Hard-Core Insertion in the Many-Body Problem*

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Under many conditions, short-range interparticle forces may be simulated by hard cores. The excluded-volume condition which this implies is equivalent to a single restriction upon the microscopic pair distribution. A short-range nonsingular equivalent potential plays a dominant role in this formulation, and its precise value depends upon the approximation used for the remaining long-range forces. A few of these approximations are examined; they yield simplifications of well-known integral equations in the theory of fluids. Possible perturbation solutions are investigated. For example, the corrections to plasma distributions due to short-range cores can be found in this fashion. The method is generalized by using a single condition on the mean radial distribution, permitting application to quantum mechanics, to mixtures, and to external forces. The special case of the Bose hard-sphere fluid is considered.

I. INTRODUCTION

A LARGE number of perturbation-type methods are available[1] for analyzing the properties of many-body systems in thermal equilibrium when the interaction forces are sufficiently weak. However, effective criteria for sufficient weakness are lacking, and one finds very often that a comparatively naive approach based self-consistently upon some model yields empirically far better results. The types of forces which one meets with in practice, weak long range together with strong short range, would in fact appear to possess a built-in unsuitability with respect to formal and unmotivated expansion procedures. Fortunately, techniques do exist for taking advantage of approximations specifically designed for weak long-range forces to include short-range repulsion as well, when the repulsion is of the hard-core variety. It is the purpose of this paper to indicate how this insertion of hard-core interactions may be carried out.

In Sec. II, we discuss the extent to which simulation of strong short-range forces by hard cores is reasonable. This is followed in Sec. III by development of the principal technique for replacing hard cores by approximation-dependent classical equivalent potentials. Section IV applies these results in principle to a few approximation methods, for which practical expansions are presented in Sec. VI which allows extension to quantum mechanics, mixtures, etc. This is then applied in Sec. VII to the special case of the hard-core Bose ground state.

II. APPEARANCE OF HARD CORE

Let us consider a system in thermal equilibrium at a sufficiently high temperature that explicit quantum many-body effects can be neglected. Nonetheless, the interaction between any two particles is basically quantum mechanical and can only be interpreted as an equivalent classical potential. Of course, the temperature must be low enough at the given density that the coordinates used to describe each particle are sufficient, i.e., that no further internal degrees of freedom are excited. Consider now a pair of particles with no bound state, as is often the case in atom-atom interactions. Suppose further that each is sufficiently massive that the uncertainty principle effectively does not apply to its center of mass [the thermal de Broglie wavelength $\lambda=(h/2mkT)^{1/2}$ is very small]. The classical potential is then the energy with respect to infinite separation, of the pair ground state with centers of mass fixed. This generally results[2] in a short-range highly repulsive (Coulomb plus exchange) potential together with long-range Van der Waals-type forces. For light particles, such as free electrons, interacting via long-range forces alone, λ should be small in comparison with mean separation: $\rho^{1/3}\lambda<1$ for density ρ. Then the true potential attains classical significance.

In the presence of pair bound states, as in ion-electron interaction, one can proceed by insisting that the equivalent potential reproduce the radial distribution which the true quantized pair exhibits at temperature T. In other words, switching to relative coordinates, we require

$$(1/V)e^{-\beta v(\mathbf{r})}=\sum|\psi_{\mathbf{n}}(\mathbf{r})|^2e^{-\beta E_{\mathbf{n}}}/\Sigma e^{-\beta_{\mathbf{n}}} \tag{2.1}$$

for volume V and temperature $T=1/k\beta$, $\sum$ denoting both summation and integration. The qualitative character of $v(\mathbf{r})$ is a function principally of the magnitude of r. We first note that the WKB contribution to the continuum part of (2.1) coincides with the classical evaluation [thus, for example $\rho(\mathbf{x})\propto 1/p(\mathbf{x};E)$ in one dimension for both microcanonical and WKB]; both

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[1] See, e.g., E. Meeron, J. Math. Phys. 1, 192 (1960).

[2] See, e.g., J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1065.

yield, for a basic interaction $v_0(\mathbf{r})$,

$$\int\int_0^\infty e^{-\beta E}\delta\left(\frac{p^2}{2m}+v_0(\mathbf{r})-E\right)dEd\mathbf{p}$$
$$=\int\int_{-p^2/2m}^\infty e^{-\beta(E+p^2/2m)}\delta[v_0(\mathbf{r})-E]dEd\mathbf{p}$$
$$=e^{-\beta v_0(\mathbf{r})}\int_{p^2/2m>-v_0(\mathbf{r})} e^{-\beta p^2/2m}d\mathbf{p}$$
$$\equiv e^{-\beta v_0^*(\mathbf{r})}(\hbar/\lambda)^3, \quad (2.2)$$

where $v_0^*(\mathbf{r})=v_0(\mathbf{r})$ when $v_0(\mathbf{r})>0$, but is quenched when v_0 tries to descend below zero. Hence, simplifying to a single bound state, (2.1) becomes

$$(1/V)e^{-\beta v(\mathbf{r})}=(\psi_0(\mathbf{r})^2e^{-\beta E_0}+\lambda^{-3}e^{-\beta v_0^*(\mathbf{r})})/(V\lambda^{-3}),$$

or

$$\beta v(\mathbf{r})=-\ln(e^{-\beta v_0^*(\mathbf{r})}+\lambda^3\psi_0{}^{(\mathbf{r})^2}e^{-\beta E_0}). \quad (2.3)$$

If $v_0(r)$ has an inner repulsive (Coulomb plus exchange) region, then ϕ_0 is exponentially small there and $v=\psi_0$. When v_0 becomes negative, $v_0^*\sim 0$, and $v(\mathbf{r})=E_0-\beta^{-1}\times\ln(\lambda^3\psi_0{}^2)$, an effective trapping potential, but generally $>-|E_0|$. Finally, at long range, if ψ is of range l, one has $\psi(\mathbf{r})^2\sim l^{-3}\exp[-(2/\hbar)(2m|E_0|)^{\frac{1}{2}}r]$, so that again the regime $v=v_0$ takes over for

$$r>(\beta E_0)^{\frac{1}{2}}\lambda+3\lambda\ln[(\lambda/l)/(\beta E_0)^{\frac{1}{2}}].$$

