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superposition of micellar layers. For such samples we find a series of relatively sharp (00*l*) reflections extending out to relatively large angles, and series of (*h**h**l*) bands near 20°, 35°, and 40°. Most of the lines which have been called short spacings or side spacings are merely high orders of the (00*l*) series. From arguments presented earlier we may also expect randomness of orientation of the large ions in the micellar layers. If this randomness is also present, we expect that the only strong band will be the band system near 20°. In part, the weakness or absence of the other bands may be due to anisotropic thermal vibrations.

It is also clear that any attempt to use such powder diagrams in phase studies of the soaps is, at best, beset by the gravest of uncertainties. Thus a sample of unchanging composition might give a great range of distinguishably different diffraction patterns corresponding to varying degrees of order. Since these will in general not be equilibrium arrangements, although they may have a long temporal stability, there is at least a serious doubt as to whether they should properly be called phases in the thermodynamic sense. In the strictest sense, thermodynamics and the notion of a phase involve equilibrium concepts.

Radial Distribution Functions and the Equation of State of a Fluid Composed of Rigid Spherical Molecules*

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The integral equation for the radial distribution function of a fluid of rigid spherical molecules has been integrated numerically in the Kirkwood approximation and in the Born-Green approximation over a wide range of densities. The distribution functions so obtained have been used to calculate the equation of state and excess entropy of the fluid. The results are compared with those obtained by means of the free volume theory of the liquid state.

I.

IN the statistical-mechanical theory of liquids composed of molecules possessing a potential of intermolecular force of the form,

$$V_N = \sum_{i < k=1}^N V(R_{ik}), \quad (1)$$

the average density $\rho^{(2)}(\mathbf{R}_1, \mathbf{R}_2)$ in the configuration space of molecular pairs plays a central role. In the fluid states of aggregation, gas or liquid, it is possible to define a function $g(R_{12})$, called the radial distribution function, by the relation,

$$\begin{aligned} \rho^{(2)} &= [\rho^{(1)}]^2 g(R_{12}), \\ \rho^{(1)} &= N/v, \end{aligned} \quad (2)$$

where the average number density $\rho^{(1)}$ in singlet space is uniform and equal to the reciprocal of the volume per molecule, and R_{12} is the scalar distance in the relative configuration space of a representative molecular pair. As is well known, the radial distribution function may be determined experimentally by the x-ray scattering technique.¹

* This work was carried out under Task Order XIII of Contract N6onr-244 between the ONR and the California Institute of Technology.

¹ F. Zernike and J. A. Prins, *Zeits. f. Physik* **41**, 184 (1927); P. Debye and H. Menke, *Physik. Zeits.* **31**, 797 (1930); B. E. Warren, *J. App. Phys.* **8**, 645 (1937); A. Eisenstein and N. S. Gingrich, *Phys. Rev.* **62**, 261 (1942).

The thermodynamic functions of a liquid are related to the potential of intermolecular force $V(R)$ and the radial distribution function by the theories of Kirkwood,² Born and Green,³ Mayer,⁴ and Yvon,⁵ which are basically equivalent although differing in certain details. The equation of state is given by

$$\frac{pv}{NkT} = 1 - \frac{2\pi N}{3vkT} \int_0^\infty R^3 \frac{dV}{dR} g(R) dR, \quad (3)$$

the internal energy by

$$\frac{E}{NkT} = -\frac{3}{2} + \frac{2\pi N}{vkT} \int_0^\infty R^2 V(R) g(R) dR, \quad (4)$$

and the chemical potential by

$$\begin{aligned} \frac{\mu}{NkT} &= \log p + \frac{\mu^E}{NkT} + \frac{\mu^*(T)}{NkT}; \quad \mu^*(T) = \lim_{p \rightarrow 0} [\mu - NkT \log p] \\ \mu^E &= -\frac{4\pi N^2}{v} \int_0^1 \int_0^\infty R^2 V(R) g(R, \xi) dR d\xi \\ &\quad - NkT \log \frac{pv}{NkT}, \end{aligned} \quad (5)$$

² J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

³ M. Born and H. S. Green, *Proc. Roy. Soc. A* **188**, 10 (1946).

⁴ J. E. Mayer, *J. Chem. Phys.* **15**, 187 (1947).

⁵ J. Yvon, *Actualités Scientifiques et Industrielles* (Hermann et Cie, Paris, 1935), p. 203. Because of its relative inaccessibility, the pioneering work of Yvon has been largely overlooked by other investigators.

where $g(R, \xi)$ is the radial distribution function for a pair of molecules, one of which, i , is partially coupled to those of the rest of the fluid, corresponding to a potential of intermolecular force,

$$V_N(\xi) = V_{N-1} + \xi \sum_{k=1}^N V(R_{ik}). \quad (6)$$

$\mu^*(T)$ is the ideal gas reference value of the chemical potential, depending on temperature alone.

