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Exact Solution of Generalized Percus-Yevick Equation for a Mixture of Hard Spheres*

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The Percus-Yevick approximate equation for the radial distribution function of a fluid is generalized to an m-component mixture. This approximation which can be formulated by the method of functional Taylor expansion, consists in setting $\exp[-\beta\varphi_{ij}(r)]C_{ij}(r)$ equal to $g_{ij}(r)[e^{-\beta\varphi_{ij}(r)}-1]$, where C_{ij}, g_{ij}, and φ_{ij} are the direct correlation function, the radial distribution function and the binary potential between a molecule of species i and a molecule of species j. The resulting equation for C_{ij} and g_{ij} is solved exactly for a mixture of hard spheres of diameters R_i. The equation of state obtained from $C_{ij}(r)$ via a generalized Ornstein-Zernike compressibility relation has the form $p/kT=\{[\sum\rho_i][1+\xi+\xi^2]-18/\pi\ \sum_{i<j}\eta_i\eta_j(R_i-R_j)^2\times[R_i+R_j+R_iR_j(\sum\eta_lR_l^2)]\}(1-\xi)^{-3}$, where $\eta_i=\pi/6$ times the density of the ith component and $\xi=\sum\eta_lR_l^3$. This equation yields correctly the virial expansion of the pressure up to and including the third power in the densities and is in very good agreement with the available machine computations for a binary mixture. For a one-component system our solution for $C(r)$ and $g(r)$ reduces to that found previously by Wertheim and Thiele and the equation of state becomes identical with that found on the basis of different approximations by Reiss, Frisch, and Lebowitz.

RECENTLY, Wertheim[1] and Thiele[2] succeeded in obtaining an exact solution of the Percus-Yevick (P.Y.) integral equation[3,4] for the radial distribution function $g(r)$ of a fluid of hard spheres. The equation of state obtained from their $g(r)$ through the use of the Ornstein-Zernike compressibility relation[5] coincided with that obtained previously by Reiss, Frisch, and Lebowitz[6] (R.F.L.) and is in very good agreement with the machine computations[7] for the whole range of "fluid" densities. The R.F.L. theory which does not involve $g(r)$ directly is based on approximating the work necessary to add a hard sphere of diameter R_2 to a fluid of hard spheres of diameter R_1 and density ρ_1. (The temperature $T=(k\beta)^{-1}$ will not be indicated explicitly in most cases.) This work is essentially the chemical potential $\mu_2(\rho_1,R_1,\rho_2,R_2)$ in the limit $\rho_2\to 0$, which is equal to the chemical potential of the single-component fluid when $R_2=R_1$ and thus yields the equation of state of a single-component fluid also found by Wertheim and Thiele. The P.Y. approximation for a hard-sphere fluid, on the other hand, is completely characterized[8] by assuming that the direct correlation function[4,9] $C(r)$, introduced by Ornstein and Zernike[5] vanishes for r greater than the diameter of the spheres. The identity of the equations of state for a single-component hard-sphere fluid obtained from these apparently unrelated theories led us to a generalization of the P.Y. equation to fluid mixtures. We shall present here the explicit solution of this generalized P.Y. equation for a binary mixture of hard spheres of diameters R_1, R_2 and densities ρ_1 and ρ_2, and briefly the results for a general mixture of m components. The chemical potential μ_2 obtained from this solution agrees, when $\rho_2\to 0$, with that obtained by R.F.L.[6] for all values of R_2. The reason underlying this

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[1] M. Wertheim, Phys. Rev. Letters 8, 321 (1963).

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[3] J. K. Percus and G. J. Yevick, Phys. Rev. **110**, 1 (1957).

[4] J. K. Percus, Phys. Rev. Letters 8, 462 (1962).

[5] L. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam **17**, 793 (1914).

[5] L. Ornstein and F. Zernike, Proc. Acad. Sci. Amsterdam **17**, 793 (1914).

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

[7] B. Alder and T. Wainwright, J. Chem. Phys. **33**, 1439 (1960).

[8] G. Stell, Physica **29**, 517 (1963).