In general, then, classical potentials of interest will have long-range attractive or repulsive tails. Except for the case of electron-proton interaction, an attractive tail is always accompanied by a strong (temperature-dependent) short-range repulsion. It is convenient to provide still another equivalence, more in the nature of an idealization, and this is to replace the repulsive core by a rigid core of infinite amplitude but finite range a. The nature of the equivalence is determined by the projected use, but matters are particularly simple if we are interested in thermodynamics, e.g., equation of state of a field. Here we need only recall[3] that under a change of internal potential δv the Helmholtz free energy is changed by

$$\delta F=-\rho\beta\int g(\mathbf{r})e^{\beta v(\mathbf{r})}\delta(e^{-\beta v(\mathbf{r})}-1)d\mathbf{r}, \quad (2.4)$$

where $g(\mathbf{r})$ is the radial distribution function. Hence a tail plus repulsive short-range v is replaceable by a hard core plus tail $\bar{v}$ provided that

$$\int\bar{g}(\mathbf{r})\exp[\beta\bar{v}(\mathbf{r})]\{\exp[-\beta\bar{v}(\mathbf{r})]-1\}d\mathbf{r}$$
$$=\int\bar{g}(\mathbf{r})\exp[\beta\bar{v}(\mathbf{r})]\{\exp[-\beta v(\mathbf{r})]-1\}d\mathbf{r}, \quad (2.5)$$

a self-consistent determination of the core radius.

[3] J. L. Lebowitz and J. K. Percus, Phys. Rev. 122, 1675 (1961).

III. FUNDAMENTAL RELATION

Suppose then that a classical fluid, which at this time will be taken as a single component comprised of point particles, is interacting via a long-range nonsingular potential $\phi(\mathbf{r})$ augmented by a hard-core repulsion $\phi_{\text{hc}}(\mathbf{r})$ of range a:

$$\begin{aligned}\phi_{\text{hc}}(\mathbf{r})&=\infty, \quad r\leq a\\ \phi_{\text{hc}}(\mathbf{r})&=0, \quad r>a.\end{aligned} \quad (3.1)$$

Uniformity is to be invoked by placing the system in a periodic box of volume V. We desire to compute the thermodynamic properties and distribution functions in thermal equilibrium for the combined potential. As is well known, the two-body distribution function describes all of equilibrium statistical mechanics. Our problem now becomes that of taking into account the very strong hard-core potential, but doing it in such a way that methods appropriate for weak long-range potentials can be used.

For the hard-core potential of (3.1) in an N-particle system, the normalized N-body Gibbs distribution[4] vanishes whenever cores penetrate:

If $\rho_N(\mathbf{x}_1,\cdots\mathbf{x}_N)$
$$=\exp\{-\beta\textstyle\sum_{i>j}[\phi(\mathbf{x}_i-\mathbf{x}_j)+\Phi_{\text{hc}}(\mathbf{x}_i-\mathbf{x}_j)]\}/Z,$$
$$\rho_N=0 \quad\text{when any}\quad (\mathbf{x}_i-\mathbf{x}_j)\leq a, \quad (3.2)$$

and, consequently, the lower order distributions vanish as well. In particular, if $\langle\ \rangle$ denotes expectation,

$$\begin{aligned}\rho_2(\mathbf{x},\mathbf{y})&=\langle\sum_{i\neq j}\delta(\mathbf{x}_i-\mathbf{x})\delta(\mathbf{x}_j-\mathbf{y})\rangle\\ &=0 \quad\text{if}\quad |\mathbf{x}-\mathbf{y}|\leq a.\end{aligned} \quad (3.3)$$

Conversely, if we define the microscopic pair distribution function

$$\hat{\rho}_2(\mathbf{x},\mathbf{y})\equiv\sum_{i\neq j}\delta(\mathbf{x}_i-\mathbf{x})\delta(\mathbf{x}_j-\mathbf{y}), \quad (3.4)$$

then the hard-core factor $\exp[-\beta\sum_{i>j}\phi_{\text{hc}}(\mathbf{x}_i-\mathbf{x}_j)]$ in ρ_N can be dropped if we adopt the restriction on configuration space that

$$\rho_N=0 \quad\text{unless}\quad \hat{\rho}_2(\mathbf{x},\mathbf{y})=0 \quad\text{whenever}\quad |\mathbf{x}-\mathbf{y}|\leq a. \quad (3.5)$$

A brief way of imposing the excluded volume condition (3.5) is to introduce a test function $W(x)$ which satisfies

$$\begin{aligned}W(\mathbf{x})&>0 \quad\text{for}\quad x\leq a,\\ &=0 \quad\text{for}\quad x>a.\end{aligned} \quad (3.6)$$

Then clearly, (3.5) is equivalent to

$$\rho_N=0\ \text{unless}\int\hat{\rho}_2(\mathbf{x},\mathbf{y})W(\mathbf{x}-\mathbf{y})d\mathbf{x}d\mathbf{y}=0. \quad (3.7)$$

[4] See, e.g., K. Huang, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1963), p. 297.