Systems of integro-differential equations for the average densities in the configuration space of subsets of n molecules of a liquid have been developed in equivalent forms by Kirkwood,² Born and Green,³ Mayer,⁴ and Yvon.⁵ In general, one has

$$\rho^{(n)} = \frac{N!}{(N-n)!} \frac{1}{v^n} e^{-\beta W^{(n)}} \\ \beta = 1/(kT), \quad (7)$$

where $W^{(n)}$ is the potential of average force acting on the molecular subset n , the resultant of their direct interaction and their average interactions with the other $N-n$ molecules of the liquid. When $W^{(3)}$ (123) is approximated by

$$W^{(3)}(123) = W^{(2)}(12) + W^{(2)}(13) + W^{(2)}(23), \quad (8)$$

where 1, 2, 3 denote the coordinates of a molecular triplet, the several sets of integro-differential equations may be closed to give an integral equation for the pair function and thus for the radial distribution function. This approximation, superposition of mean forces between pairs in a set of triplets may be regarded as analogous to the Hartree approximation in quantum mechanics, applied to the density $\rho^{(3)}$ in the space of triplets as the product of the densities $\rho^{(2)}$ for the sets in the space of molecular pairs. As has been shown by one of us,⁶ the corresponding Hartree-like approximation in singlet space leads to the free-volume theory of liquids.

The resulting integral equation for the radial distribution function for a pair of molecules, one of which is partially coupled to other molecules of the fluid according to the potential of Eq. (6), takes the form

$$\log g(R, \xi) = -\beta \xi V(R) \\ + \frac{\pi N}{vR} \int_0^\infty [K(R-r, \xi) - K(R+r, \xi)] r [g(r) - 1] dr, \\ K(t, \xi) = -2\beta \int_0^\xi \int_{|t|}^\infty s V(s) g(s, \xi) ds d\xi; \quad \text{K} \\ K(t, \xi) = \beta \xi \int_{|t|}^\infty (s^2 - t^2) \frac{dV}{ds} g(s, \xi) ds; \quad \text{BGY} \quad (9)$$

⁶ J. G. Kirkwood, J. Chem. Phys. **18**, 380 (1950).

where now as henceforth $g(r)$ denotes $g(r, 1)$, with $\xi=1$. The kernel designated by K refers to the Kirkwood theory and that designated by BGY refers to the Born-Green-Yvon theory. Although the original sets of integro-differential equations in the two theories are exact, the superposition approximation, Eq. (8), leads to the two different kernels of Eq. (9). The numerical discrepancies, reflecting the influence of the superposition approximation are not great and will be discussed later. Since the essentials of the derivation of Eqs. (9) have been given elsewhere^{2,3,7} they will not be reproduced here.

The potential of intermolecular force $V(R)$ is conveniently expressed in the form,

$$V(R) = \epsilon \gamma(x), \\ x = R/a, \quad (10)$$

where ϵ is an energy and a is a length characteristic of the molecules. Thus for a Lennard-Jones potential, we have

$$\gamma(x) = (1/x^n) - (1/x^6) \quad (11)$$

where n is an exponent in the neighborhood of 12 and a and ∞ are the two values of R for which $V(R)$ vanishes. For rigid spheres,

$$\lim_{x \rightarrow \infty} e^{-\beta \epsilon \gamma(x)} = 0; \quad 0 \leq x \leq 1, \\ = 1; \quad x > 1, \quad (12)$$

where a is the diameter of the spheres. If we define a function $\psi(x)$ by the relation

$$g(x, \xi) = e^{-\beta \xi \epsilon \gamma(x) + [\psi(x, \xi)/\xi]}, \\ g(-x) = g(x), \\ \gamma(-x) = \gamma(x), \\ \psi(-x) = -\psi(x), \quad (13)$$

and extend the definitions of $g(x)$ and $\gamma(x)$ to the negative real axis by means of the last three of Eqs. (13), the integral equation, Eq. (9), becomes

$$\psi(x, \xi) = \frac{\lambda_0}{4} \int_{-\infty}^\infty K(x-s, \xi) s [g(s) - 1] ds \\ \lambda_0 = (4\pi N a^3)/v \\ K(t, \xi) = -2\beta \epsilon \int_{|t|}^\infty \int_0^\xi s \gamma(s) g(s, \xi) d\xi ds; \quad \text{K} \\ K(t, \xi) = \xi \beta \epsilon \int_{|t|}^\infty (s^2 - t^2) \frac{d\gamma(s)}{ds} g(s, \xi) ds; \quad \text{BGY.} \quad (14)$$

The solution of Eq. (14) with the Lennard-Jones potential, Eq. (11), by numerical methods with the use of International Business Machine equipment is at present under investigation. Since direct iterative operation on a sequence of trial functions $g(s)$ with the integral

⁷ J. G. Kirkwood and E. M. Boggs, J. Chem. Phys. **10**, 394 (1942).

operator $\int_{-\infty}^{\infty} ds K(x-s)$ in general fails to give convergent results for values of λ_0 appropriate to liquid densities, other methods are being developed, which depend on starting with a relatively good zero approximation to $g(s)$. In order to obtain a set of trial functions for the zero approximation base, as well as for their intrinsic interest, we have undertaken the integration of Eq. (14) for fluids composed of rigid spheres.