[9] J. L. Lebowitz and J. K. Percus, J. Math. Phys. 4, 116 (1963); 4, 248 (1963).

agreement and a more complete discussion of this equation will be presented elsewhere.

The P.Y. equation for a mixture may be derived in complete analogy with that of a single-component fluid[4] by using the methods of functional Taylor expansion. We consider a binary system confined to a volume V which is represented by a grand canonical ensemble with chemical potentials μ_1 and μ_2. The particles interact via a pair potential $\varphi_{ij}(r)$ and are subject to an external potential $U_i(r)$ where $i, j=1, 2$. Let Ξ be the grand partition function of this system. It is then easy to show[9] that,

$$\frac{\delta \ln\Xi}{\delta(-\beta U_i(\mathbf{r}))}=n_i(\mathbf{r}), \tag{1}$$

$$\frac{\delta n_i(\mathbf{r})}{\delta(-\beta U_j(\mathbf{r}'))}=\frac{\delta^2 \ln\Xi}{\delta(-\beta U_j(\mathbf{r}'))\delta(-\beta U_i(\mathbf{r}))}=n_i(\mathbf{r})n_j(\mathbf{r}')\times[g_{ij}(\mathbf{r},\mathbf{r}')-1]+n_i(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\delta_{ij}, \tag{2}$$

where $n_i(\mathbf{r})$ is the density of the ith species at $\mathbf{r}$ and $g_{ij}(\mathbf{r},\mathbf{r}')$ is the radial distribution function between an i particle at $\mathbf{r}$ and a j particle at $\mathbf{r}'$, $g_{ij}(\mathbf{r},\mathbf{r}')=g_{ji}(\mathbf{r}',\mathbf{r})$. Defining now the direct correlation functions $C_{ij}(\mathbf{r},\mathbf{r}')$ by the equations,

$$\frac{\delta(-\beta U_i(\mathbf{r}))}{\delta n_j(r')}=\delta_{ij}\frac{\delta(\mathbf{r}-\mathbf{r}')}{n_i(r)}-C_{ij}(\mathbf{r},\mathbf{r}'), \tag{3}$$

we obtain immediately the relations[10]

$$[g_{ij}(\mathbf{r},\mathbf{r}')-1]=C_{ij}(\mathbf{r},\mathbf{r}')+\sum_{l=1,2}\int[g_{il}(\mathbf{r},\mathbf{y})-1]n_l(\mathbf{y})C_{lj}(\mathbf{y},\mathbf{r}')d\mathbf{y}, \tag{4}$$

$$C_{ij}(\mathbf{r},\mathbf{r}')=C_{ji}(\mathbf{r}',\mathbf{r}). \tag{5}$$

When there is no external potential, $U_i(\mathbf{r})=0$, and the system is sufficiently large, $V\rightarrow\infty$, then $n_i(\mathbf{r})=\rho_i$, the average density, and $g_{ij}(\mathbf{r},\mathbf{r}')$, $C_{ij}(\mathbf{r},\mathbf{r}')$ depend only on $|\mathbf{r}-\mathbf{r}'|$.

We consider now the behavior of the function $n_i(r)e^{\beta[U_i(r)-\varphi_{ij}(r)]}$ as the external potential $U_i(r)$ is "turned on" from zero to its final value $\varphi_{ij}(r)$, i.e., at the end there is a particle of the jth species held fixed at the origin. Then,

$$\begin{aligned} n_i(r)e^{\beta[U_i(r)-\varphi(r)]}&=\rho_i e^{-\beta\varphi_{ij}(r)}, &&\text{initially},\\ &=\rho_i g_{ij}(r), &&\text{finally}. \end{aligned} \tag{6}$$

Expanding the final value of this function about its initial value in a functional Taylor series in the density[4,9] we obtain, using (2) and (3),

$$\rho_i g_{ij}(r)=\rho_i e^{-\beta\varphi_{ij}(r)}\left[1+\sum_{l=1}^{2}\int C_{il}(\mathbf{r}-\mathbf{r}')\times\rho_l[g_{lj}(r')-1]d\mathbf{r}'+\dots\right]. \tag{7}$$