Since (3.7) may be achieved by appending a Kronecker δ function (unity at vanishing argument), we conclude that the expectation of any quantity Q in the ensemble interacting via $\phi+\phi_{hc}$ can also be expressed as

$$\langle Q\rangle_{\phi+\phi_{hc}}=\left\langle Q\delta_{Kr}\left(\int \hat{\rho}_2(\mathbf{x},\mathbf{y})W(\mathbf{x}-\mathbf{y})d\mathbf{x}d\mathbf{y}\right)\right\rangle_\phi \Big/ \left\langle \delta_{Kr}\left(\int \hat{\rho}_2(\mathbf{x},\mathbf{y})W(\mathbf{x}-\mathbf{y})d\mathbf{x}d\mathbf{y}\right)\right\rangle_\phi \quad (3.8)$$

a ratio of expectations over the tail potential interaction alone. But if we use the representation

$$\delta_{Kr}(z)=\lim_{S\to\infty}\frac{1}{2S}\int_{-S}^{S} e^{i\beta sz}ds\,, \quad (3.9)$$

and observe that

$$\int \hat{\rho}_2(\mathbf{x},\mathbf{y})W(\mathbf{x}-\mathbf{y})d\mathbf{x}d\mathbf{y}=\sum_{i\neq j} W(\mathbf{x}_i-\mathbf{x}_j)\,,$$

so that

$$\rho_N(\mathbf{x}_1,\cdots\mathbf{x}_N)_\phi \exp\left(i\beta s\int \hat{\rho}_2(\mathbf{x},\mathbf{y})W(\mathbf{x}-\mathbf{y})d\mathbf{x}d\mathbf{y}\right) =\rho_N(\mathbf{x}_1,\cdots\mathbf{x}_N)_{\phi-2isW}Z_{\phi-2isW}/Z_\phi\,, \quad (3.10)$$

(3.8) also achieves the more transparent form

$$\langle Q\rangle_{\phi+\phi_{hc}}=\lim_{S\to\infty}\int_{-S}^{S}\langle Q\rangle_{\phi-2isW}Z_{\phi-2isW}ds \Big/ \int_{-S}^{S} Z_{\phi-2isW}ds\,. \quad (3.11)$$

It is tempting to evaluate (3.11) by steepest descent,[5] but first the integrands must be found. For this purpose, when the "potential" $\phi-2isW$ no longer has a hard-core singularity, we can utilize our favorite superior approximation for weak long-range forces. Whatever that is, it will have the consequence[6] that (consistently indicating results of the approximation by bars)

$$\bar{Z}_{\phi-2isW}=\exp(-N\beta\mathfrak{F}_{\phi-2isW})\,, \quad (3.12)$$

where the free energy per particle $\bar{\mathfrak{F}}=\bar{F}/N$ remains constant as $N\to\infty$ at fixed mean density ρ. Hence, if $\bar{\mathfrak{F}}_{\phi-2isW}$ has saddle points in the complex s plane, with that one of minimum real part at $s=\frac{1}{2}is_0$, an expansion of (3.11) about $s=\frac{1}{2}is_0$ becomes exact as $N\to\infty$. Under these circumstances, (3.11) reduces simply to

$$\langle Q\rangle_{\phi+\phi_{hc}}=\langle\bar{Q}\rangle_{\phi+\phi'}\,,\quad \phi'=s_0W\,, \quad (3.13)$$

with the interpretation that exact expectations with potential $\phi+\phi_{hc}$ are to be computed as approximate expectations with potential $\phi+\phi'$.

The effective hard-core potential $\phi'=s_0W$ is not at all arbitrary, but is determined by the approximation made. Indeed, the condition that $\bar{\mathfrak{F}}_{\phi-2isW}$ have a saddle point at all is not trivial. We require $\partial\bar{F}_{\phi+s_0W}/\partial s_0=0$; by explicit differentiation, $\frac{1}{2}\langle\sum_{i\neq j}s_0W(\mathbf{x}_i-\mathbf{x}_j)\rangle_{\phi+s_0W}=0$, or $\int\bar{\rho}_2(\mathbf{x},\mathbf{y})_{\phi+\phi'}\phi(\mathbf{x}-\mathbf{y})d\mathbf{x}d\mathbf{y}=0$. In a uniform system, $\bar{\rho}_2(\mathbf{x},\mathbf{y})=\bar{\rho}_2(x-y)$, so that

$$\int \bar{\rho}_2(\mathbf{r})_{\phi+\phi'}\phi'(\mathbf{r})d\mathbf{r}=0\,. \quad (3.14)$$

Since $\phi'>0$ inside the core and $\bar{\rho}_2\geq 0$ always, Eq. (3.14) is not a single condition but a global one: $\phi'=s_0W$ must be chosen so that the pair distribution $\bar{\rho}_2$ resulting from the approximation [i.e., from (3.13)] vanish inside the core. In other words, assembling (3.8), (3.13), and (3.14) and defining

$$g(\mathbf{r})=\rho_2(\mathbf{r})/\rho^2\,, \quad (3.15)$$

the result of inserting a hard-core interaction ϕ_{hc} into a system with interparticle potential ϕ is the approximation

$$g(\mathbf{r})_{\phi+\phi_{hc}}=\bar{g}(\mathbf{r})_{\phi+\phi'}\,,$$

where

$$\begin{aligned} r\leq a:&\quad g(\mathbf{r})=0\,,\quad \phi'(\mathbf{r})>0\,,\\ r>a:&\quad \phi'(\mathbf{r})=0\,. \end{aligned} \quad (3.16)$$

Equations (3.16) will generally determine the effective hard core ϕ' uniquely, the particular form depending, of course, on the basic approximation hidden in the bar notation. The basic approximation is designed with the tail ϕ in mind. As it improves, the saddle point $s_0\to\infty$ for any acceptable W of (3.6); thus in this limit, ϕ' coincides with ϕ_{hc}, as it must. It is to be noted that if the basic approximation itself produces a g vanishing inside the core when the true potential $\phi+\phi_{hc}$ is used, (3.16) is solved by $\phi'=\phi_{hc}$, and our method is powerless to effect further improvement.