For rigid spheres, Eq. (14) becomes,

$$\begin{aligned}\psi(x) &= -\frac{\lambda}{4} \int_{-\infty}^{\infty} K_0(x-s) s [g(s) - 1] ds \\ g(s) &= e^{\psi(s)/s} \quad |s| \geq 1 \\ &= 0 \quad |s| < 1 \\ K_0(t) &= t^2 - 1 \quad |t| \leq 1 \\ &= 0 \quad |t| > 1\end{aligned}\quad (15)$$

where $\psi(x)$ denotes $\psi(x, 1)$. The parameter λ is related to the density in different ways according to the Kirkwood theory and the Born-Green theory (see Appendix).

$$\begin{aligned}[g_1(\lambda)]^{-1} \int_0^{\lambda} [g_1(\lambda')]^{-1} d\lambda' &= 4\pi\sqrt{2}v_0/v; \quad \text{K} \\ [g_1(\lambda)]^{-1}\lambda &= 4\pi\sqrt{2}(v_0/v); \quad \text{BG} \\ v_0 &= Na^3/\sqrt{2},\end{aligned}\quad (16)$$

where v_0 is the close-packed volume of the system of spheres and $g_1(\lambda)$ denotes $g(1+\epsilon, \lambda)$ as $\epsilon \rightarrow +0$. The two systems of integro-differential equations underlying the Kirkwood and the Born and Green theories are equivalent and exact. However, the superposition approximation in the space of triplets leads to different equations in the space of pairs. The discrepancy reflected in Eq. (16) is thus a measure of the error produced by this approximation.

Equation (15), linearized with respect to the function $\psi(x)$, assumes the form,

$$\begin{aligned}\psi(x) &= -\frac{\lambda}{4} \int_{-\infty}^{\infty} K_0(x-s) [A\{|s| - 1\} \psi(s) \\ &\quad - [1 - A\{|s| - 1\}] s] ds, \\ A\{t\} &= 1 \quad t \geq 0, \\ &= 0 \quad t < 0,\end{aligned}\quad (17)$$

where $A(t)$ is the unit step-function. Equation (17) has been given approximate analytical solutions by Kirkwood and Boggs⁷ for several values of λ . The present numerical solutions of the non-linear equation, Eq. (15), cover a wider range of the parameter λ than those of Kirkwood and Boggs. For the same values of λ in the linear approximation, they are found to agree with the analytical solutions for large values of x and to correct the latter in the neighborhood of the first peak of the radial distribution function.

II.

We shall now describe the methods employed in the numerical solution of Eq. (15), which we write in the form

$$\begin{aligned}\psi(x) &= -\frac{\lambda}{4} \int_{-\infty}^{\infty} K_0(x-s) \varphi(s) ds \\ \varphi(x) &= x[g(x) - 1] \\ g(x) &= A(|x| - 1) e^{\psi(x)/x}.\end{aligned}\quad (18)$$

The resolvent kernel $k(t)$ of $K_0(t)$ may be expressed in the form⁸

$$\begin{aligned}k(t) &= -\frac{\lambda}{\pi} \int_0^{\infty} \frac{G(u)}{1 - \lambda G(u)} \cos u t du \\ G(u) &= -\frac{1}{4} \int_{-\infty}^{\infty} K_0(t) e^{iut} dt = \frac{u \cos u - \sin u}{u^3}.\end{aligned}\quad (19)$$

By the method of Fourier transforms, we obtain from Eq. (18)

$$\begin{aligned}\psi(x) &= -\int_{-\infty}^{\infty} k(x-s) f(s) ds \\ f(x) &= \varphi(x) - \psi(x)\end{aligned}\quad (20)$$

from which $\psi(x)$ may be determined for $x > 1$ when $f(x)$ is known. An alternative form of Eq. (20) is

$$f(x) = \varphi(x) + \int_{-\infty}^{\infty} k(x-s) f(s) ds. \quad (21)$$

In the linear approximation,

$$\begin{aligned}\varphi_0(x) &= A\{|x| - 1\} \psi_0(x) - [1 - A\{|x| - 1\}] x \\ f_0(x) &= 0; \quad x > 1 \\ \varphi_0(x) &= -x; \quad x \leq 1\end{aligned}\quad (22)$$

and Eqs. (20) and (21) become

$$\begin{aligned}f_0(x) &= -x + \int_{-1}^{+1} k(x-s) f_0(s) ds; \quad x < 1 \\ \psi_0(x) &= -\int_{-1}^{+1} k(x-s) f_0(s) ds; \quad x > 1.\end{aligned}\quad (23)$$

The first of Eqs. (23) determines $f_0(x)$ and the second determines the linear approximation $\psi_0(x)$ for $x > 1$. In this approximation the determination of $g(x)$ thus reduces to the solution of a linear integral equation for $f_0(x)$ on the finite interval $-1 < x < +1$, with the resolvent kernel $k(t, \lambda)$.

