y}_1)} \cdots \delta e^{\gamma(\mathbf{y}_s)} = e_s(\mathbf{y}^s)\Xi\left[\gamma - \beta \sum_1^s \phi_{\mathbf{y}_i}\right], \tag{3.3}$$

which is our literal starting point. If (3.3) is differentiated k times, it generalizes to

[10] See, for example, J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 137.

[11] See, for example, J. L. Lebowitz and J. K. Percus, Phys. Rev. **122**, 1675 (1961).

$$\frac{\delta^{k+s}\Xi[\gamma]}{\delta e^{\gamma(\mathbf{x}_1)}\cdots\delta e^{\gamma(\mathbf{x}_k)}\delta e^{\gamma(\mathbf{y}_1)}\cdots\delta e^{\gamma(\mathbf{y}_s)}} = \frac{e_{k+s}(\mathbf{y}^s\mathbf{x}^k)}{e_k(\mathbf{x}^k)}\,\frac{\delta^k\Xi\left[\gamma-\beta\sum_1^s\phi_{\mathbf{y}_j}\right]}{\delta e^{\gamma(\mathbf{x}_1)-\beta\sum\phi(\mathbf{x}_1\mathbf{y}_j)}\cdots\delta e^{\gamma(\mathbf{x}_k)-\beta\sum\phi(\mathbf{x}_k\mathbf{y}_j)}}, \tag{3.4}$$

where we have made use of the relation

$$e_s(\mathbf{y}^s)\exp\left[-\beta\sum\phi(\mathbf{y}_i,\mathbf{x}_i)\right] = e_{s+k}(\mathbf{y}^s\mathbf{x}^k)/e_k(\mathbf{x}^k).$$

Equation (3.4), in fact, when written as[12]

$$\frac{n_{k+s}(\mathbf{x}^k\mathbf{y}^s,[\gamma])}{n_s\,\mathbf{y}^s,[\gamma])} = n_k\left(\mathbf{x}^k,\left[\gamma-\beta\sum_1^s\phi_{\mathbf{y}_j}\right]\right), \tag{3.5}$$

is precisely the conditional distribution relation alluded to above.

We now wish to relate distributions of different orders for the same system. This requires elimination of the external potential which enters into such as (3.5) and may be accomplished by turning on the external potential in a series expansion of the form (1.3). To this end, we set

$$\begin{aligned} e^{\gamma(\mathbf{r}|0)} &= z \\ e^{\gamma(\mathbf{r}|\alpha)} &\equiv z\left\{1+\alpha\left(\exp\left[-\beta\sum_1^s\phi(\mathbf{y}_i,\mathbf{r})\right]-1\right)\right\} \\ &\equiv z\{1+\alpha f(\mathbf{y}^s;\mathbf{r})\} \\ e^{\gamma(\mathbf{r}|1)} &\equiv z\exp\left[-\beta\sum_1^s\phi(\mathbf{y}_i,\mathbf{r})\right], \end{aligned} \tag{3.6}$$

$f(\mathbf{y}^s;\mathbf{r})$ being a generalized Mayer f function, and follow the corresponding transition of a quantity we shall refer to as $G_{k,s}(\alpha)$:

$$\begin{aligned} G_{k,s}(\mathbf{r}^k\mathbf{y}^s|0) &= \Xi(0)z^{-k}n_k(\mathbf{r}^k), \\ G_{k,s}(\mathbf{r}^k\mathbf{y}^s|\alpha) &\equiv \delta^k\Xi(\alpha)/\delta e^{\gamma(\mathbf{r}_1|\alpha)}\cdots\delta e^{\gamma(\mathbf{r}_k|\alpha)}, \\ &= \Xi(\alpha)\prod_1^k e^{-\gamma(\mathbf{r}_i|\alpha)}n_k(\mathbf{r}^k|\alpha), \end{aligned} \tag{3.7}$$

$$G_{k,s}(\mathbf{r}^k\mathbf{y}^s|1) = \Xi(0)z^{-(k+s)}n_{k+s}(\mathbf{r}^k\mathbf{y}^s)e_k(\mathbf{r}^k)/e_{k+s}(\mathbf{r}^k\mathbf{y}^s).$$

Here $\Xi(\alpha)$ denotes $\Xi[\gamma(\ |\alpha)]$, etc.

Direct application of (1.3) now yields

$$\begin{aligned} G_{k,s}(1) &= \sum_{j=0}^{\ell}\frac{1}{j!}\int\frac{\delta^jG_{k,s}(\alpha)}{\delta e^{\gamma(\mathbf{r}_1)}\cdots\delta e^{\gamma(\mathbf{r}_j)}}\bigg|_{\alpha=0} \\ &\times\prod_1^j[zf(\mathbf{y}^s;\mathbf{r}_i)]\,d\mathbf{r}^j \\ &+\iint_0^1\frac{(1-\alpha)^\ell}{\ell!}\,\frac{\delta^{\ell+1}G_{k,s}(\alpha)}{\delta\exp[\gamma(\mathbf{r}_1|\alpha)]\cdots\delta\exp[\gamma(\mathbf{r}_{\ell+1}|\alpha)]} \\ &\times\prod_1^{\ell+1}[zf(\mathbf{y}^s;\mathbf{r}_i)]\,d\mathbf{r}^{\ell+1}\,d\alpha, \end{aligned} \tag{3.8}$$

or employing

$$\delta^jG_{k,s}(\mathbf{x}^k\mathbf{y}^s|\alpha)/\delta e^{\gamma(\mathbf{r}_1|\alpha)}\cdots\delta e^{\gamma(\mathbf{r}_j|\alpha)} = G_{k+j,s}(\mathbf{x}^k\mathbf{r}^j,\mathbf{y}^s|\alpha) \tag{3.9}$$

and the definition of $G_{k,s}$,

$$\begin{aligned} \frac{n_{k+s}(\mathbf{x}^k\mathbf{y}^s)e_k(\mathbf{x}^k)}{e_{k+s}(\mathbf{x}^k\mathbf{y}^s)z^s} &= \sum_{j=0}^{\ell}\frac{1}{j!}\int n_{k+j}(\mathbf{x}^k\mathbf{r}^j)\prod_{i=1}^j f(\mathbf{y}^s;\mathbf{r}_i)\,d\mathbf{r}^j \\ &+z^{\ell+1}\int_0^1\frac{(1-\alpha)^\ell}{\ell!}\,\frac{\Xi(\alpha)}{\Xi(0)}\prod_1^k e^{-\gamma(\mathbf{x}_i|\alpha)} \\ &\times\left\{\int\prod_1^{\ell+1}[f(\mathbf{y}^s;\mathbf{r}_i)e^{-\gamma(\mathbf{r}_i|\alpha)}]n_{k+\ell+1}(\mathbf{x}^k\mathbf{r}^{\ell+1}|\alpha)\,d\mathbf{r}^{\ell+1}\right\}d\alpha \\ &= N_{k,s}^{(\ell)}+R_{k,s}^{(\ell)}. \end{aligned} \tag{3.10}$$

If this series converges, so that the remainder term $R_{k,s}^{(\ell)}$ vanishes when ℓ goes to infinity, then for any choice of $k\geq 0$, we get a set of recursive equations for the distributions *in the original system without external potential*, as s is varied. Similarly, for any choice of $s\geq 1$ (the choice $s=0$ leads to an identity), we obtain a set of equations for different k. In particular, the choice $k=0$ recovers the Mayer–Montroll equations, while $s=1$ gives the Kirkwood–Salsburg equations. Equation (3.10), with $\ell=\infty$, is equivalent to Eq. (54′) of Mayer.[6]