Truncating this expansion after the second term and using (4) yields the generalized P.Y. equation for mixtures,

$$g_{ij}(r)(e^{-\beta\varphi_{ij}(r)}-1)=e^{-\beta\varphi_{ij}(r)}C_{ij}(r). \tag{8}$$

Thus, as in the case of a single component fluid, the P.Y. approximation for a mixture states that the range of $C_{ij}(r)$ is equal to the range of $\varphi_{ij}(r)$. In particular for a fluid of hard spheres,

$$\begin{aligned} e^{-\beta\varphi_{ij}(r)}&=0, \quad r<R_{ij}\equiv(R_i+R_j)/2,\\ &=1, \quad r>R_{ij}. \end{aligned} \tag{9}$$

Equations (8) and (9) state that $C_{ij}(r)$ vanishes for $r>(R_i+R_j)/2$ and $g_{ij}(r)$ vanishes for $r<(R_i+R_j)/2$. The approximation is of course in the first statement the latter being rigorously true.[11] We may define now,

$$\begin{aligned} \sigma_{ij}(r)&=-12(\eta_i\eta_j)^{1/2}rC_{ij}(r), \quad r\leq R_{ij},\\ &=12(\eta_i\eta_j)^{1/2}rg_{ij}(r), \quad r\geq R_{ij}, \end{aligned} \qquad \eta_i=\pi\rho_i/6, \tag{10}$$

and write Eq. (4) in terms of σ alone. Doing this and going over in the integrations into bipolar coordinates yields,

$$\sigma_{ij}(r)=A_{ij}r-\sum_{l=1,2}\int_{R_{il}}^{\infty}dy\,\sigma_{il}(y)\int_{|r-y|}^{[r+y,R_{lj}]}\sigma_{lj}(x)dx, \tag{11}$$

where $[r+y, R_{lj}]$ indicates that the smaller of these two numbers is to be taken as the upper limit of the integration. Here

$$A_{ij}=12(\eta_i\eta_j)^{1/2}a_j \tag{12}$$

and

$$a_j=1-\sum_{l=1,2}\rho_l\int C_{lj}(\mathbf{r})d\mathbf{r}=\sum_{l=1,2}\left[\rho_l\frac{\partial\beta\mu_l(\rho_1,\rho_2)}{\partial\rho_j}\right]=\beta\frac{\partial p(\rho_1,\rho_2)}{\partial\rho_j}, \tag{13}$$

where p is the pressure. The second equality in (13) follows from (3) upon integration with respect to r' in a uniform system when it is realized that the chemical and external potential enter the grand partition function in the combination μ_i-U_i. The last equality follows from thermodynamics. These equalities may also be derived from consideration of fluctuations in a binary system[10] and are a generalization of the Ornstein-Zernike compressibility relation for a one component system.

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[10] F. J. Pearson and G. S. Rushbrooke, Proc. Roy. Soc. Edinburgh A64, 305 (1957).

[11] For a one-dimensional mixture of hard rods the exact $C_{ij}(r)$ vanishes for $r>R_{ij}$ and Eq. (8) is exact, [c.f., J. L. Lebowitz, J. K. Percus, and I. J. Zucker, Bull. Am. Phys. Soc. **7**, 415 (1962), where this was shown for a one-component system].

Let us assume, for definiteness that $R_2 \geq R_1$. The upper bound on the second integral in (11) will then be R_{ij} except for the case $(i,j)=(1,2)$. Taking the derivative with respect to r of (11) yields

$$\sigma_{ij}^{(1)}(r)=A_{ij}-\sum_l\Bigg[\int_{|r-x|\geq R_{il},\ -R_{lj}\leq x\leq 0}\sigma_{il}(r-x)\sigma_{lj}(x)dx - \int_{|r-x|\geq R_{il},\ 0\leq x\leq R_{lj}}\sigma_{il}(r-x)\sigma_{lj}(x)dx\Bigg]-P_{ij}(r)\,, \quad (14)$$

where

$$P_{ij}(r)=\delta_{i1}\delta_{j2}P(r)\,,$$

$$\begin{aligned} P(r)&=\sum_{l=1,2}\int_{R_{1l}+r}^{R_{l2}}\sigma_{1l}(r-z)\sigma_{l2}(z)dz\,, & r&\leq(R_2-R_1)/2\equiv\lambda\,, \quad (15)\\ &=0\,, & r&\geq\lambda\,. \end{aligned}$$