The resolvent kernel $k(t, \lambda)$ was calculated for a suitable range of the parameter, $\lambda = 5, 10, 20, 27.4$, with the use of IBM equipment and the file of punched cards of *sinut* employed in these laboratories for electron

⁸ E. C. Titchmarsh, *Introduction to the Theory of Fourier Integrals* (Oxford University Press, London, 1948), pp. 303-305.

TABLE I.* Radial distribution functions for several values of parameter λ . $x[g(x)-1]$ as a function of x .

| λ x | 5 | 10 | 20 | 27.4 | 33 |
|------------------|-------|-------|-------|-------|-------|
| 1.00 | 0.45 | 0.80 | 1.36 | 1.66 | 1.85 |
| 1.08 | 0.39 | 0.66 | 1.08 | 1.36 | 1.62 |
| 1.16 | 0.32 | 0.53 | 0.83 | 1.04 | 1.25 |
| 1.24 | 0.26 | 0.40 | 0.59 | 0.73 | 0.87 |
| 1.32 | 0.20 | 0.29 | 0.37 | 0.44 | 0.47 |
| 1.40 | 0.15 | 0.18 | 0.18 | 0.16 | 0.11 |
| 1.48 | 0.09 | 0.09 | 0.01 | -0.08 | -0.19 |
| 1.56 | 0.05 | 0.01 | -0.12 | -0.26 | -0.41 |
| 1.64 | 0.01 | -0.05 | -0.22 | -0.39 | -0.56 |
| 1.72 | -0.02 | -0.10 | -0.29 | -0.46 | -0.64 |
| 1.80 | -0.04 | -0.13 | -0.31 | -0.48 | -0.63 |
| 1.88 | -0.05 | -0.13 | -0.28 | -0.41 | -0.52 |
| 1.96 | -0.05 | -0.10 | -0.18 | -0.25 | -0.29 |
| 2.04 | -0.03 | -0.05 | -0.03 | 0.02 | 0.10 |
| 2.12 | -0.02 | -0.01 | 0.09 | 0.24 | 0.44 |
| 2.20 | 0.00 | 0.02 | 0.16 | 0.34 | 0.63 |
| 2.28 | 0.00 | 0.04 | 0.18 | 0.38 | 0.65 |
| 2.36 | 0.01 | 0.04 | 0.17 | 0.32 | 0.52 |
| 2.44 | 0.01 | 0.04 | 0.13 | 0.22 | 0.30 |
| 2.52 | 0.01 | 0.03 | 0.07 | 0.09 | 0.06 |
| 2.60 | 0.01 | 0.02 | 0.01 | -0.03 | -0.16 |
| 2.68 | 0 | 0.01 | -0.04 | -0.13 | -0.32 |
| 2.76 | | 0.00 | -0.07 | -0.20 | -0.42 |
| 2.84 | | -0.01 | -0.09 | -0.24 | -0.45 |
| 2.92 | | -0.01 | -0.09 | -0.21 | -0.38 |
| 3.00 | | -0.01 | -0.07 | -0.15 | -0.25 |
| 3.08 | | -0.01 | -0.04 | -0.06 | -0.03 |
| 3.16 | | -0.01 | 0.00 | 0.03 | 0.14 |
| 3.24 | | 0 | 0.02 | 0.09 | 0.29 |
| 3.32 | | | 0.04 | 0.15 | 0.41 |
| 3.40 | | | 0.05 | 0.17 | 0.36 |
| 3.48 | | | 0.05 | 0.14 | 0.28 |
| 3.56 | | | 0.04 | 0.09 | 0.14 |
| 3.64 | | | 0.02 | 0.03 | 0.00 |
| 3.72 | | | 0.00 | -0.02 | -0.12 |
| 3.80 | | | -0.01 | -0.06 | -0.23 |
| 3.88 | | | -0.02 | -0.10 | -0.28 |
| 3.96 | | | -0.02 | -0.11 | -0.26 |
| 4.04 | | | -0.02 | -0.08 | -0.20 |
| 4.12 | | | -0.02 | -0.05 | -0.11 |
| 4.20 | | | -0.01 | -0.02 | 0.00 |
| 4.28 | | | 0.00 | 0.02 | 0.11 |
| 4.36 | | | 0.00 | 0.04 | 0.18 |
| 4.44 | | | 0.01 | 0.06 | 0.24 |
| 4.52 | | | 0.01 | 0.07 | 0.22 |
| 4.60 | | | 0.01 | 0.06 | 0.15 |
| 4.68 | | | 0.01 | 0.03 | 0.08 |
| 4.76 | | | 0.01 | 0.01 | -0.01 |
| 4.84 | | | 0 | -0.01 | -0.09 |
| 4.92 | | | | -0.03 | -0.15 |
| 5.00 | | | | -0.03 | -0.19 |
| 5.08 | | | | -0.03 | -0.18 |