IV. SOME EXAMPLES

The prototype approximation for very long-range, e.g., Coulomb forces is the Debye-Hückel equation,[7] which itself can be simplified in several ways. It arises from the fact that the one-body density when a particle is fixed at $\mathbf{y}$ is given by

$$\rho(\mathbf{x})=\rho g(\mathbf{x}-\mathbf{y})\,, \quad (4.1)$$

but is also given approximately by the Boltzmann factor for the average excess potential acting at $\mathbf{x}$:

$$\begin{aligned} u_{av}(\mathbf{x})&=\phi(\mathbf{x}-\mathbf{y})+\int\rho(\mathbf{z})\phi(\mathbf{x}-\mathbf{z})d_{\mathbf{z}}+K'\,,\\ \rho(\mathbf{x})&=\rho e^{-\beta u_{av}(\mathbf{x})}\,. \end{aligned} \quad (4.2)$$

[5] See e.g., P. M. Morse and H. Feshbach, *Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), p. 434.

[6] See, e.g., H. Callen, *Thermodynamics* (John Wiley & Sons, Inc., New York, 1960), p. 98.

[7] See, e.g., R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, England, 1939), p. 390.

Combining (4.1) and (4.2) leads to the desired

$$g(\mathbf{x}-\mathbf{y};\phi)=K\{\exp[-\beta\phi(\mathbf{x}-\mathbf{y})]\}\times\left\{\exp\left[-\beta\rho\int g(\mathbf{z}-\mathbf{y};\phi)\phi(\mathbf{x}-\mathbf{z})d\mathbf{z}\right]\right\} \quad (4.3)$$

with normalization constant $K=\exp[\beta\rho\int\phi(\mathbf{z})d\mathbf{z}]$, so that $g\to 1$ asymptotically. Interestingly, (4.3) cannot be used with (3.16) because it will never create a g vanishing inside the hard core for any effective $\phi+\phi'$.

Suppose, however, that $g-1$ is small. Then taking the logarithm of (4.3) and linearizing,

$$g(\mathbf{x}-\mathbf{y};\phi)-1=-\beta\phi(\mathbf{x}-\mathbf{y})-\rho\beta\int[g(\mathbf{z}-\mathbf{y};\phi)-1]\phi(\mathbf{x}-\mathbf{z})d\mathbf{z}, \quad (4.4)$$

the linearized Debye-Hückel approximation. A considerably more convenient representation is in terms of the direct correlation function c of Ornstein and Zernike,[8] which is defined by the integral relation

$$g(\mathbf{x})=1+c(\mathbf{x})+\rho\int c(\mathbf{x}-\mathbf{y})(g(\mathbf{y})-1)d\mathbf{y}, \quad (4.5)$$

equivalent to an algebraic relation between Fourier coefficients,

$$c_{\mathbf{k}}=(g-1)_{\mathbf{k}}/(1-\rho(g-1)_{\mathbf{k}}). \quad (4.5')$$

Equation (4.4) then reduces simply to

$$c(\mathbf{r};\phi)=-\beta\phi(\mathbf{r}). \quad (4.6)$$

Consequently, on inserting a hard core, our approximation (3.16) becomes $c(\mathbf{r})=-\beta\phi(\mathbf{r})-\beta\phi'(\mathbf{r})$ where $\phi'(\mathbf{r})=0$ for $r>a$, which we may write as

$$\begin{aligned} c(\mathbf{r})&=\beta\phi(\mathbf{r}) \quad \text{for} \quad r>a,\\ g(\mathbf{r})&=0 \quad \text{for} \quad r\leq a. \end{aligned} \quad (4.7)$$

For no tail at all, $\phi=0$, (4.7) simplifies to $c(\mathbf{r})=0$ for $r>a$, $g(\mathbf{r})=0$ for $r<a$, and is thus identical with the hard sphere Percus-Yevick (PY) equation, whose accuracy has been well attested to.[9] More generally, (4.7) bears a close similarity both to the PY equation.[10]

$$\begin{aligned} c(\mathbf{r})&=(1-e^{\beta\phi(\mathbf{r})})g(\mathbf{r}) \quad \text{for} \quad r>a,\\ g(\mathbf{r})&=0 \quad \text{for} \quad r\leq a \end{aligned} \quad (4.8)$$

and the Broyles-Sahlin equation[11]

$$c(\mathbf{r})=c)_{\text{hs}}(\mathbf{r})-\beta\phi(\mathbf{r}). \quad (4.9)$$

For potentials which become weakly infinite at the origin, such as the Coulomb, the linearized Debye-Hückel equation (4.4) has the unfortunate trait of producing a large negative g at the origin. However, an infinite potential is not as potent as this linearization indicates, and it may be shown that a suitable adjustment is to replace $-\beta\phi$ by the Mayer f factor $f(\mathbf{r};\phi)=e^{-\beta\phi(\mathbf{r})}-1$. Thus, (4.7) is replaced by

$$\begin{aligned} c(\mathbf{r})&=e^{-\beta\phi(\mathbf{r})}-1 \quad \text{for} \quad r>a\\ g(\mathbf{r})&=0 \quad \text{for} \quad r\leq a, \end{aligned} \quad (4.10)$$

a result which indeed coincides with the PY equation (4.8) when g is approximated by the pair Boltzmann factor $e^{-\beta\phi}$.