Taking the Laplace transform of (14) yields

$$s[G_{ij}(s)+F_{ij}(s)]=A_{ij}/s-\sum G_{il}(s)\times[F_{lj}(-s)-F_{lj}(s)]+\Gamma_{ij}(s)\,, \quad (16)$$

where

$$G_{ij}(s)=\int_{R_{ij}}^{\infty}e^{-sr}\sigma_{ij}(r)dr\equiv 12(\eta_i\eta_j)^{1/2}\times\int_{R_{ij}}^{\infty}e^{-sr}rg_{ij}(r)dr=G_{ji}(s)\,, \quad (17)$$

$$F_{ij}(s)=\int_0^{R_{ij}}e^{-sr}\sigma_{ij}(r)dr\equiv -12(\eta_i\eta_j)^{1/2}\times\int_0^{R_{ij}}e^{-sr}rC_{ij}(r)dr=F_{ji}(s)\,, \quad (18)$$

$$\Gamma_{ij}(s)=\delta_{i1}\delta_{j2}\Gamma_{12}(s)=\delta_{i1}\delta_{j2}[P(-s)-P(s)]\,, \quad (19)$$

$$P(s)=\int_0^{\lambda}e^{-sr}P(r)dr\,. \quad (20)$$

Solving for $G_{ij}(s)$ we obtain, in matrix notation,

$$\begin{aligned}\mathbf{G}(s)&=[\mathbf{A}+s\mathbf{\Gamma}(s)-s^2\mathbf{F}(s)]\cdot[s^2\mathbf{I}-s\mathbf{F}^{\pm}(s)]^{-1}\\&=\mathbf{H}(s)\cdot\mathbf{K}(s)\,, \quad (21)\\ \mathbf{F}^{\pm}(s)&=\mathbf{F}(s)-\mathbf{F}(-s)\,,\end{aligned}$$

where $\mathbf{I}$ is the unit matrix. More explicitly

$$G_{ij}(s)=N_{ij}(s)/D(s)\,, \quad (22)$$

where

$$D(s)=\{[s^2-sF_{22}^{\pm}(s)][s^2-sF_{11}^{\pm}(s)]-s^2F_{12}^{\pm}(s)F_{21}^{\pm}(s)\}\,, \quad (23)$$

$$N_{ij}(s)=\sum_{l=1,2}\{[A_{il}+s\Gamma_{il}(s)-s^2F_{il}(s)]\times[s^2\delta_{l'j'}-(-1)^{l+j}sF_{l'j'}^{\pm}(s)]\} \quad (24)$$

and $1'=2$, $2'=1$. The requirement that $\mathbf{G}$ and $\mathbf{F}$ be symmetric determines the value of Γ_{12}. This value of Γ_{12} also ensures that we can obtain σ_{11} from σ_{22} by simply interchanging η_1, R_1 with η_2, R_2.

The solutions of Eq. (11) which are physically meaningful are those for which $g_{ij}(r)\rightarrow 1$ as $r\rightarrow\infty$ in such a way that $\int r|g_{ij}(r)-1|dr$ exists.[12] This requires that $G_{ij}(s)-12(\eta_i\eta_j)^{1/2}s^{-2}$ have no singularities in the closed right-hand plane of the complex s plane. Now the symmetry of $\mathbf{G}$ and $\mathbf{F}$ imply, using (20), that

$$\begin{aligned}\mathbf{G}(s)=\mathbf{H}(s)\cdot\mathbf{K}^T(s)(s)=\mathbf{G}^T(s)&=\mathbf{K}^T(s)\cdot\mathbf{H}^T(s)\\&=\mathbf{K}(s)\cdot\mathbf{H}^T(s)\,, \quad (25)\end{aligned}$$