A different but equivalent set of integral equations may be obtained by instead expanding $G_{k,s}(0)$ about its value at $\alpha=1$ [corresponding to setting $\alpha=1-\delta$ in (3.6) and expanding about $\delta=0$]. This procedure leads to the equations

$$\begin{aligned} z^sn_k(\mathbf{x}^k) &= \sum_{j=0}^{\ell}\frac{(-1)^j}{j!}\int n_{k+s+j}(\mathbf{x}^k\mathbf{y}^s\mathbf{r}^j)\prod_{i=1}^j f(\mathbf{y}^s;\mathbf{r}_i) \\ &\times e_{k+j}(\mathbf{x}^k\mathbf{r}^j)/e_{k+s+j}(\mathbf{x}^k\mathbf{y}^s\mathbf{r}^j)\,d\mathbf{r}^j \\ &+\frac{z^{k+\ell+s+1}(-1)^{\ell+1}}{\Xi(0)}\int\prod_1^{\ell+1}f(\mathbf{y}^s;\mathbf{r}_i) \\ &\times\int_0^1 G_{k+\ell+1,s}(\mathbf{x}^k\mathbf{r}^{\ell+1}\mathbf{y}^s|\alpha)\,\frac{\alpha^\ell}{\ell!}\,d\alpha\,d\mathbf{r}^{\ell+1}. \end{aligned} \tag{3.11}$$

It should be noted that the left-hand side of (3.11) contains, in contrast to (3.10), z raised to a positive power. Eq. (3.11) is formally the inverse or "solution" of (3.10).

The fugacity (z) expansion[3] implicit in (3.10) may be avoided if we consider instead the expansion of the function

[12] See, e.g., J. K. Percus, Phys. Rev. Letters **8**, 462 (1962).

$$\tilde{G}_{k,s}(\alpha) = \prod_{i=1}^{k} e^{-\gamma(\mathbf{r}_i|\alpha)} \mathfrak{F}_k(\mathbf{r}^k|\alpha) = \frac{\delta^k \ln \Xi(\alpha)}{\delta e^{\gamma(\mathbf{r}_1|\alpha)} \cdots \delta e^{\gamma(\mathbf{r}_k|\alpha)}}. \quad (3.12)$$

For $k = 0$, $\tilde{G}_{0,s}(\alpha) = \ln \Xi(\alpha)$, we find

$$\ln \left[\frac{n_s(\mathbf{y}^s)}{z^s e_s(\mathbf{y}^s)}\right] = \sum_{j=0}^{\ell} \frac{1}{j!} \int \mathfrak{F}_j(\mathbf{r}^j) \prod_{i=1}^{j} f(\mathbf{y}^s; \mathbf{r}_i)\, d\mathbf{r}^j + z^{\ell+1} \int_0^1 \frac{(1-\alpha)^\ell}{\ell!} \times \int \tilde{G}_{\ell+1,s}(\mathbf{r}^{\ell+1}\mathbf{y}^s|\alpha) \prod_{i=1}^{\ell+1} f(\mathbf{y}^s; \mathbf{r}_i)\, d\mathbf{r}^i\, d\alpha, \quad (3.13)$$

while for $k \geq 1$,

$$\tilde{F}_{k/s}(\mathbf{x}^k; \mathbf{y}^s) \frac{e_s(\mathbf{y}^s) e_k(\mathbf{x}^k)}{e_{s+k}(\mathbf{y}^s\mathbf{x}^k)} = \sum_0^{\ell} \frac{1}{j!} \int \mathfrak{F}_{k+j}(\mathbf{x}^k\mathbf{r}^j) \prod_1^j f(\mathbf{y}^s; \mathbf{r}_i)\, d\mathbf{r}^j + z^{k+\ell+1} \int_0^1 \frac{(1-\alpha)^\ell}{\ell!} \int \tilde{G}_{k+\ell+1,s}(\mathbf{x}^k\mathbf{r}^{\ell+1}\mathbf{y}^s|\alpha) \times \prod_1^{\ell+1} f(\mathbf{y}^s; \mathbf{r}_i)\, d\mathbf{r}^i\, d\alpha. \quad (3.14)$$

Here $\tilde{F}_{k/s}(\mathbf{x}^k; \mathbf{y}^s)$ is the Ursell function for k particles when s particles are fixed, and corresponds to replacing the densities $n_j(\mathbf{x}^j)$ appearing in $\mathfrak{F}_k$ by the conditional densities $n_{j+s}(\mathbf{x}^j\mathbf{y}^s)/n_s(\mathbf{y}^s)$. Thus,

$$\tilde{F}_{1/1}(\mathbf{x}; \mathbf{y}) = n_2(\mathbf{x}\mathbf{y})/n_1(\mathbf{y}), \quad (3.15)$$

$$\tilde{F}_{2/1}(\mathbf{x}_1\mathbf{x}_2; \mathbf{y}) = n_3(\mathbf{x}_1\mathbf{x}_2\mathbf{y})/n_1(\mathbf{y}) - n_2(\mathbf{x}_1\mathbf{y})n_2(\mathbf{x}_2\mathbf{y})/n_1(\mathbf{y})^2.$$

Equation (3.14) may now be used to develop a virial expansion in the density for the Ursell functions in a manner similar to the fugacity expansion obtainable from (3.10).[3] Unfortunately, however, the left-hand side of (3.14) is not linear in the F's—see, e.g., (3.15)—and this will lead to quite complicated recurrence relations for the coefficients in the density expansion. For completeness, we indicate how the relation between $\mathfrak{F}_k$ and $\tilde{F}_{k/1}$ may be obtained. If, for a test function $g(\mathbf{x})$, we set

$$\mathfrak{F}_k = \int \mathfrak{F}_k(\mathbf{x}^k) \prod_1^k g(\mathbf{x}_i)\, d\mathbf{x}^k/k!,$$
$$n_k = \int n_k(\mathbf{x}^k) \prod_1^k g(\mathbf{x}_i)\, d\mathbf{x}^k/k!, \quad (3.16)$$
$$\tilde{F}_{k/1}(\mathbf{y}) = \int \tilde{F}_{k/1}(\mathbf{x}^k\mathbf{y}) \prod_1^k g(\mathbf{x}_i)\, d\mathbf{x}^k/k!,$$
$$n_{k/1}(\mathbf{y}) = \int n_{k+1}(\mathbf{x}^k\mathbf{y}) \prod_1^k g(\mathbf{x}_i)\, d\mathbf{x}^k/(k!n_1(\mathbf{y})),$$

then from the generating function relation (2.17), we have

$$\sum_1^\infty \mathfrak{F}_k = \ln\left(1 + \sum_1^\infty n_k\right) = \ln\left[1 + \left(\int g(x)\, \delta/\delta g(x)\, dx\right)^{-1} \sum_1^\infty k n_k\right] = \ln\left[1 + \left(\int g\, \delta/\delta g\right)^{-1} \cdot \int g(\mathbf{y}) n_1(\mathbf{y}) \sum_0^\infty n_{k/1}(\mathbf{y})\, d\mathbf{y}\right],$$

so that

$$\sum_1^\infty \mathfrak{F}_k = \ln\left[1 + \left(\int g\, \delta/\delta g\right)^{-1} \int g(\mathbf{y}) n_1(\mathbf{y}) \times \exp\left(\sum_1^\infty \tilde{F}_{k/1}(\mathbf{y})\right) d\mathbf{y}\right], \quad (3.17)$$

which can be expanded out. Equation (3.13) and the first of Eqs. (3.14), without a remainder term, were also obtained, using a different method, by Green.[7]

IV. INEQUALITIES FOR POSITIVE POTENTIAL

We have already indicated that (3.10) may be used, when $\ell \to \infty$, to obtain series expansions of the distribution functions in powers of z. The purpose of this section is to obtain rigorous inequalities on the distribution functions, valid for all values of z, by securing upper and lower bounds on the remainder term $R_{k,s}^{(\ell)}$ in (3.10). We repeat for convenience

$$\frac{n_{k+s}(\mathbf{x}^k\mathbf{y}^s)e_k(\mathbf{x}^k)}{e_{k+s}(\mathbf{x}^k\mathbf{y}^s)z^s} = N_{k,s}^{(\ell)} + R_{k,s}^{(\ell)}. \quad (4.1)$$