The linearized Debye-Hückel equation can be sequentially corrected in a number of ways to approach the exact pair distribution. Consistent with the technique we have here developed, an asymptotic expansion in the range of force would be called for, with the insertion method correcting for the intense short-range forces. For this purpose, one may use the standard diagrammatic expansion[12] of c in potential bonds $(-\beta\phi)$ and vertex contributions ρ, allowing only connected diagrams which do not decompose on excision of a vertex. For very long-range forces, a suitable ordering parameter[13] is the number of links minus number of vertices, starting with the lowest possible value of -1, and explicitly summing each order of diagrams. This yields the series, in condensed notation,

$$c(12,\phi)=-\beta\phi(12)+[\tfrac{1}{2}h_0(12,\phi)^2+\left[\tfrac{1}{6}h_0(12,\phi)^3+\rho(h_0(1.2,\phi)\int h_0(13,\phi)^2h_0(32,\phi)d3+\tfrac{1}{2}\rho^2\int\int h_0(13,\phi)h_0(14,\phi)h_0(23,\phi)\times h_0(24,\phi)h_0(34,\phi)d3d4\right]+\cdots, \quad (4.11)$$

where $h_0=g_0-1$ is the solution of (4.4):

$$h_{0\mathbf{k}}(\phi)=-\beta\phi_{\mathbf{k}}/(1+\rho\beta\phi_{\mathbf{k}}). \quad (4.12)$$

Alternatively, (4.11) can be inverted to read

$$\beta\phi(12)=-c(12,\phi)+[\tfrac{1}{2}h(12,\phi)^2]+\left[\tfrac{1}{3}h(12,\phi)^3+\rho h(12,\phi)\int h(13,\phi)^2h(32,\phi)d3+\tfrac{1}{2}{}^2\rho\int\int h(13,\phi)h(14,\phi)h(23,\phi)\times h(24,\phi)h(34,\phi)d3d4\right]+\cdots. \quad (4.13)$$

Choosing the direct relation (4.11), the next order cor-

[8] L. S. Ornstein and F. Z. Zernike, Proc. Acad. Sci. Amsterdam **17**, 793 (1914).
[9] A. A. Broyles, J. Chem. Phys. **35**, 493 (1961) and seq.
[10] J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1958).
[11] A. A. Broyles and H. Sahlin, and D. D. Carley, Phys. Rev. Letters **10**, 319 (1963).
[12] See, e.g., J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Chap. 13.
[13] D. L. Bowers and E. E. Salpeter, Phys. Rev. **119**, 1180 (1960).

rection to (4.7) becomes

$$c(\mathbf{r})=-\beta\phi(\mathbf{r})-\beta\phi'(\mathbf{r})+\tfrac{1}{2}h_0(\mathbf{r};\phi+\phi')^2, \quad (4.14)$$

where $r>a$: $\phi'(\mathbf{r})=0$, $r\leq a$: $g(\mathbf{r})=0$, and one may continue in this fashion.

It is to be noted that whereas (4.7) states that $c(\mathbf{r})=0$ outside the range of force, (4.14) suggests [and its analog using (4.13) demands] that

$$c(\mathbf{r})=\tfrac{1}{2}[g(\mathbf{r})-1]^2, \quad (4.15)$$

which can lead to quite different results in transition regions. The result (4.15) also happens to be false in the solvable case of one-dimensional hard spheres where there is of course no transition.

V. HARD-CORE PERTURBATION EXPANSIONS

Let us examine the Debye-Hükel based set (4.7) in further detail. To do so most effectively, it is best written as a single equation. From (4.5) it is clear that the difference $g=c$ remains continuous and even differentiable in the face of discontinuities in g and c. Therefore we consider the combination

$$\tau(\mathbf{r})\equiv g(\mathbf{r})-c(\mathbf{r})-\beta\phi(\mathbf{r}), \quad (5.1)$$

which, from (4.7), coincides with g outside the core and extends it inside. If we further introduce the Mayer f function for the core

$$f(\mathbf{r})=e^{-\beta\phi_{\mathrm{hc}}(\mathbf{r})}-1=-1, \quad r\leq a$$
$$=0, \quad r>a, \quad (5.2)$$

it is seen that, again from (4.7),

$$g(\mathbf{r})=[1+f(\mathbf{r})]\tau(r),$$
$$c(\mathbf{r})=f(\mathbf{r})(\mathbf{r})-\beta\tau(r). \quad (5.3)$$

Substituting (5.3) into (4.5) and separating powers of f,

$$(\tau-1)(\mathbf{r})+\rho\int\beta\phi(\mathbf{r}-\mathbf{r}')(\tau-1)(\mathbf{r}')d\mathbf{r}'$$
$$=-\beta\phi(\mathbf{r})+\rho\int f(\mathbf{r}-\mathbf{r}')\tau(r-r')(\tau-1)(\mathbf{r}')d\mathbf{r}'$$
$$-\rho\int f(\mathbf{r}-\mathbf{r}')\tau(\mathbf{r}-\mathbf{r}')\beta\phi(\mathbf{r}')d\mathbf{r}'$$
$$+\rho\int f(\mathbf{r}-\mathbf{r}')\tau(\mathbf{r}-\mathbf{r}')f(r')\tau(\mathbf{r}')d\mathbf{r}', \quad (5.4)$$

the desired single equation.

With the aim of iterating (5.4) in an f series, we must solve for $\tau-1$ on its left-hand side. This is done by observing again from (4.5) and (4.6) that the coreless distribution is given by

$$(g_0-1)_{\mathbf{k}}=-\beta\phi_{\mathbf{k}}/(1+\beta\rho\phi_{\mathbf{k}}), \quad (5.5)$$

from which it follows that

$$(\delta+\rho\beta\phi)^*[\delta+\rho(g_0-1)]=\delta. \quad (5.6)$$

Here we have used the convolution notation

$$(a^*b)(\mathbf{r})\equiv\int a(\mathbf{r}-\mathbf{r}')b(\mathbf{r}')d\mathbf{r}'. \quad (5.7)$$

Thus, applying $[\delta+\rho(g_0-1)]^*$ to (5.4) yields

$$\tau=g_0+\rho(f\tau)^*[g_0-1+\tau-1+\rho(\tau-1)^*(g_0-1)]$$
$$+\rho(f\tau)^*[f\tau+\rho(f\tau)^*(g_0-1)]; \quad (5.8)$$

and so, on iteration,

$$\tau=g_0+\rho(fg_0)^*[2(g_0-1)$$
$$+\rho(g_0-1)^*(g_0-1)]+\cdots. \quad (5.9)$$