where the superscript T indicates the transpose of a matrix and the last equality follows from the symmetry of K. Multiplying (25) by $\mathbf{H}^T(-s)$ and noting that $\mathbf{K}(s)=\mathbf{K}(-s)$, gives

$$\begin{aligned}\mathbf{L}(s)\equiv\mathbf{G}(s)\cdot\mathbf{H}^T(-s)&=[\mathbf{H}(s)\cdot\mathbf{K}(s)]\cdot\mathbf{H}^T(-s)\\&=\mathbf{H}(s)\cdot[\mathbf{H}(-s)\cdot\mathbf{K}(-s)]\\&=\mathbf{H}(s)\cdot\mathbf{G}(-s)=\mathbf{L}^T(-s)\,. \quad (26)\end{aligned}$$

It is seen from the definition of $\mathbf{H}(s)$ that it (i.e., each of its elements) is an entire function of s. Hence, since $\mathbf{H}(0)=\mathbf{A}$, we have, by our assumption on the nature of $\mathbf{G}(s)$, that

$$\begin{aligned}\mathbf{L}(s)-s^{-2}\mathbf{A}'&=\mathbf{G}(s)\cdot\mathbf{H}^T(-s)-s^{-2}\mathbf{A}'\\&=\mathbf{H}(s)\cdot\mathbf{G}(-s)-s^{-2}\mathbf{A}'\,, \quad (27)\end{aligned}$$

where $A_{ij}'=12\sum_l(\eta_i\eta_l)^{1/2}A_{jl}=(12)^2(\eta_i\eta_j)^{1/2}\sum\eta_l a_l=A_{ij}'$, has no singularities anywhere in the s plane and is therefore an entire function. It follows from (14) that

$$\begin{aligned}\sigma_{ij}^{(1)}(0)&=A_{ij}\,, \quad i=1,\,2\\ \sigma_{21}(r)&=\sigma_{12}(r)=A_{21}r\,, \quad r\leq\lambda\,,\end{aligned} \quad (28)$$

and $\sigma_{21}^{(1)}(r)$ is continuous at $r=\lambda$. An examination of the behavior of the entire function

$$L_{22}(s)-A_{22}'s^{-2}=\frac{N_{21}(s)H_{21}(-s)+N_{22}(s)H_{22}(-s)}{D(s)}-A_{22}'s^{-2} \quad (29)$$

now shows that it is bounded along every ray in the s plane. Hence it must be a constant[13] which we shall call $2B_{22}$. Thus, using (27),

$$\begin{aligned}G_{21}(s)F_{21}(-s)+G_{22}(s)F_{22}(-s)&\\=\{A_{21}G_{21}(s)+A_{22}G_{22}(s)\}s^{-2}&\\-12\left\{\frac{A_{21}(\eta_2\eta_1)^{1/2}+A_{22}\eta_2}{s^4}\right\}-\frac{2B_{22}}{s^2}&\,. \quad (30)\end{aligned}$$

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[12] This method is a generalization of that developed by M. Wertheim for the one-component system [J. Math. Phys. (to be published)].

[13] See, e.g., E. C. Titchmarsh, *The Theory of Functions* (Oxford University Press, London, 1939).

If we take the inverse Laplace transform of (30) then for $r \leq R_{21} < R_2$ the first two terms on the right side will not contribute since $G_{ij}(s)$ goes as $e^{-sR_{ij}}$ for real part of s large positive and has no singularities in the right plane. Thus we can close the contour on that side. The Laplace transform of the left side of (30) is precisely the first term in the bracket on the right side of (14) for $\sigma_{22}^{(1)}(r)$ [cf., first term in bracket on right side of (16)]. On the other hand, the second term in the bracket on the right side of (14) makes no contribution to $\sigma_{22}^{(1)}(r)$ for $r < R_{12}$. Therefore, adding the inversely Laplace transformed Eq. (30) to Eq. (14), we obtain

$$\sigma_{22}^{(1)}(r) = A_{22} + 2B_{22}r + 2[A_{21}(\eta_2\eta_1)^{1/2} + A_{22}\eta_2]r^3, \quad r < R_{21}, \tag{31}$$

while for $R_{21} \leq r \leq R_2$, we find after taking two more derivatives and using (28),

$$\sigma_{22}^{(3)}(r) = 12[A_{21}(\eta_2\eta_1)^{1/2} + A_{22}\eta_2]r = 24D_{22}r. \tag{32}$$

Hence,

$$\sigma_{22}(r) = A_{22}r + B_{22}r^2 + D_{22}r^4, \quad r \leq R_2, \tag{33}$$

which is of the same functional form, i.e., a quartic polynomial in r, as that found by Wertheim and Thiele for a one-component system.