It is simplest to consider first the case of positive potential, $\phi(\mathbf{y}, \mathbf{r}) > 0$, so that $-1 \leq f(\mathbf{y}^s; \mathbf{r}) \leq 0$. This was first studied by a very different method by Lieb,[1] who obtained the bounds given in Eq. (4.10). In this case, since $n_{k+\ell+1}$ is always nonnegative, the remainder $R_{k,s}^{(\ell)}$ has the sign $(-1)^{\ell+1}$. Thus, $R_{k,s}^{(\ell)} \geq 0$ for ℓ odd, $R_{k,s}^{(\ell)} \leq 0$ for ℓ even, and we have at once the result

$$\frac{n_{k+s}(\mathbf{x}^k\mathbf{y}^s)e_k(\mathbf{x}^k)}{e_{k+s}(\mathbf{x}^k\mathbf{y}^s)z^s} \begin{matrix} \geq \\ \leq \end{matrix} \left\{ N_{k,s}^{(\ell)}(\mathbf{x}^k\mathbf{y}^s) \quad \begin{matrix} \ell & \text{odd} \\ \ell & \text{even} \end{matrix} \right\}, \quad (4.2)$$

with eventual steady decrease in the interval hemmed in by successive bounds, if the series $N_{k,s}^{(\ell)}$ converges as $\ell \to \infty$, but rigorous bounds under all circumstances.

A stronger inequality for the same value of ℓ is obtained by noting that $G_{m,n}(\alpha)$ is a monotonically decreasing function of α, for $\phi \geq 0$, since

$$\partial G_{m,n}(\mathbf{x}^m\mathbf{y}^n|\alpha)/\partial\alpha = z \int f(\mathbf{y}^n; \mathbf{r}) G_{m+1,n}(\mathbf{x}^m\mathbf{r}\mathbf{y}^n|\alpha)\, d\mathbf{r} \leq 0 \quad \text{for} \quad f \leq 0. \quad (4.3)$$

Thus, $0 \leq G_{m,n}(1) \leq G_{m,n}(\alpha) \leq G_{m,n}(0)$. Using $G_{m,n}(1)$ as a lower bound in the remainder, (4.2) is then strengthened to

$$R_{k,s}^{(\ell)}(x^k y^s) \left.\begin{matrix}\geq\\ \leq\end{matrix}\right\} \frac{1}{\ell + 1!} \frac{1}{z^s} \int n_{k+\ell+s+1}(\mathbf{x}^k \mathbf{r}^{\ell+1} \mathbf{y}^s)$$

$$\times \frac{e_{k+\ell+1}(\mathbf{x}^k \mathbf{r}^{\ell+1})}{e_{k+\ell+s+1}(\mathbf{x}^k \mathbf{r}^{\ell+1} \mathbf{y}^s)} \prod_1^{\ell+1} f(\mathbf{y}^s; \mathbf{r}_i)\, d\mathbf{r}^{\ell+1} \left.\begin{matrix}\ell \text{ odd}\\ \ell \text{ even}\end{matrix}\right\}. \quad (4.4)$$

On the other hand, using $G_{m,n}(0)$ as an upper bound succeeds only in converting the inequality for ℓ into the original one for $\ell + 1$. Still stronger inequalities can be obtained by noting that $G(\alpha)$ is convex, since successive derivatives with respect to α alternate in sign.

By setting $e^{\gamma(\mathbf{r}|0)}$ in (3.6) equal to z, we have implicitly removed any external potential from the interior of our system. Thus, if $\phi(\mathbf{y}, \mathbf{r}) = \phi(\mathbf{y} - \mathbf{r})$ and we adopt periodic boundary conditions, the system will be uniform and the constant density $\rho = n_1(\mathbf{r})$ one of its thermodynamic parameters. We, henceforth, restrict our attention to uniform systems (although this restriction is for most of our purposes inessential). We now proceed to obtain actual bounds upon the distributions and not merely relations between them. As a prototype, (4.2) may be truncated at $\ell = 0$ to yield

$$\frac{n_{k+s}(\mathbf{x}^k \mathbf{y}^s)}{e_{k+s}(\mathbf{x}^k \mathbf{y}^s)} \leq z^s \frac{n_k(\mathbf{y}^k)}{e_k(\mathbf{y}^k)}, \quad (4.5)$$

and, in particular,

$$n_s/e_s \leq \rho z^{s-1} \leq z^s. \quad (4.5')$$

The last form of the inequality was obtained originally by Groeneveld.[2]

Successively finer inequalities now involve truncating at higher ℓ and eliminating all distributions but one. The process may, however, be carried out in numerous ways. Consider first the Kirkwood–Salsburg sequence $s = 1$, $k = 0, 1, 2, \cdots$. We have from (4.4),

$$\frac{\rho}{z} \leq 1 + z \int f(\mathbf{r}) \frac{n_2(\mathbf{r})}{z^2} e^{\beta\phi(\mathbf{r})}\, d\mathbf{r} \leq 1, \quad (4.6a)$$

$$\frac{\rho}{z} \geq 1 + z \int \frac{\rho}{z} f(\mathbf{r})\, d\mathbf{r} + \frac{z^2}{2!} \int f(\mathbf{r}_1 - \mathbf{y}) f(\mathbf{r}_2 - \mathbf{y})$$

$$\times \frac{n_3(\mathbf{r}_1\mathbf{r}_2\mathbf{y})}{z^3} \frac{e_2(\mathbf{r}_1\mathbf{r}_2)}{e_3(\mathbf{r}_1\mathbf{r}_2\mathbf{y})}\, d\mathbf{r}_1\, d\mathbf{r}_2 \geq 1 + \rho \int f(\mathbf{r})\, d\mathbf{r}, \quad (4.6b)$$

$$\frac{\rho}{z} \leq 1 + z \int \frac{\rho}{z} f(\mathbf{r})\, d\mathbf{r}$$

$$+ \frac{z^2}{2!} \int f(\mathbf{r}_1 - \mathbf{y}) f(\mathbf{r}_2 - \mathbf{y}) \frac{n_2(\mathbf{r}_1\mathbf{r}_2)}{z^2}\, d\mathbf{r}_1\, d\mathbf{r}_2$$

$$+ \frac{z^3}{3!} \int fff \frac{n_4}{z^4} \frac{e_3}{e_4}\, d\mathbf{r}_1\, d\mathbf{r}_2\, d\mathbf{r}_3 \leq 1 + \rho \int f(\mathbf{r})\, d\mathbf{r}$$

$$+ \frac{z^2}{2!} \int f(\mathbf{r}_1 - \mathbf{y}) f(\mathbf{r}_2 - \mathbf{y}) \frac{n_2(\mathbf{r}_1, \mathbf{r}_2)}{z^2}\, d\mathbf{r}_1\, d\mathbf{r}_2, \quad (4.6c)$$

$$\frac{n_2(\mathbf{x}\mathbf{y})}{z^2} e^{\beta\phi(\mathbf{x}-\mathbf{y})} \leq \frac{\rho}{z}$$

$$+ z \int f(\mathbf{r} - \mathbf{y}) \frac{n_3(\mathbf{x}\mathbf{r}\mathbf{y})}{z^3} \frac{e_2(\mathbf{x}\mathbf{r})}{e_3(\mathbf{x}\mathbf{r}\mathbf{y})}\, d\mathbf{r} \leq \rho/z, \quad (4.7a)$$

$$\frac{n_2(\mathbf{x}\mathbf{y})}{z^2} e^{\beta\varphi} \geq \frac{\rho}{z} + z \int f(\mathbf{r} - \mathbf{y}) \frac{n_2(\mathbf{x}\mathbf{r})}{z^2}\, d\mathbf{r}$$