We can now ask for the modified equation of state due to the hard-core influence, regarding f as a perturbation. A particularly effective method for obtaining this from any approximation to g is by the Ornstein-Zernike compressibility relation[14]

$$\rho\int(g-1)(\mathbf{r})d\mathbf{r}=\partial\rho/\partial\beta p-1. \quad (5.10)$$

Multiplying (5.9) by $\rho(1+f)$ and retaining first order in f,

$$\rho(g-1)=\rho(g_0-1)+\rho(fg_0)^*(\delta+\rho(g_0-1)^*$$
$$\times(\delta+\rho(g_0-1))+\cdots, \quad (5.11)$$

or integrating over all space,

$$\frac{\partial\rho}{\partial\beta p}\frac{\partial\rho}{\partial\beta p_0}\left[1-\frac{\partial\rho}{\partial\beta p_0}\int_{r<a}g_0(\mathbf{r})d\mathbf{r}+\cdots\right]. \quad (5.12)$$

The reciprocal of (5.12),

$$\frac{\partial\beta p}{\partial\rho}=\frac{\partial\beta p_0}{\partial\rho}+\int_{r<a}g_0(\mathbf{r})d\mathbf{r}+\cdots, \quad (5.13)$$

then integrates at once to the modified equation

$$\beta p=\beta p_0+\left(\frac{1}{2\pi}\right)^3\int f_{\mathbf{k}}\ln(1+\beta\rho\phi_{\mathbf{k}})d\mathbf{k}+\cdots. \quad (5.14)$$

Of course, it is clear that the replacement of $-\beta\phi$ by $f_\phi=e^{-\beta\phi}-1$, as in (4.10), results in precisely the same replacement throughout the preceding.

For $\partial\beta p/\partial\rho$ not far from unity, an additional order of accuracy in this difference is obtainable with no additional effort. We first observe, from (4.5), that (5.10)

[14] See Ref. 8.

also implies

$$-\rho\int c(\mathbf{r})d\mathbf{r}=\frac{\partial\beta p}{\partial\rho}-1. \quad (5.15)$$

Hence, τ of (5.1) satisfies

$$\rho\int[\tau(\mathbf{r})-g_0(\mathbf{r})]d\mathbf{r}$$
$$=\left(\frac{\partial\rho}{\partial\beta p}-2+\frac{\partial\beta p}{\partial\rho}\right)-\left(\frac{\partial\rho}{\partial\beta p_0}-2+\frac{\partial\beta p_0}{\partial\rho}\right). \quad (5.16)$$

But then from (5.9) we have immediately

$$\left[\left(\frac{\partial\rho}{\partial\beta p}\right)^{\frac{1}{2}}-\left(\frac{\partial\beta p}{\partial\rho}\right)^{\frac{1}{2}}\right]^2=\left[\left(\frac{\partial\rho}{\partial\beta p_0}\right)^{\frac{1}{2}}-\left(\frac{\partial\beta p_0}{\partial\rho}\right)^{\frac{1}{2}}\right]^2$$
$$-\left[\int_{r<a}g_0(\mathbf{r})d\mathbf{r}\right]\left[\left(\frac{\delta\rho}{\delta\beta p_0}\right)^2-1\right]+\cdots, \quad (5.17)$$

which indeed determines $\partial\beta p/\partial\rho$ to one higher (mixed) order.

Proceeding to the opposite extreme, that in which only hard cores are present, one may test the adequacy of the present approach by making an expansion of g or c, and consequently of p, in powers of density. To this end, the various truncations based upon (4.11) or (4.13) may be employed, or their modifications with $f(r;\phi)$ instead of ϕ entering. The common zero-order truncation (4.7) leads, as we know, to the hard-core PY equation, with exact first three virial coefficients and very accurate fourth and fifth. For the next stage, the first-order f expansion corresponding to (4.11) and (4.13) becomes

$$c(12;\phi)=f(12;\phi)+\tfrac{1}{2}[g_0(12;\phi)-1-f(12;\phi)]^2$$
$$+f(12;\phi)[g(12;\phi)-1-f(12;\phi)]+\cdots, \quad (5.18)$$
$$f(12;\phi)=c(12;\phi)-\tfrac{1}{2}[g(12;\phi-1-c(12;\phi)]^2$$
$$-c(12;\phi)[g(12;\phi)-1-c(12;\phi)]+\cdots,$$

where g_0 requires f to replace $-\beta\phi$ in (4.11). Thus, for hard cores, instead of (4.14),

$$r\leq a:\ g(\mathbf{r})=0,$$
$$r>a:\ c(\mathbf{r})-\tfrac{1}{2}[g(\mathbf{r})-1-c(\mathbf{r})]^2$$
$$-c(\mathbf{r})[g(\mathbf{r})-1-c(\mathbf{r})]=0, \quad (5.19)$$

which may be coupled, using the hard-core f, to read

$$(1-\tau)c=f+\tfrac{1}{2}(1-f)\tau^2, \quad (5.20)$$

where $\tau\equiv g-c-1$ or $\tau=\rho c^*(\tau+c)$. A virial expansion of τ can now be carried out; it appears that, e.g., the fourth virial coefficient is not correctly reproduced until one order above the truncation (5.18) is employed.

VI. GENERALIZATION

One is not compelled to use the microscopic restriction (3.7) to simulate hard-core interactions. Indeed, since $\bar{\rho}_2\geq 0$, the vanishing of the mean pair distribution (3.3) is clearly sufficient to ensure that two particles never penetrate into a prohibited region. Thus, it is sufficient to reduce the equivalence of (3.4) and (3.7) to that of (3.3) and

$$\int\rho_2(\mathbf{x},\mathbf{y})W(\mathbf{x}-\mathbf{y})d\mathbf{x}d\mathbf{y}=\langle\sum_{i\neq j}W(\mathbf{x}_i-\mathbf{x}_j)\rangle=0 \quad (6.1)$$

for W defined as in (3.6). Condition (6.1), interpreted as a supplementary condition or distribution, wave function, on density matrix, is universally applicable to representing the hard-core restriction.