We can carry through a similar analysis for the function

$$L_{21}(s)e^{\lambda s}A_{21}'[s^{-2} + \lambda s^{-1}] = \left[\frac{N_{21}(s)H_{11}(-s) + N_{22}(s)H_{12}(-s)}{D(s)}\right] \times e^{\lambda s} - A_{21}'(s^{-2} + \lambda s^{-1}). \tag{34}$$

This function is also an entire function of s which is bounded on every ray. [From (19) $\Gamma_{12}(s)$ is an even function of s which goes as $s^{-2}e^{\lambda s}$ for real part of s large positive.] Hence, it is equal to a constant; $2B_{21}$. In a manner similar to (30), we now find

$$\begin{aligned} G_{21}(s)F_{11}(-s) &+ G_{22}(s)F_{12}(-s) \\ &= [A_{11}G_{21}(s) + A_{12}G_{22}(s)]s^{-2} + \Gamma_{12}(s)G_{22}(s)s^{-1} \\ &\quad - \left\{24\left(\frac{\eta_1}{\eta_2}\right)^{1/2} D_{22}[s^{-4} + \lambda s^{-3}] + 2B_{21}/s^2\right\}e^{-s\lambda}. \end{aligned}$$

Taking the inverse Laplace transform of (35) and adding it to the equation for $\sigma_{21}^{(1)}(r)$ in (14) we obtain, (using $F_{21} = F_{12}$),

$$\begin{aligned} \sigma_{21}(r) = \sigma_{12}(r) &= A_{21}r, \quad r \leq \lambda \\ &= A_{21}r + B_{21}x + 2(R_2 - R_1)\left(\frac{\eta_1}{\eta_2}\right)^{1/2} D_{22}x^3 \\ &\quad + \left(\frac{\eta_1}{\eta_2}\right)^{1/2} D_{22}x^4, \quad \lambda \leq r \leq R_{21}, \end{aligned} \tag{36}$$

where $x = r - \lambda$. The coefficients A_{ij} and B_{ij} may be found from (13) and from the continuity of $\sigma_{ij}(r)$ and its first two derivatives at R_{ij}. We find

$$\begin{aligned} -C_{ii}(r) &= a_i + b_i r + dr^3, \quad r < R_i, \quad i = 1, 2 \\ -C_{12}(r) = -C_{21}(r) &= a_1, \quad r \leq \lambda \\ &= a_1 + [bx^2 + 4\lambda dx^3 + dx^4]/r, \\ &\qquad \lambda \leq r \leq R_{21} \end{aligned} \tag{37}$$

and vanish in this approximation[14] for $r > R_{ij}$. Here,

$$\begin{aligned} a_i &= \frac{\partial[\beta p(\rho_1, \rho_2)]}{\partial \rho_i}, \\ b_1 &= -6[\eta_1 R_1^2 g_{11}^2(R_1) + \eta_2 R_{12}^2 g_{12}^2(R_{12})], \\ b &= -6[\eta_1 R_1 g_{11}(R_1) + \eta_2 R_2 g_{22}(R_2)]R_{12} g_{12}(R_{12}), \\ d &= \tfrac{1}{2}[\eta_1 a_1 + \eta_2 a_2], \end{aligned} \tag{38}$$

$$\begin{aligned} \beta p = \Big\{ &(\rho_1 + \rho_2)[1 + \xi + \xi^2] \\ &- \frac{18}{\pi}\eta_1\eta_2(R_2 - R_1)^2[(R_1 + R_2) \\ &+ R_1R_2(\eta_1 R_1^2 + \eta_2 R_2^2)]\Big\}(1 - \xi)^{-3}, \end{aligned} \tag{39}$$