$$+ \frac{z^2}{2!} \int f(\mathbf{r}_1 - \mathbf{y}) f(\mathbf{r}_2 - \mathbf{y}) \frac{n_4(\mathbf{x}\mathbf{r}_1\mathbf{r}_2\mathbf{y})}{z^4} \frac{e_3(\mathbf{x}\mathbf{r}_1\mathbf{r}_2)}{e_4(\mathbf{x}\mathbf{r}_1\mathbf{r}_2\mathbf{y})}\, d\mathbf{r}_1\, d\mathbf{r}_2$$

$$\geq \frac{\rho}{z} + z \int f(\mathbf{r} - \mathbf{y}) \frac{n_2(\mathbf{x}, \mathbf{r})}{z^2}\, d\mathbf{r}, \quad (4.7b)$$

$$\frac{n_3(\mathbf{x}_1\mathbf{x}_2\mathbf{y})}{z^3} e^{\beta[\phi(\mathbf{x}_1-\mathbf{y})+\phi(\mathbf{x}_2-\mathbf{y})]} \leq \frac{n_2(\mathbf{x}_1\mathbf{x}_2)}{z^2}$$

$$+ z \int f(\mathbf{r} - \mathbf{y}) \frac{n_4(\mathbf{x}_1\mathbf{x}_2\mathbf{r}\mathbf{y})}{z^4} \frac{e_3(\mathbf{x}_1\mathbf{x}_2\mathbf{r})}{e_4(\mathbf{x}_1\mathbf{x}_2\mathbf{r}\mathbf{y})}\, d\mathbf{r}$$

$$\leq n_2(\mathbf{x}_1, x_2)/z^2. \quad (4.8)$$

We can now also obtain bounds on ρ/z, n_2/z^2, etc., which do not contain any distribution functions but only ρ and z and explicitly known quantities. Perhaps the simplest consistent (but not necessarily "best") manner of doing this is to *consider only the second* (*weaker*) *inequalities* in Eqs. (4.6)–(4.8). Then we utilize (4.7a) to eliminate n_2 from (4.6c), (4.7b), and (4.8c). This yields (4.9c), (4.15b), and (4.16), . . . etc., —the key to the maintenance of the inequality in each case being that $f < 0$. We thus find

$$\rho \leq z, \qquad \rho \geq z + \rho z \int f(\mathbf{r})\, d\mathbf{r}, \quad (4.9a, b)$$

$$\rho \leq z + \rho \left\{ z \int f(\mathbf{r})\, d\mathbf{r} + \frac{z^2}{2!} \int e^{-\beta\varphi(\mathbf{r})} f(\mathbf{y}) f(\mathbf{r} - \mathbf{y})\, d\mathbf{r}\, d\mathbf{y} \right\}. \quad (4.9c)$$

This process was carried out in detail by Penrose,[13] and leads to a general set of inequalities, Lieb's inequalities are of the form

$$\rho \left.\begin{matrix}\leq\\ \geq\end{matrix}\right\} z + \rho \sum_{i=1}^{\ell} a_i z^i \quad \left.\begin{matrix}\ell \text{ even}\\ \ell \text{ odd}\end{matrix}\right\}, \quad (4.10)$$

which, as long as $\sum_1^\ell a_i z^i < 1$, can be written as

[13] O. Penrose, J. Math. Phys. 4, 1488 (1963) (previous paper).

$$\rho \begin{matrix}\le\\ \ge\end{matrix} \Big\} z \Big/ \Big(1 - \sum_1^{\ell} a_i z^i\Big). \tag{4.11}$$

The coefficients a_i in (4.10) and (4.12) may be found in terms of the more customary quantities b_k occurring in the fugacity expansions of pressure and density,

$$\begin{aligned}\beta p &= \sum_1^{\infty} b_k z^k,\\ \rho &= \sum_1^{\infty} k b_k z^k.\end{aligned} \tag{4.12}$$

Since the a_i do not depend[13] upon ℓ, one need only take the $\ell = \infty$ limit of (4.11) and equate coefficients:

$$z \Big/ \Big(1 - \sum_1^{\infty} a_i z^i\Big) = \sum_1^{\infty} k b_k z^k. \tag{4.13}$$

Making use of a well-known formula[14] for the power series representing the quotient of two power series, one finds

$$a_i = (-1)^{i+1} \times \begin{vmatrix} 2b_2 & 1 & 0 & \cdots & 0\\ 3b_3 & 2b_2 & 1 & \cdots & 0\\ \cdot & 3b_3 & 2b_2 & \cdots & 0\\ \cdot & \cdot & \cdot & & \cdot\\ \cdot & \cdot & \cdot & & 1\\ (j+1)b_{j+1} & jb_j & (j-1)b_{j-1} & & 2b_2 \end{vmatrix}. \tag{4.14}$$

The same process which led to (4.9), leads directly to the analogous sequence

$$n_2(\mathbf{xy})/z^2 \le (\rho/z) e^{-\beta\phi(\mathbf{x}-\mathbf{y})}, \tag{4.15a}$$

$$\frac{n_2(\mathbf{x}, \mathbf{y})}{z^2} \ge \frac{\rho}{z}\Big[e^{-\beta\phi(\mathbf{x}-\mathbf{y})} + z\int e^{-\beta\phi(\mathbf{x}-\mathbf{r})} f(\mathbf{r}-\mathbf{y})\, d\mathbf{r}\Big], \cdots, \tag{4.15b}$$

$$\frac{n_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{y})}{z^3} \le \rho e_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{y}), \cdots. \tag{4.16}$$

In general, one derives, in this fashion, inequalities of the form[13]

$$n_k(\mathbf{x}^k) \begin{matrix}\le\\ \ge\end{matrix} \Big\} \rho z^{k-1} \sum_{j=0}^{\ell} a_{k,j}(\mathbf{x}^k) z^j \quad \begin{matrix}\ell \text{ even}\\ \ell \text{ odd}\end{matrix}, \tag{4.17}$$

and the $a_{k,j}$ can again be obtained by letting $\ell \to \infty$, then equating (4.17) to the usual fugacity expansion of n_k:

$$n_k(\mathbf{x}^k) = \rho z^{k-1} \sum_0^{\infty} a_{k,j}(\mathbf{x}^k) z^j = z^k \sum_0^{\infty} n_{k,j}(\mathbf{x}^k) z^j,$$

or

$$\sum_0^{\infty} a_{k,j}(\mathbf{x}^k) z^j = \sum_0^{\infty} n_{k,j}(\mathbf{x}^k) z^j \Big/ \sum_0^{\infty} (j+1) b_{j+1} z^j. \tag{4.18}$$

A somewhat simpler set of inequalities, which however are not always as strong as (4.11) and (4.17), is available from the Mayer–Montroll equations, i.e., $k = 1$ in (4.1). For this purpose, we iterate as before, but also eliminate $\rho = n_1(\mathbf{r})$ in terms of z and f. This yields directly[13]

$$n_k(\mathbf{x}^k) \begin{matrix}\le\\ \ge\end{matrix} \Big\} z^k \sum_0^{\ell} n_{k,j}(\mathbf{x}^k) z^j \quad \begin{matrix}\ell \text{ even}\\ \ell \text{ odd}\end{matrix}, \quad k \ge 1. \tag{4.19}$$

In particular, for $k = 1$, since $p = \int (\rho/z)\, dz$ we have both

$$\rho \begin{matrix}\le\\ \ge\end{matrix} \Big\} \sum_0^{\ell-1} j b_j z^j \quad \begin{matrix}\ell \text{ odd},\\ \ell \text{ even}\end{matrix}$$

and

$$\beta p \begin{matrix}\le\\ \ge\end{matrix} \Big\} \sum_0^{\ell-1} b_j z^j. \quad \begin{matrix}\ell \text{ odd}.\\ \ell \text{ even}\end{matrix} \tag{4.20}$$