Consider, for example, quantum statistical mechanics. This may be described by the minimum principle of free energy[15]

$$F=U-TS$$
$$=\mathrm{Min}_\Gamma(\mathrm{Tr}\Gamma H+(1/\beta)\ \mathrm{Tr}\Gamma\ln\Gamma], \quad (6.2)$$

with $\mathrm{Tr}\Gamma=1$ and Γ the N-body density matrix, since appending $\mathrm{Tr}\Gamma=1$ by a Lagrange parameter: $\lambda(\mathrm{Tr}\Gamma-1)$, leads directly to

$$\Gamma=e^{-\beta H}/\mathrm{Tr}e^{-\beta H},\quad \lambda=F-1/\beta$$
$$F=-(1/\beta)\ \ln\mathrm{Tr}e^{-\beta H}. \quad (6.3)$$

Suppose now that we further append the restriction (6.1) in the form

$$\mathrm{Tr}\Gamma W=0,$$
$$W=\tfrac{1}{2}\sum_{i\neq j}W(\mathbf{x}_i-\mathbf{x}_j), \quad (6.4)$$

by means of a Lagrange parameter $s\ \mathrm{Tr}\Gamma W$. Equation (6.2) instead becomes

$$F=\mathrm{Min}_\Gamma[\mathrm{Tr}\Gamma(H+\Phi')+(1/\beta)\ \mathrm{Tr}\Gamma\ln\Gamma]$$

with $\mathrm{Tr}\Gamma=1$, $\mathrm{Tr}\Gamma W=0$, where $\Phi'=\frac{1}{2}\sum_{i\neq j}\phi'(\mathbf{x}_i-\mathbf{x}_j;)$, $\phi'(\mathbf{x})=sW(\mathbf{x})$. If an approximate minimization is carried out, resulting in approximate reduced density matrices so designated again by bars, one will again be unable to satisfy $\mathrm{Tr}\Gamma W=0$ merely by suitable choice of s unless W has a specific and generally unique form determined by the approximation. Hence (3.16) for an internal potential Φ generalizes immediately to

$$\langle\mathbf{x}_1\mathbf{x}_2|\Gamma_2|\mathbf{x}_1\mathbf{x}_2\rangle_{\phi+\phi_{\mathrm{hc}}}=\langle\mathbf{x}_1\mathbf{x}_2|\bar{\Gamma}_2|\mathbf{x}_1\mathbf{x}_2\rangle_{\phi+\phi'}, \quad (6.6)$$

where $\langle\mathbf{x}_1\mathbf{x}_2|\Gamma_2|\mathbf{x}_1\mathbf{x}_2\rangle=0$ for $|\mathbf{x}_1-\mathbf{x}_2|\leq a$ and $\phi'(\mathbf{x})>0$ for $x\leq a$, $\phi'(\mathbf{x})=0$ for $x>a$. Here Γ_2 is the two-body

[15] See, e.g., Ref. 6, p. 105.

reduced density matrix:

$$\langle \sum_{i\neq j} f(i,j)\rangle = \mathrm{Tr}_{1,2} f(1,2)\Gamma_2(1,2)\,. \qquad (6.7)$$

Special cases of (6.6) abound. It applies to quantum mechanical ground states, and for that matter extends to excited states as well, and even (suitably modified) to dynamics. It reduces in the classical equilibrium limit to (3.16), and shows that with external forces, the only required modification is that one should not reduce $g(\mathbf{x}_1,\mathbf{x}_2)=\rho_2(\mathbf{x}_1,\mathbf{x}_2)/\rho(\mathbf{x}_1)\rho(\mathbf{x}_2)$ to its translationally invariant relative coordinate form. The manner of derivation of (6.6) also suggests further generalization, for example, to mixtures. In this case, particles of type μ and type ν cannot penetrate more closely than some $a_{\mu\nu}$, which if classical hard cores were involved, would necessarily have the form $a_{\mu\nu}=\frac{1}{2}(a_\mu+a_\nu)$. Clearly, (6.6) now requires

$$\langle \mathbf{x}_1\mu\mathbf{x}_2\nu|\Gamma_2|\mathbf{x}_1\mu x_2\nu\rangle=0 \quad \text{for} \quad |\mathbf{x}_1-\mathbf{x}_2|\leq a_{\mu\nu} \qquad (6.8)$$

and $\phi'_{\mu\nu}(\mathbf{x})>0$ for $x\leq a_{\mu\nu}$, $\phi'_{\mu\nu}(\mathbf{x})=0$ for $x>a_{\mu\nu}$. For instance, using the classical linearized Debye-Hückel approximation,

$$c_{\mu\nu}(\mathbf{x}_1\mathbf{x}_2)=-\beta\phi_{\mu\nu}(\mathbf{x}_1\mathbf{x}_2)\,,$$

where

$$g_{\mu\nu}(\mathbf{x}_1\mathbf{x}_2)-\delta_{\mu\nu}=c_{\mu\nu}(\mathbf{x}_1\mathbf{x}_2) +\sum\nolimits_\lambda \int c_{\mu\lambda}(\mathbf{x}_1\mathbf{x}_3)\rho_\lambda(\mathbf{x}_3)(g_{\lambda\nu}(\mathbf{x}_2\mathbf{x}_3)-\delta_{\lambda\nu})d\mathbf{x}_3 \qquad (6.9)$$

and $g_{\mu\nu}(\mathbf{x}_1\mathbf{x}_2)\equiv\rho_{2\mu\nu}(\mathbf{x}_1\mathbf{x}_2)/\rho_\mu(\mathbf{x}_1)\rho_\mu(\mathbf{x}_2)$, Eq. (4.7) becomes, for mixtures,

$$\begin{aligned} c_{\mu\nu}(\mathbf{x}_1\mathbf{x}_2)&=-\beta\phi_{\mu\nu}(\mathbf{x}_1\mathbf{x}_2) \quad \text{for} \quad r_{12}>a_{\mu\nu} \\ g_{\mu\nu}(\mathbf{x}_1\mathbf{x}_2)&=0 \quad \text{for} \quad r_{12}\leq a_{\mu\nu}\,. \end{aligned} \qquad (6.10)$$