* The solutions $g(x)$ were checked by direct iteration in Eq. (15) at intervals of 0.04 in x . The input $g(x)$ checked with the output $g(x)$ to ± 0.005 for $\lambda=5, 10$, and 20 , and to ± 0.02 for $\lambda=27.4$ and 33 .

diffraction calculation.⁹ For these calculations it was transformed by partial integration in the following manner,

$$k(t) = -\frac{\lambda}{\pi t} \int_0^\infty \frac{3uG(u) + \sin u}{u^2[1 - \lambda G(u)]^2} \sin u t du. \quad (24)$$

Convolution operations with the kernel $k(x-s)$ involved in the solution of Eqs. (23) were then carried out on desk calculators.

Since, except for small values of λ , the kernel $k(t)$

⁹ Shaffer, Schomaker, and Pauling, J. Chem. Phys. **14**, 659 (1946).

TABLE I.—Continued.

| λ x | 5 | 10 | 20 | 27.4 | 33 |
|------------------|---|----|----|-------|-------|
| 5.16 | | | | -0.03 | -0.13 |
| 5.24 | | | | -0.02 | -0.06 |
| 5.32 | | | | 0.00 | 0.01 |
| 5.40 | | | | 0.01 | 0.07 |
| 5.48 | | | | 0.02 | 0.12 |
| 5.56 | | | | 0.02 | 0.16 |
| 5.64 | | | | 0.02 | 0.14 |
| 5.72 | | | | 0.02 | 0.10 |
| 5.80 | | | | 0.01 | 0.05 |
| 5.88 | | | | 0.00 | -0.01 |
| 5.96 | | | | 0.00 | -0.06 |
| 6.04 | | | | 0.00 | -0.10 |
| 6.12 | | | | 0.00 | -0.13 |
| 6.20 | | | | -0.01 | -0.12 |
| 6.28 | | | | -0.01 | -0.08 |
| 6.36 | | | | -0.01 | -0.03 |
| 6.44 | | | | -0.01 | 0.01 |
| 6.52 | | | | 0 | 0.05 |
| 6.60 | | | | | 0.08 |
| 6.68 | | | | | 0.09 |
| 6.76 | | | | | 0.08 |
| 6.84 | | | | | 0.05 |
| 6.92 | | | | | 0.02 |
| 7.00 | | | | | 0.00 |
| 7.08 | | | | | -0.02 |
| 7.16 | | | | | -0.07 |
| 7.24 | | | | | -0.07 |
| 7.32 | | | | | -0.06 |
| 7.40 | | | | | -0.05 |
| 7.48 | | | | | -0.02 |
| 7.56 | | | | | 0.00 |
| 7.64 | | | | | 0.02 |
| 7.72 | | | | | 0.03 |
| 7.80 | | | | | 0.04 |
| 7.88 | | | | | 0.04 |
| 7.96 | | | | | 0.03 |
| 8.04 | | | | | 0.02 |
| 8.12 | | | | | 0.01 |
| 8.20 | | | | | -0.01 |
| 8.28 | | | | | -0.02 |
| 8.36 | | | | | -0.02 |
| 8.44 | | | | | -0.02 |
| 8.52 | | | | | -0.02 |
| 8.60 | | | | | -0.01 |
| 8.68 | | | | | -0.01 |
| 8.76 | | | | | 0.00 |
| 8.84 | | | | | 0.00 |
| 8.92 | | | | | 0.00 |
| 9.00 | | | | | 0.01 |
| 9.08 | | | | | 0.01 |
| 9.16 | | | | | 0.01 |
| 9.24 | | | | | 0.01 |
| 9.32 | | | | | 0.01 |
| 9.40 | | | | | 0.01 |
| 9.48 | | | | | 0 |

possesses one or more eigenvalues less than unity,¹⁰ solution of Eq. (23) by direct iteration fails to give convergent results (see Appendix). In order to overcome this difficulty, $k(t)$ is expressed in the form

$$k(t) = k_0(t) + k_1(t), \\ k_0(t) = A_0 + A_1 \cos \gamma_1 t + A_2 \cos \gamma_2 t, \quad (25)$$

where the parameters A_0, A_1, A_2, γ_1 , and γ_2 are chosen by trial to give $\int_0^\infty k_1(t)^2 dt$ a sufficiently small value to raise all of the eigenvalues of $k_1(t)$, which may be shown