$$\begin{aligned} g_{11}(R_1) &= \{[1 + \tfrac{1}{2}\xi] + \tfrac{3}{2}\eta_2 R_2^2(R_1 - R_2)\}(1 - \xi)^{-2} \\ &= -C_{11}(R_1), \\ g_{12}(R_{12}) &= [R_2 g_{11}(R_1) + R_1 g_{22}(R_2)]/2R_{12} \\ &= -C_{12}(R_{12}), \\ \xi &= \eta_1 R_1^3 + \eta_2 R_2^3, \end{aligned} \tag{40}$$

and b_2, $g_{22}(R_2)$ are obtained from b_1, $g_{11}(R_1)$ by interchanging η_1, R_1 with η_2, R_2. The Laplace transforms of $rg_{ij}(r)$, $[12(\eta_i\eta_j)^{1/2}]^{-1}G_{ij}(s)$ are found from (20) or (26):

$$\begin{aligned} G_{11}(s) &= s[h - L_2(s)e^{sR_2}]/\mathfrak{D}(s), \\ G_{21}(s) = G_{12}(s) &= (\eta_1\eta_2)^{1/2}s^2 e^{sR_{12}}\{[\tfrac{3}{4}(\eta_2 R_2^3 - \eta_1 R_1^3) \\ &\quad \times (R_2 - R_1) - R_{12}(1 + \tfrac{1}{2}\xi)]s - (1 + 2\xi)\}/\mathfrak{D}(s), \end{aligned} \tag{41}$$

where

$$\mathfrak{D}(s) = h - L_1(s)e^{sR_1} - L_2(s)e^{sR_2} + S(s)e^{s(R_1+R_2)}, \tag{42}$$

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[14] The exact one-dimensional direct correlation functions for a one-dimensional mixture of hard rods are (c.f., Ref. 11),

$$\begin{aligned} -C_{11}(r) &= [1 - \rho_2(R_2 - R_1) - (\rho_1 + \rho_2)r](1 - \rho_1 R_1 - \rho_2 R_2)^{-2}, \quad r < R_1 \\ -C_{12}(r) &= [1 - \rho_2(R_2 - R_1)](1 - \rho_1 R_1 - \rho_2 R_2)^{-2}, \quad r \leq \lambda \\ &= [1 - \rho_2(R_2 - R_1)] - (\rho_1 + \rho_2)[r - (R_2 - R_1)/2] \\ &\qquad \times (1 - \rho_1 R_1 - \rho_2 R_2)^{-2}, \quad \lambda \leq r \leq R_{12}. \end{aligned}$$

The resemblance to (37) is very striking.

and

$$
\begin{aligned}
h&=36\eta_1\eta_2(R_2-R_1)^2\,,\\
L_1(s)&=12\eta_2[(1+\tfrac{1}{2}\xi)+\tfrac{3}{2}\eta_1R_1^2(R_2-R_1)]R_2s^2\\
&\qquad+[12\eta_2(1+2\xi)-hR_1]s+h\,,\\
S(s)&=h+[12(\eta_1+\eta_2)(1+2\xi)-h(R_1+R_2)]s\\
&\qquad-18(\eta_1R_1^2+\eta_2R_2^2)^2s^2-6(\eta_1R_1^2+\eta_2R_2^2)\\
&\qquad\times(1-\xi)s^3-(1-\xi)^2s^4\,,
\end{aligned}
\tag{43}
$$

and $G_{22}(s)$, $L_2(s)$ can be found from $G_{11}(s)$ and $L_1(s)$ by interchanging η_1, R_1 with η_2, R_2. We may now verify explicitly our previous assumptions on $G_{ij}(s)$ as well as its correct behavior when η_1 or R_1 vanishes or $R_1=R_2$.