V. INEQUALITIES FOR GENERAL POTENTIAL

When the pair potential $\phi(\mathbf{r})$ is not everywhere positive (or zero) we must obtain bounds for both the product of the f's and $n(\alpha)$ in the remainder in (4.1). Separating the potential into a positive and negative part:

$$\begin{gathered}\phi(\mathbf{r}) = \phi_+(\mathbf{r}) + \phi_-(\mathbf{r}),\\ \phi_+ \ge 0, \quad \phi_- \le 0, \quad \phi_-\phi_+ = 0,\end{gathered} \tag{5.1}$$

we can thereby obtain also for f

$$f(\mathbf{y}^s; \mathbf{r}) \equiv f_+(\mathbf{y}^s; \mathbf{r}) - f_-(\mathbf{y}^s; \mathbf{r}), \tag{5.2}$$

where $f_+ \ge 0$, $f_- \ge 0$, $f_+f_- = 0$. Correspondingly, in the factor $\prod f$ in (3.10), we may collect separately the positive and negative terms:

$$\prod_1^{\ell+1} [f_+(\mathbf{y}^s; \mathbf{r}) - f_-(\mathbf{y}^s; \mathbf{r})] = F_+(\mathbf{y}^s; \mathbf{r}^{\ell+1}) - F_-(\mathbf{y}^s; \mathbf{r}^{\ell+1}), \tag{5.3}$$

with $F_+ \ge 0$, $F_- \ge 0$.

To estimate the quantity $n_{k+\ell+1}(\mathbf{x}^k \mathbf{r}^{\ell+1} \mid \alpha)\, \Xi(\alpha)$ in the remainder of (4.1), we recall [Eq. (3.2)] that

$$\Xi[\gamma] \prod_1^{t} e^{-\gamma(\mathbf{x}_i)} n_t(\mathbf{x}^t, [\gamma]) = e_t(\mathbf{x}^t)\, \Xi\Big[\gamma - \beta \sum_1^{t} \phi_{\mathbf{x}_i}\Big]. \tag{5.4}$$

[14] See, for example, I. S. Gradstein and I. M. Riezhic, *Collection of Formulas* (Four Continent Publishing Company, Inc., New York, 1962).

Now in the present instance, $t = k + \ell + 1$, and in the integrand of $\Xi[\gamma - \beta \sum_1^s \phi_{x_i}]$ we have (with $0 \leq \alpha \leq 1$)

$$\prod_1^N e^{\gamma(\mathbf{r}_i|\alpha)} = z^N \prod_1^N (1 + \alpha f(\mathbf{y}^s; \mathbf{r}_i))$$
$$\leq z^N \prod_1^N (1 + f_+(\mathbf{y}^s; \mathbf{r}_i)) \tag{5.5}$$
$$= z^N \exp\left[-\beta \sum_{j=1}^N \sum_{i=1}^s \phi_-(\mathbf{y}_i - \mathbf{r}_j)\right].$$

It has been shown by Penrose[3] that when the particles have hard cores and $\phi(\mathbf{r})$ falls off sufficiently rapidly as $r \to \infty$, then in the domain of nonvanishing Boltzmann factor,

$$\sum_{j=1}^N \phi(\mathbf{y} - \mathbf{r}_j) \geq -2\Phi', \qquad N = 1, 2, \cdots, \tag{5.6}$$

where Φ' is some constant. The same argument shows that

$$\sum_{j=1}^N \phi_-(\mathbf{y} - \mathbf{r}_j) \geq -2\Phi'. \tag{5.7}$$

It follows then from (5.4) that

$$\Xi[\gamma] \prod_1^t e^{-\gamma(\mathbf{x}_i)} n_t(\mathbf{x}^t, [\gamma])$$
$$\leq \Xi[\ln z] z^{-t} n_t(\mathbf{x}^t, [\ln z]) e^{2\beta s\Phi'}, \tag{5.8}$$

or

$$\left(\frac{\Xi(\alpha)}{\Xi(0)}\right) \prod_1^k e^{-\gamma(\mathbf{x}_i|\alpha)} \prod_1^{\ell+1} e^{-\gamma(\mathbf{r}_i|\alpha)} n_{k+\ell+1}(\mathbf{x}^k\mathbf{r}^{\ell+1}|\alpha)$$
$$\leq z^{-k-\ell-1} e^{2\beta s\Phi'} n_{k+\ell+1}(\mathbf{x}^k\mathbf{r}^{\ell+1}), \tag{5.8'}$$

and, hence (performing the α integration), that the remainder term of (4.1) is bounded from both sides:

$$R_{k,s}^{(\ell)} \left.\begin{matrix}\leq\\ \geq\end{matrix}\right\} \pm e^{2\beta s\Phi'} \int \frac{n_{k+\ell+1}(\mathbf{x}^k\mathbf{r}^{\ell+1})}{(\ell+1)!} \left.\begin{matrix} F_+(\mathbf{y}^s\mathbf{r}^{\ell+1}) \\ F_-(\mathbf{y}^s\mathbf{r}^{\ell+1})\end{matrix}\right\} d\mathbf{r}^{\ell+1}, \tag{5.9}$$

F_+ being used for the upper bound, F_- for the lower.

Equations (4.1) and (5.9) may be treated by successive elimination in the fashion of (4.6)–(4.9) to obtain somewhat more complicated bounds on the distribution functions.[13] In the special case $k = 0$, $s = 1$, one has directly

$$\rho/z \leq 1 + \rho e^{2\beta\Phi'} \int f_+(\mathbf{r})\, d\mathbf{r},$$
$$\rho/z \geq 1 - \rho e^{2\beta\Phi'} \int f_-(\mathbf{r})\, d\mathbf{r}. \tag{5.10}$$

For positive potentials, where $\Phi' = 0$, $f_+ = 0$, $f_- = -f$, (5.9) implies the previous (4.2).

It is to be noted that, by the same reasoning used to derive (5.8), one may obtain

$$n_{k+s}(\mathbf{x}^k\mathbf{y}^s) \leq z^s \frac{e_{k+s}(\mathbf{x}^k\mathbf{y}^s)}{e_k(\mathbf{x}^k)} n_s(\mathbf{y}^s) e^{2s\beta\Phi'}$$
$$\leq z^{k+s} e_{k+s}(\mathbf{x}^k\mathbf{y}^s) e^{2(k+s)\beta\Phi'}. \tag{5.11}$$

The last inequality was first obtained by Groeneveld.[2] As a special case, one has the simple

$$\rho \leq z e^{2\beta\Phi'}. \tag{5.12}$$

VI. APPLICATION TO HARD SPHERES

In this section, we shall evaluate explicitly our rigorous inequalities on the thermodynamic parameters and radial distribution function for a gas of hard spheres of diameter a, and compare them with machine computations and approximate theories.

Consider first the bounds (4.11) and (4.20) for the function $\rho(z)$. For hard spheres of diameter a, the first five virial coefficients are known:

$$B = \tfrac{2}{3}\pi a^3, \qquad C = \tfrac{5}{8}B^2,$$
$$D = 0.2869\, B^3, \qquad E = 0.115\, B^4 \tag{6.1}$$

(E is only known to within 15%), thus yielding the corresponding irreducible cluster integrals

$$\beta_1 = -2B, \qquad \beta_2 = -\tfrac{15}{16}B^2,$$
$$\beta_3 = -0.3825\, B^3, \qquad \beta_4 = -0.144\, B^4, \tag{6.2}$$

and connected cluster integrals, in units of B,

$$b_2 = -1, \qquad b_3 = 1.689,$$
$$b_4 = -3.555, \qquad b_5 = 8.467. \tag{6.3}$$

We note parenthetically the relation of (6.3) to rigorous upper bounds which have been derived[2]: $|b_3| \leq 2$, $|b_4| \leq \frac{16}{3}$, $|b_5| \leq \frac{50}{3}$.