¹⁰ R. Courant and D. Hilbert, *Methoden der Mathematischen Physik* (Interscience Publishers, Inc., New York), Vol. I, pp. 104-110, 1943.

to be bounded below by $[2\int_0^2(2-t)k_1^2(t)dt]^{-1/2}$, above unity.¹⁰ When this condition is fulfilled, $f_0(x)$ may be represented by the convergent sum

$$f_0(x) = \sum_{n=0}^{\infty} f_{0,n}(x), \quad (26)$$

where

$$\begin{aligned} f_{0,n}(x) &= \sigma_{0,n}(x) + \int_{-1}^{+1} k_0(x-s)f_{0,n}(s)ds, \\ \sigma_{0,0}(x) &= -x, \\ \sigma_{0,n}(x) &= \int_{-1}^{+1} k_1(x-s)f_{0,n-1}(s)ds. \end{aligned} \quad (27)$$

Since the approximate kernel $k_0(x-s)$ is chosen in degenerate form, the sequence of integral equations, Eq. (27), are solvable in closed form,

$$\begin{aligned} f_{0,n}(x) &= \sigma_{0,n}(x) + 2A_1M_{1,n}\sin\gamma_1x + 2A_2M_{2,n}\sin\gamma_2x, \\ M_{1,n} &= \int_0^1 f_{0,n}(s)\sin\gamma_1sds, \\ M_{2,n} &= \int_0^1 f_{0,n}(s)\sin\gamma_2sds, \end{aligned} \quad (28)$$

where the $M_{\alpha,n}$ are to be determined in each case by solving a set of two linear equations, following from their definition and the first of Eqs. (28). Several iterations, the number increasing with increasing values of λ , suffice to determine $f_0(x)$, which upon substitution in Eq. (23) yields the desired solution of the linearized problem.

In the non-linear case, $f(x)$ of Eqs. (20) and (21) no longer vanishes outside the interval $-1 \leq x \leq +1$. Nevertheless, we write Eq. (21) in the form

$$\begin{aligned} f(x) &= \sigma(x) + \int_{-1}^{+1} k(x-s)f(s)ds, \\ \sigma(x) &= -x + \int_1^{\infty} k(x-s)f(s)ds \\ &\quad + \int_{-\infty}^{-1} k(x-s)f(s)ds \quad x \leq 1, \end{aligned} \quad (29)$$

and consider the sequence of integral equations,

$$\begin{aligned} f_n(x) &= \sigma_n(x) + \int_{-1}^{+1} k(x-s)f_n(s)ds \quad x \leq 1, \\ \sigma_n(x) &= -x + \int_1^{\infty} k(x-s)f_{n-1}(s)ds \\ &\quad + \int_{-\infty}^{-1} k(x-s)f_{n-1}(s)ds, \\ f_n(x) &= x[e^{\lambda\psi_n(x)/x} - 1] - \psi_n(x) \quad x > 1, \end{aligned}$$

$$\begin{aligned} \psi_n(x) &= - \int_{-1}^{+1} k(x-s)f_n(s)ds - \int_1^{\infty} k(x-s)f_{n-1}(s)ds \\ &\quad - \int_{-\infty}^{-1} k(x-s)f_{n-1}(s)ds. \end{aligned} \quad (30)$$

Starting with the solution of Eq. (23) as $f_0(x)$ with $\sigma_0(x) = -x$, and solving each of the linear integral equations, Eq. (30), by the method employed in the solution of Eq. (23), we find that the sequence $\psi_n(x)$ converges to the solution $\psi(x)$ of the non-linear integral equation, Eq. (18). All solutions are finally tested by direct iteration with the kernel $K_0(x-s)$ of Eq. (18).

For large values of the parameter λ , convergence is slow by the method of solution described here. However, when a moderately good approximation $\psi^0(x)$ has been obtained by this method, it may be refined by the following iterative procedure. If we linearize Eq. (18) with respect to the error $\omega(x)$, equal to $\psi(x) - \psi^0(x)$, we find,

$$\psi(x) = \psi^0(x) + \omega(x),$$

$$\omega(x) = L\omega + O(\omega^2),$$

$$\begin{aligned} L\omega &= \nu(x) + \frac{\lambda}{4} \int_{-\infty}^{\infty} K_0(x-s)A\{|s|-1\} \\ &\quad \times \exp\left[\frac{\psi^0(s)}{s}\right]\omega(s)ds \end{aligned}$$

$$\nu(x) = \frac{\lambda}{4} \int_{-\infty}^{\infty} K_0(x-s)\varphi^0(s)ds - \psi^0(x) \quad (31)$$

where L is an inhomogeneous linear operator and $\nu(x)$ is the iterative defect of the trial function $\psi^0(x)$. Let us consider the sequence