For pure hard cores, this reduces to the PY equation for mixtures, and has recently been solved.[16]

VII. BOSON GROUND STATE

As an application of (6.6) to the quantum mechanical domain, let us examine the case of a Bose system at zero temperature—the ground state—interacting via both weak long-range and hard-core forces. We must first devise a suitable long-range approximation, and for this will choose what is effectively an extended linearized Debye-Hückel approximation. As one of numerous ways of deriving this approximation,[17] let us choose an approach used by Zilsel.[18]

In second quantization, the standard many-boson Hamiltonian takes the form

$$H=(\hbar^2/2m)\int \nabla\psi^*(\mathbf{x})\cdot\nabla\psi(\mathbf{x})d\mathbf{x} +\tfrac{1}{2}\int\int \phi(\mathbf{x}-\mathbf{y})\psi^*(\mathbf{x})\psi^*(\mathbf{y})\psi(\mathbf{x})d\mathbf{x}d\mathbf{y} \qquad (7.1)$$

with only $[\psi(\mathbf{x}),\psi^*(\mathbf{y})]=\delta(\mathbf{x}-\mathbf{y})$ nonvanishing. We can then transform to new variables, at least formally,

$$\psi(\mathbf{x})=e^{i\pi(\mathbf{x})/\hbar}\rho^{1/2}(\mathbf{x}), \quad \psi^*(\mathbf{x})=\rho^{1/2}(\mathbf{x})e^{-i\pi(\mathbf{x})/\hbar}, \qquad (7.2)$$

where only $[\pi(\mathbf{x}),\rho(\mathbf{y})]=\delta(\mathbf{x}-\mathbf{y})\neq 0$, in terms of which (7.1) becomes

$$H=\frac{1}{2m}\int\Bigg[\rho(\mathbf{x})\nabla\pi(\mathbf{x})\cdot\nabla\pi(\mathbf{x}) +\frac{1}{4}\hbar^2\frac{1}{\rho(\mathbf{x})}\nabla\rho(\mathbf{x})\cdot\nabla\rho(\mathbf{x})\Bigg]d\mathbf{x}+\frac{1}{2}\int\int\phi(\mathbf{x}-\mathbf{y}) \times[\rho(\mathbf{x})\rho(\mathbf{y})-\rho(\mathbf{x})\delta(\mathbf{x}-\mathbf{y})]d\mathbf{x}d\mathbf{y}+\text{const.} \qquad (7.3)$$

For weak long-range forces, we neglect the fluctuations of the density and thus write $\rho(\mathbf{x})=\rho$, the mean density, in the kinetic energy coefficients. The Fourier transformation

$$\begin{aligned} \rho(\mathbf{x})&=(1/V)\sum \rho_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{x}}, \quad [\pi_{\mathbf{k}},\rho_{\mathbf{l}}]=\delta_{\mathbf{kl}} \\ \pi(\mathbf{x})&=\qquad\quad \sum \pi_{\mathbf{k}}e^{-i\mathbf{k}\cdot\mathbf{x}}, \end{aligned} \qquad (7.4)$$

then diagonalizes the Hamiltonian, and we find

$$H=\sum(Nk^2/2m)\pi_{\mathbf{k}}\pi_{-\mathbf{k}}+\sum(\hbar^2k^2/8mN)\rho_{\mathbf{k}}\rho_{-\mathbf{k}} +\sum(1/2V)\phi_{\mathbf{k}}\rho_{\mathbf{k}}\rho_{-\mathbf{k}}+\text{const}, \qquad (7.5)$$

a set of uncoupled harmonic oscillators.

Since the radial distribution Fourier coefficients are readily shown to be

$$g_{\mathbf{k}}=(1/\rho N)\langle\rho_{\mathbf{k}}\rho_{-\mathbf{k}}-1\rangle\,, \qquad (7.6)$$

a direct evaluation in the ground state of (7.5) yields

$$g_{\mathbf{k}}(\phi)=\frac{1}{\rho}\left\{\left[1+\frac{2\rho\phi_{\mathbf{k}}}{\hbar^2k^2/2m}\right]^{-\frac{1}{2}}-1\right\}\,. \qquad (7.7)$$

Thus, taking advantage of (6.6) and the fact that the coordinate diagonal elements of Γ_2 precisely constitute the pair distribution $\rho_2=\rho^2 g$, we can add a hard core to ϕ and obtain the approximation for the Bose ground state.

$$1+\rho g_{\mathbf{k}}=[1+(4m\rho/\hbar^2k^2)(\phi_{\mathbf{k}}+\phi'_{\mathbf{k}})]^{-1/2}, \qquad (7.8)$$

where $\phi'(\mathbf{r})=0$ for $r>a$. In the absence of a long-range force at all, this generalizes the classical PY equation, and is strongly suggested by Ref. 19. However, the full consequences of (7.8) remain to be delineated.

[16] J. L. Lebowitz, Phys. Rev. **133**, A895 (1964).

[17] See, e.g., J. K. Percus, editor, *Many-Body Problem* (John Wiley & Sons, Inc., New York, 1963), Chap. XIII.

[18] P. R. Zilsel in Ref. 17, Chap. XXVI.

[19] J. K. Percus and G. J. Yevick in Ref. 17, Chap. XVIII.