To determine the coefficients a_i, we employ (4.14) in the form

$$1 - \sum_1^\infty a_j z^j = 1\Big/\left(1 + \sum_2^\infty b_k z^{k-1}\right), \tag{6.4}$$

and find that,

$$a_1 = -2, \qquad a_2 = 1.063,$$
$$a_3 = -1.950, \qquad a_4 = 4.617. \tag{6.5}$$

We, therefore, have the following upper bounds $\rho^{(i)}(z)$ and lower bounds $\rho_{(i)}(z)$ on ρ [from (4.12) and (4.20)]:

$$\rho^{(1)}(z) = z, \qquad \rho^{(2)}(z) = z,$$
$$\rho^{(3)}(z) = z/(1 + 2z - 1.063z^2),$$
$$\rho^{(4)}(z) = z - 2z^2 + 5.063z^3, \tag{6.6}$$

$$\begin{aligned}
\rho^{(5)}(z) &= z/(1 + 2z - 1.063z^2 + 1.950z^3 - 4.617z^4),\\
\rho^{(6)}(z) &= z - 2z^2 + 5.063z^3 - 14.222z^4 + 42.335z^5,\\
\rho_{(1)}(z) &= z/(1 + 2z), \qquad \rho_{(2)}(z) = z - 2z^2,\\
\rho_{(3)}(z) &= z/(1 + 2z - 1.063z^2 + 1.950z^3), \qquad (6.7)\\
\rho_{(4)}(z) &= z - 2z^2 + 5.063z^3 - 14.222z^4.
\end{aligned}$$

The fractional expressions are valid until the denominators change sign.

The lowest upper bound of (6.6) and greatest lower bound of (6.7) are plotted in Fig. 1, for the range $0 \le z \le 3$. They bracket ρ to within 1% for $z < 0.25$ ($\rho < 0.17$), to within 25% for $z < 1.0$ ($\rho < 0.5$), and thereafter diverge rapidly (close packing occurs at $\rho \sim 3$ in these units). We may use the bounds of (6.6) and (6.7) to test approximate equations of state. The approximation for hard spheres obtained on the basis of thermodynamic arguments by Reiss, Frisch, and Lebowitz,[15] and by Wertheim[16] and Thiele[16] from the exact solution of the Percus–Yevick[16] approximate integral equation for the radial distribution function,

$$\beta_p = \rho[1 + \tfrac{1}{4}\rho + (\tfrac{1}{4}\rho)^2]/(1 - \tfrac{1}{4}\rho)^3, \qquad (6.8)$$

is in very good agreement with machine computations[17] of the pressure over the whole range of "fluid" densities, $\rho < 1.6$. From (6.8), the fugacity z is obtained by means of

$$\ln z = \ln \rho + \int_0^\rho \frac{\partial(\beta p - \rho)}{\partial \rho} \frac{d\rho}{\rho}, \qquad (6.9)$$

or

$$z = \frac{\rho}{1 - \frac{1}{4}\rho} \exp\left\{\frac{\frac{1}{4}\rho}{(1 - \frac{1}{4}\rho)^3}\left[7 - \tfrac{13}{2}(\tfrac{1}{4}\rho) + \tfrac{5}{2}(\tfrac{1}{4}\rho)^2\right]\right\}, \qquad (6.10)$$

which, when plotted on the same graph as the bounds, fits snugly in the center for $z < 1$.

For the radial distribution function $g(r, z) = n_2(r, z)/\rho^2$, we find from Eqs. (4.17)–(4.18)

$$\begin{aligned}
\rho g(r) &\le z a_{2,0}(r) = z n_{2,0} = z e^{-\beta\varphi(r)},\\
\rho g(r) &\ge z a_{2,0}(r) + z^2 a_{2,1}(r)\\
&= (z + 2z^2) n_{2,0}(r) + z^2 n_{2,1}(r) \qquad (6.11)\\
&= e^{-\beta\varphi}[z + (g_1 - 2)z^2],\\
\rho g(r) &\le z a_{2,0}(r) + z^2 a_{2,1}(r) + z^3 a_{2,2}(r)\\
&= e^{-\beta\varphi(r)}[z + (g_1 - 2)z^2 + (3b_3 - 4g_1 + g_2)z^3],
\end{aligned}$$

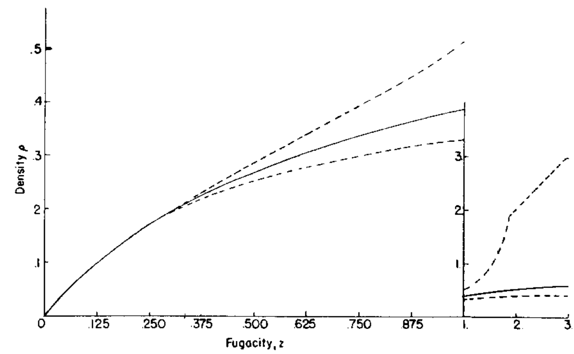

FIG. 1. Bounds on the density. Dotted lines are least upper bound and greatest lower bound for $\rho(z)$ obtained from (6.6) and (6.7); solid line is $\rho(z)$ given by R–F–L and P–Y, Eq. (6.10).

where we have used (4.18) and the relation

$$g(r) = e^{-\beta\varphi(r)}[1 + g_1\rho + g_2\rho^2 + \cdots]. \qquad (6.12)$$

On the other hand, we have from (4.19)

$$\begin{aligned}
\rho g(r) &\le (z/\rho) z n_{2,0}(r),\\
\rho g(r) &\ge (z/\rho)(z n_{2,0}(r) + z^2 n_{2,1}(r)), \qquad (6.13)
\end{aligned}$$

which may be completed to ρ-independent inequalities for $\rho g(r)$ by application of (4.20). For a hard-sphere gas, the values of g_k and $n_{2,k}$ for $k = 0, 1, 2$ are known from the work of Nijboer and Van Hove.[18] In Fig. 2, we have plotted the lowest upper bound and greatest lower bound of (6.11) [(6.12) turns out to be inferior in each case] for $z = \frac{1}{4}$ and $z = \frac{1}{2}$ and the value of $\rho g(r)$ obtained by Wertheim,[16] for $z = \frac{1}{4}$, $r \le 2$.

One can also look, e.g., at (4.6) from the viewpoint of integral inequalities on $\rho g(r)$. Thus, from the first and third equations of (4.6) (dropping the last term in the latter), one has

$$\begin{aligned}
1 &\le \frac{z}{\rho} + \int f(r) e^{\beta\phi(r)} \rho g(r)\, d\mathbf{r},\\
1 &\le \frac{z}{\rho} + z \int f(r)\, d\mathbf{r} \qquad (6.14)\\
&\quad + \frac{1}{2} z \int f(r_1) f(r_2) \rho g(\mathbf{r}_1 - \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2,
\end{aligned}$$

or in the case of hard spheres,

$$\begin{aligned}
&\int_{|r| \le a} \rho g(r) e^{\beta\phi(r)}\, d\mathbf{r} \le \frac{z}{\rho} - 1,\\
&\frac{1}{2}\left\{\int_{|r_1| \le a,\, |r_2| \le a,\, |r_{12}| \ge a} \rho g(\mathbf{r}_1 - \mathbf{r}_2)\, d\mathbf{r}_1\, d\mathbf{r}_2\right\} \qquad (6.15)\\
&\qquad \ge \tfrac{4}{3}\pi a^3 + \frac{1}{z} - \frac{1}{\rho}.
\end{aligned}$$