$$\psi^{(n)}(x) = \psi^{(n-1)}(x) + \omega^{(n)}(x)$$

$$\omega^{(n)}(x) = L^{(n)}\omega^{(n)}$$

$$\begin{aligned} L^{(n)}\omega^{(n)} &= \nu^{(n)}(x) + \frac{\lambda}{4} \int_{-\infty}^{\infty} K_0(x-s)A\{|s|-1\} \\ &\quad \times \exp\left[\frac{\psi^{(n-1)}(s)}{s}\right]\omega^{(n)}(s)ds \end{aligned}$$

$$\nu^{(n)}(x) = \frac{\lambda}{4} \int_{-\infty}^{\infty} K_0(x-s)\varphi^{(n-1)}(s)ds - \psi^{(n-1)}(x), \quad (32)$$

where $\omega^{(n)}$ exactly satisfies the linear equation, $L^{(n)}\omega^{(n)} = \omega^{(n)}$, and $\psi^0(x)$ is the first member of the sequence $\psi^{(n)}$. We now define a sequence

$$\begin{aligned} \omega_0^{(n)} &= \nu^{(n)}(x), \\ \omega_1^{(n)} &= L^{(n)}\omega_0^{(n)}, \\ \omega_2^{(n)} &= L^{(n)}\omega_1^{(n)}, \\ \omega_3^{(n)} &= \alpha^{(n)}\omega_1^{(n)} + (1-\alpha^{(n)})\omega_0^{(n)}, \end{aligned}$$

$$\Delta_{kk'}^{(n)} = \int_{-\infty}^{\infty} \chi_k^{(n)} \chi_{k'}^{(n)} dx; \chi_k^{(n)} = L^{(n)} \omega_k^{(n)} - \omega_k^{(n)}. \quad (33)$$

The value of α which minimizes $\Delta_{33}^{(n)}$ is given by

$$\alpha^{(n)} = (\Delta_{00}^{(n)} - \Delta_{01}^{(n)}) / (\Delta_{11}^{(n)} + \Delta_{00}^{(n)} - 2\Delta_{01}^{(n)})$$

$$\frac{\Delta_{33}^{(n)}}{\Delta_{00}^{(n)}} = 1 - \epsilon^{(n)} \quad \epsilon^{(n)} = \frac{1}{\Delta_{00}^{(n)}} \frac{[\Delta_{00}^{(n)} - \Delta_{01}^{(n)}]^2}{\Delta_{11}^{(n)} + \Delta_{00}^{(n)} - 2\Delta_{01}^{(n)}}. \quad (34)$$

The denominator in the expression for $\epsilon^{(n)}$ is positive by the Schwarz inequality. Thus $\epsilon^{(n)}$ is positive and we have,

$$0 \leq \Delta_{33}^{(n)} / \Delta_{11}^{(n)} \leq 1. \quad (35)$$

Repetition of this cycle will, except in singular cases, lead to a sequence $\omega_k^{(n)}(x)$ which converges in the mean to the solution $\omega^{(n)}(x)$ of the linear equation, $L^{(n)}\omega^{(n)} = \omega^{(n)}$, of Eq. (32). However, the most economical path to a solution of the non-linear problem is through the sequence

$$\psi_3^{(n)} = \psi_3^{(n-1)} + \omega_3^{(n)}, \quad (36)$$

where $\omega_3^{(n)}$ is given by Eqs. (33) and (34). Except in singular cases $\psi_3^{(n)}$ converges to the solution $\psi(x)$ of the non-linear equation Eq. (18).

III.

The methods described in Section II have been used to calculate $g(x, \lambda)$ for the fluid of rigid spheres for values of the parameter λ equal to 5, 10, 20, 27.4, and 33. The results of the calculations are presented in Table I and Fig. 1. In Fig. 2, the linear and non-linear solutions of Eq. (18) are compared for $\lambda=27.4$. It will be observed that they are appreciably different only in the neighborhood of $x=1$. A comparison of the linear solution for $\lambda=27.4$, with the approximate analytical solution of Kirkwood and Boggs,⁷ shows the latter to be somewhat inaccurate in the neighborhood of $x=1$.

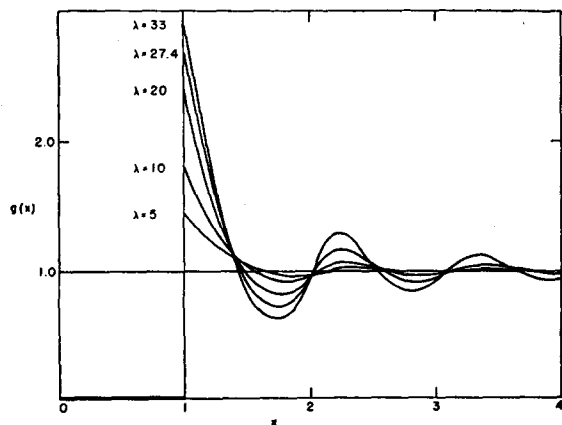


FIG. 1. Radial distribution functions for several values of the parameter λ .