The pressure given in (39), which comes from the compressibility relation (13), yields correctly the first three virial coefficients,[15] i.e., coefficients of $\rho_1{}^l\rho_2{}^k$ for $l+k\leq 3$. It is also in very good agreement with the Monte-Carlo computations[16] of the pressure done for $R_1=\frac{3}{5}R_2$, $\rho_1=\rho_2$, $\xi<0.2$. The reduced volume of mixture is always negative which implies that there is no phase separation of the components.[17] The pressure may be obtained from $g_{ij}(r)$, in addition to the compressibility relation (13), also by use of the virial theorem. For a mixture of hard spheres this has the form,[18]

$$\beta p^v=\rho_1+\rho_2+\tfrac{2}{3}\pi\sum_{i,j}\rho_i\rho_jR_{ij}{}^3g_{ij}(R_{ij})\,. \tag{44}$$

For the correct g_{ij} the two relations, (13) and (44), will yield the same result. For our approximate g_{ij} we find from (40),

$$\beta p^v=\beta p-\frac{18}{\pi}\frac{\xi}{(1-\xi)^3}(\eta_1R_1^2+\eta_2R_2^2)^3\,, \tag{45}$$

where we continue to label the compressibility pressure (39) by p. The generalization of the above results to an m-component mixture of hard spheres is immediate. The generalization of Eqs. (39), (45), and (40) are

$$
\begin{aligned}
\beta p=\Bigg\{&[\sum_{i=1}^{m}\rho_i][1+\xi+\xi^2]-\frac{18}{\pi}\sum_{i<j}\eta_i\eta_j(R_i-R_j)^2\\
&\times[2R_{ij}+R_iR_j(\sum\eta_lR_l^2)]\Bigg\}(1-\xi)^{-3}\,,
\end{aligned}
\tag{46}
$$

$$\beta p^v=\beta p-\frac{18\xi}{\pi}[\sum_{l=1}^{m}\eta_lR_l^2]^3(1-\xi)^{-3}\,,\quad \xi=\sum_{l=1}^{m}\eta_lR_l^3\,, \tag{47}$$

$$g_{ij}(R_{ij})=[R_jg_{ii}(R_i)+R_ig_{jj}(R_j)]/2R_{ij}\,, \tag{48}$$

$$g_{ii}(R_i)=\{(1-\xi)+\tfrac{3}{2}\,(\sum_{l=1}^{m}\eta_lR_l^2)R_i\}(1-\xi)^{-2}\,. \tag{49}$$

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[15] A. G. McLellan and B. J. Alder, J. Chem. Phys. 24, 115 (1956).

[16] E. B. Smith and K. R. Lea, Nature 186, 714 (1960).

[17] I am indebted for the above results to Professor J. S. Rowlinson. Professor Rowlinson also obtained independently the pressure (39) for the case $R_1=0$.

[18] *Note added in proof.* B. J. Alder has kindly informed me that both p and p^v are in very good agreement (with p slightly above and p^v slightly below) with Monte-Carlo computations carried out by him and his co-workers for several values of R_2/R_1, ρ_2/ρ_1, and a large range of ξ.

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Simplified Approach to the Ground-State Energy of an Imperfect Bose Gas. II. Charged Bose Gas at High Density

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Foldy, and later Girardeau, calculated the ground-state energy of a charged Bose gas at high density. We rederive the common first term obtained by these authors by using a nonperturbation method developed previously. Our aims are: (i) to establish the validity of this common result, which has not been proved; (ii) to establish the validity and usefulness of our nonperturbation method. We also show that our method will give the correct functional dependence of the ground-state energy on the density at *low* density, although the exact coefficient must await a numerical computation.

I. INTRODUCTION

ABOUT two years ago Foldy[1] suggested investigating the charged Bose gas as a possible model for superconductivity and superfluidity. He derived formulas for the ground-state energy and elementary excitation spectrum of the system at high density (weak coupling constant) by applying Bogolyubov's well-known method.[2] Foldy derived the first two terms

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[1] L. L. Foldy, Phys. Rev. 124, 649 (1961) (hereafter referred to as F). See also Errata, *ibid.* 125, 2208 (1962).

[2] N. N. Bogolyubov, J. Phys. (U.S.S.R.) 11, 23 (1947). See also *The Many Body Problem*, edited by C. DeWitt (John Wiley & Sons, Inc., New York, 1959), p. 343.