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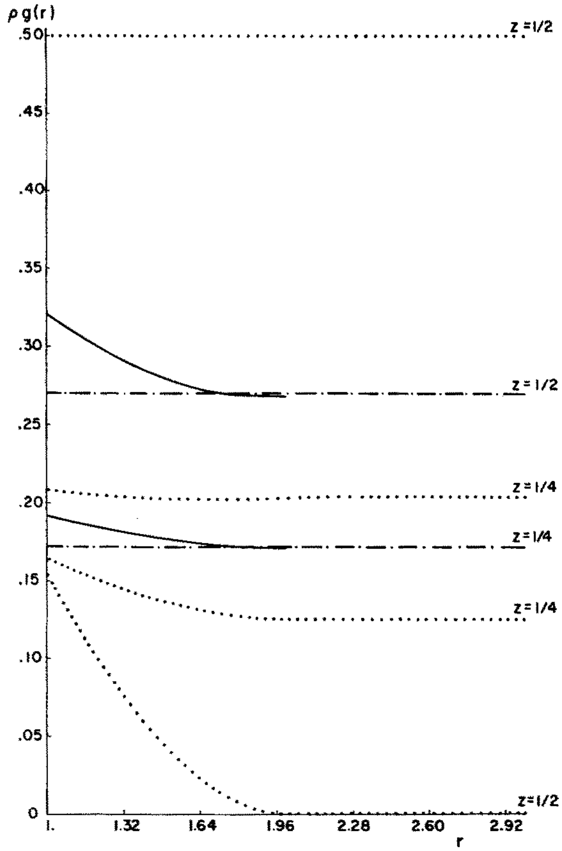

FIG. 2. Bounds on $\rho g(r)$. Dotted lines represent upper and lower bounds of $\rho g(r)$ for $z = \frac{1}{4}$ and $z = \frac{1}{2}$. Solid lines represent solution of the P–Y equation for the same values of z for $r \leq 2$. Straight dot-dash lines represent values of ρ for $z = \frac{1}{4}, \frac{1}{2}$ from (6.10), and are thus the asymptotic values of $\rho g(r)$ for $z = \frac{1}{4}, \frac{1}{2}$.

VII. OTHER INEQUALITIES

In this section we describe briefly some other bounds on the thermodynamic functions which are not obtainable directly from the general development given above. First, it is known that, for all physically reasonable potentials, $p(z)$ and $\rho(z)$ are nondecreasing functions of z.[19] When $\phi(r) \geq 0$, it was also shown by Groeneveld that $p(z_1 + z_2) \leq p(z_1) + p(z_2)$. We shall now show further that when the forces between the particles are purely repulsive, $\phi'(r) \leq 0$, then $p(z)/z$ is a monotonically decreasing function of z [since $\phi(r)$ goes to zero as $r \to \infty$, $\phi'(r) \leq 0$ implies $\phi \geq 0$]. Recalling that $\rho = \partial\beta p/\partial \ln z$, we have, on taking the derivative of $\beta p/z$,

$$\begin{aligned}(d/dz)(\beta p/z) &= (1/z^2)[\rho - \beta p] \\ &= \frac{1}{z^2}\frac{1}{6}\int r\beta\phi'(r)n_2(r)\,dr.\end{aligned} \tag{7.1}$$

The last equality follows from the virial theorem and applies to all potentials. For purely repulsive forces, however, $d(\beta p/z)/dz$ is clearly negative.

For more general forces, but with potentials such that (5.6) and the sequel are valid, we may instead obtain bounds on the pressure. Since f can always be decomposed into a difference of functions decreasing monotonically to zero, we write

$$\begin{gathered} f(r) = f^+(r) - f^-(r), \\ \frac{d}{dr}f^+ \geq 0, \qquad \frac{d}{dr}f^- \geq 0, \end{gathered} \tag{7.2}$$

$$\left(\frac{d}{dr}f^+\right)\left(\frac{d}{dr}f^-\right) = 0. \tag{7.3}$$

We then find from the virial theorem and (5.11) that

$$\begin{aligned}\beta p &= \rho + \frac{1}{6}\int e^{\beta\phi(r)}rf'(r)n_2(r)\,dr \\ &\leq \rho + \frac{1}{6}\int e^{\beta\phi(r)}r\frac{df^+}{dr}n_2(r)\,dr \\ &\leq \rho\left[1 + \frac{1}{6}ze^{2\beta\Phi'}\int r\frac{df^+}{dr}\,dr\right].\end{aligned}$$

Hence

$$\beta p \leq \rho\left[1 - \frac{1}{2}ze^{2\beta\Phi'}\int f^+(r)\,dr\right], \tag{7.4}$$

where $\int f^+(r)\,dr \leq 0$. Eliminating z or ρ from (7.4) by virtue of (5.10) thus yields

$$\beta p \leq \rho\left[1 - \frac{1}{2}\frac{\rho e^{2\beta\Phi'}\int f^+(r)\,dr}{1 - \rho e^{2\beta\Phi'}\int f_-(r)\,dr}\right] \tag{7.5}$$

$$\beta p \leq z\frac{1 - \frac{1}{2}ze^{2\beta\Phi'}\int f^+(r)\,dr}{1 - ze^{2\beta\Phi'}\int f_+(r)\,dr}. \tag{7.6}$$

For repulsive forces, (7.5) reduces to

$$\beta p \leq \rho(1 - |b_2|\,\rho)/(1 - 2\,|b_2|\,\rho). \tag{7.7}$$

Lower bounds on p may be obtained in a similar fashion.

Bounds of the form (7.5)–(7.7), unfortunately, become useless at high density. Nonetheless, the monotonicity of $\rho(z)$ alone helps establish some bounds on $p(z)$. We have

$$\begin{gathered}\beta p(z) = \beta p(z_0) + \int_{z_0}^{z}\frac{\rho}{z}\,dz \geq \beta p(z_0) + \rho(z_0)\ln(z/z_0), \\ \beta p(z) \leq \beta p(z_0) + \rho(z)\ln(z/z_0), \qquad z \geq z_0.\end{gathered} \tag{7.8}$$

Now for potentials with a hard core, $\rho(z)$ has an upper bound ρ_c, the close-packing density. An upper bound to $p(z)$ is then given by

$$\beta p(z) \leq \beta p(z_0) - \rho_c \ln z_0 + \rho_c \ln z, \qquad z \geq z_0. \tag{7.9}$$

[19] L. Van Hove, Physica 15, 951 (1949); D. Ruelle, Helv. Phys. Acta 36, 183 (1963).

We see from (7.9) that $\beta p(z) - \rho_c \ln z$ is a decreasing function of z and that $\lim_{z\to\infty} (\beta p(z)/\ln z) = \rho_c$. This suggests that we write the relation between p and z in the form

$$z = B(\beta p)e^{\beta p/\rho_c}. \tag{7.10}$$

Then $B(\beta p)$ starts out as βp, increases monotonically with p, and satisfies the equation

$$(d/d\beta p) \ln B(\beta p) = 1/\rho(p) - 1/\rho_c \geq 0. \tag{7.11}$$

One may obtain a power series expansion for $B(\beta p)$ from inversion of the series $\sum b_l z^l$. In the special case of a one-dimensional gas of hard rods, one has $B(\beta p) = \beta p$.

Finally, we shall mention one other type of inequality, which compares two systems with different potentials. Let the potential $\phi(r;\alpha)$ have the form

$$\phi(r;\alpha) = \begin{cases} \infty & r < a \\ \alpha u(r) & r \geq a \end{cases}. \tag{7.12}$$

Then the canonical partition function for N particles in a volume V becomes

$$\begin{aligned} Z_N(\alpha) &= \frac{\lambda^N}{N!}\int_{\Omega_N(V)} e^{-\beta\alpha\sum_{i>j}u(r_{ij})}\, d\mathbf{r}^N \\ &= \frac{\lambda^N}{N!}\int_{\Omega_N(V)} (e^{-\frac{1}{2}\beta\alpha\sum_{i>j}u(r_{ij})})^2\, d\mathbf{r}^N, \end{aligned} \tag{7.13}$$

where λ is a constant and $\Omega_N(V)$ the complement of the excluded volume. It follows now from Schwartz's inequality that

$$Z_N(\alpha)Z_N(-\alpha) \geq \left(\frac{\lambda^N}{N!}\int_{\Omega_N} d\mathbf{r}^N\right)^2 = Z_N(0)^2, \tag{7.14}$$

where $Z_N(0)$ is simply the partition function for hard spheres. Since the free energy per particle is given by

$$F_1(\rho;\alpha) = -\lim_{\substack{N\to\infty \\ V\to\infty \\ N/V=\rho}} \frac{\ln Z_N(V,\alpha)}{\beta N}, \tag{7.15}$$

it follows from (7.14) that

$$F_1(\rho;\alpha) + F_1(\rho;-\alpha) \leq 2F_1(\rho;0). \tag{7.16}$$

The relation (7.16) may be written in terms of the pressure

$$p(\rho;\alpha) = \rho^2 \frac{\partial F_1(\rho;\alpha)}{\partial \rho} = -\frac{\partial F_1(v;\alpha)}{\partial v}, \tag{7.17}$$

where $v = \rho^{-1}$ is the volume per particle, and becomes

$$\int_v^\infty \left[\beta p(v';\alpha) + \beta p(v';-\alpha) - \frac{2}{v'}\right] dv' \leq 2\int_v^\infty \left[\beta p(v';0) - \frac{1}{v'}\right] dv'. \tag{7.18}$$

It is interesting to note that when $u(r)$ represents a very long-range weak potential, such as the type considered by Kac, Uhlenbeck, and Hemmer,[20]

$$u(r) = -\gamma^\nu u(\gamma r), \qquad \int u(r)\, d\mathbf{r} = 1, \tag{7.19}$$

where $\nu = 1, 2, 3$ is the dimensionality of the space, then in the limit $\gamma \to 0$

$$\beta p(\rho;\alpha) = \beta p(\rho;0) + \alpha\rho^2, \tag{7.20}$$

for $\alpha < 0$, while for $\alpha > 0$, (7.20) has to be supplemented by the Maxwell rule for the two-phase region. Thus (7.18) becomes an equality for volume v outside the two-phase region.

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APPENDIX A. FUGACITY EXPANSION OF THE URSELL FUNCTION

We may use the methods developed in this paper to obtain directly the fugacity expansion, with or without a remainder, of the Ursell function $\mathfrak{F}_s(\mathbf{r}^s; z)$. We consider a "turning-on process" which takes $\exp \gamma(\mathbf{y} \mid \alpha)$ from an initial value zero to a final value z, to wit,

$$e^{\gamma(\mathbf{y}|\alpha)} = \alpha z. \tag{A1}$$

Thus expanding $\mathfrak{F}_s(\mathbf{r}^s, [\gamma]) \prod_1^s e^{-\gamma(\mathbf{r}_i|\alpha)}$ at $\alpha = 1$ about its reference value at $\alpha = 0$, we obtain with the help of (2.19)

$$\begin{aligned} \frac{\mathfrak{F}_s(\mathbf{r}^s;z)}{z^s} &= \sum_{j=0}^{\ell} \frac{z^j}{j!}\int U_{s+j}(\mathbf{r}^s\mathbf{x}^j)\, d\mathbf{x}^j \\ &+ \int_0^z dz' \frac{(z-z')^\ell}{\ell!(z')^{s+\ell+1}}\int \mathfrak{F}_{s+\ell+1}(\mathbf{r}^s\mathbf{x}^{\ell+1};z')\, d\mathbf{x}^{\ell+1}, \end{aligned} \tag{A2}$$

where

$$U_k(\mathbf{y}^k) = \lim_{z\to 0} \frac{\mathfrak{F}_k(\mathbf{y}^k;z)}{z^k} \tag{A3}$$

is the kth Mayer cluster function.[2]

When $\ell \to \infty$, (A2) yields the fugacity series for F_s. When $s = 1$, (A2) reduces to (4.13b). It was shown by Groeneveld[2] that for a positive potential, $\phi(r) \geq 0$, the U_k alternate in sign, $(-1)^k U_k \geq 0$. Thus, the coefficients in the fugacity expansion of the Ursell functions alternate in sign when $\phi \geq 0$.

[20] M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, J. Math. Phys. 4, 216 (1963).

However, unlike the case of the expansion of $\mathfrak{F}_1 = n$, or the n_k in general, stopping the series after a finite number of terms does not yield an upper or lower bound on $\mathfrak{F}_s$ for $s > 1$, i.e., the remainder term in (A2) alternates in sign only for $s = 1$.

We may however still obtain bounds on the remainder term in (A2) by decomposing $\mathfrak{F}_{s+l+1}$ into its positive and negative parts, which are products of n's, and using the bounds on the n's obtained in this paper. Unfortunately, the bounds thus derived do not have the property of approaching zero when the s particles in $\mathfrak{F}_s$ are separated into groups which are far removed from each other. This is not surprising since these bounds hold also when the system is split into two phases, in which case the Ursell functions do not approach zero asymptotically.

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Solution of Linear Integral Equations Using Padé Approximants

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It is shown that the exact solution of a nonhomogeneous linear integral equation with a kernel K of rank n is given by forming the Padé approximant $P(n, n)$ from the first $2n$ terms of the perturbation series solution. It follows that for a compact kernel K, the solution is $\lim_{n\to\infty} P(n, n)$; this gives meaning to a large class of perturbation series when the perturbation is large. The possible extension of this result to wider classes of equations is discussed.

I. INTRODUCTION

THE method of Padé approximants has been applied with considerable success to the solution of a variety of problems[1-3] in which a divergent or an apparently divergent series requires interpretation. Gammel[4] has suggested the use of this technique to solve a strong coupling problem in quantum field theory—the calculation of the magnetic moments of the nucleons from the perturbation series. This suggestion has led the author to study the realm of validity of the Padé method in perturbation theory, in particular in potential theory, and then to broaden the scope of the theory to a general study of linear integral equations.

Given a series

$$s = \sum_{r=0}^{\infty} \lambda^r m_r, \tag{1.1}$$

where m_r are complex in general, the Padé approximant

$$P(\alpha, \beta) \equiv \left(\sum_{p=0}^{\alpha} \lambda^p a_p\right)\left(\sum_{q=0}^{\beta} \lambda^q b_q\right)^{-1} \tag{1.2}$$

is defined by the identity in λ,

$$\left(\sum_{q=0}^{\beta} \lambda^q b_q\right)\left(\sum_{r=0}^{\infty} \lambda^r m_r\right) = \sum_{p=0}^{\alpha} \lambda^p a_p + O(\lambda^{\alpha+\beta+1}). \tag{1.3}$$

Thus a_p and b_q are given by

$$\sum_{q=0}^{\min(r,\beta)} b_q m_{r-q} = a_r \qquad (r = 0, 1, \cdots, \alpha), \tag{1.4}$$

and

$$\sum_{q=0}^{\min(r,\beta)} b_q m_{r-q} = 0 \qquad (r = \alpha + 1, \cdots, \alpha + \beta). \tag{1.5}$$

In general we can choose, say, $b_0 = 1$, and (1.4) then defines $b_1, \cdots, b_\beta$ uniquely; from (1.3), a_r and hence $P(\alpha, \beta)$ are defined uniquely. Further, it is clear that the formal expansion of (1.2) as a power series in λ will agree with (1.1) to $O(\lambda^{\alpha+\beta})$.

II. THE SOLUTION OF INTEGRAL EQUATIONS WITH KERNELS OF FINITE RANK

We shall first study the nonhomogeneous linear integral equation

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