All radial distribution functions exhibit their first peak at $x=1$, decreasing monotonically to the first minimum, which is followed by oscillations of diminishing amplitude resembling those of the experimentally determined radial distribution functions of real liquids.

From the values of $g_1(\lambda)$ obtained from the solutions presented in Table I, the densities corresponding to the family of distribution functions $g(x, \lambda)$ may be determined by means of Eq. (16) according to the Kirkwood theory and according to the Born and Green theory. The densities are presented as a function of λ for the two theories in Table II.

For values of λ equal to or exceeding 34.8, no solutions of Eq. (15) exist for which $x^2[g(x)-1]$ is integrable. This value of λ , corresponding to an expansion v/v_0 equal to 1.24 on the Kirkwood theory and 1.48 on the Born-Green theory evidently represents the limit of stability of a fluid phase of rigid spheres. For greater densities, a crystalline phase is the stable phase.¹¹ The transition between fluid and crystalline phases cannot be discussed quantitatively without an investigation of distribution functions in the crystalline phase itself. In the case of rigid spheres, it appears likely that the transition may be of second order rather than of first order, although at present this is no more than a surmise. It is also possible that the crystalline phase possesses some intrinsic disorder arising from the inability of rigid spheres to distinguish between next nearest neighbors and the likelihood of stacking errors leading to structures intermediate between the face-centered cubic and the hexagonal close-packed arrangements.

The equation of state, Eq. (3), becomes for rigid spheres,

$$\frac{pv}{NkT} - 1 = \frac{2\pi\sqrt{2}}{3} \frac{v_0}{v} g_1(\lambda), \quad (37)$$

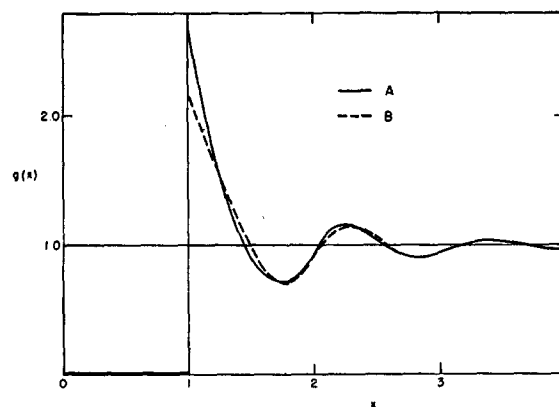


FIG. 2. Radial distribution functions for $\lambda=27.4$. A, solution of non-linear integral equation. B, solution of linear integral equation.

¹¹ J. G. Kirkwood and E. M. Boggs, J. Chem. Phys. 9, 514 (1941).

TABLE II. Fluid densities as function of λ .^a

| λ | $g_1(\lambda)$ | v/v_0 (K) | v/v_0 (BG) |
|-----------|----------------|-------------|--------------|
| 5 | 1.45 | 4.74 | 5.15 |
| 10 | 1.80 | 2.83 | 3.20 |
| 20 | 2.36 | 1.78 | 2.10 |
| 27.4 | 2.66 | 1.45 | 1.73 |
| 33 | 2.85 | 1.29 | 1.53 |
| 34.8 | 2.90 | 1.24 | 1.48 |

^a v/v_0 = ratio of volume to close packed volume of spheres.

where $g_1(\lambda)$ is given as a function of density v/v_0 in Table II. In Table III, $p v/RT - 1$ is presented as a function of v/v_0 for both the Kirkwood and the Born-Green theories. This function is also plotted in Fig. 3 together with the free volume¹² expression for rigid spheres,

$$\frac{p v}{RT} - 1 = \frac{1}{(v/v_0)^{1/3} - 1}, \quad (38)$$

where v_0 is the close-packed volume of a face-centered cubic lattice rather than that of the simple cubic lattice originally used by Eyring and Hirschfelder.

The excess molal entropy, S^E , of a fluid phase is defined by the relation,

$$\begin{aligned} S &= -R \log p + S^*(T) + S^E \\ S^E &= \int_0^p \left[\frac{R}{p} - \left(\frac{\partial v}{\partial T} \right)_p \right] dp \\ S^*(T) &= \lim_{p \rightarrow 0} [S + R \log p]. \end{aligned} \quad (39)$$

For the fluid of rigid spheres,

$$\begin{aligned} \frac{S^E}{R} &= \frac{-A^E}{RT} = -\frac{\mu^E}{RT} + \left[\frac{p v}{RT} - 1 \right], \\ \frac{S^E}{R} &= \frac{2\pi\sqrt{2}}{3} \int_{\infty}^{v/v_0} \frac{g_1(\lambda)}{y^2} dy + \log \left[1 + \frac{2\pi\sqrt{2}}{3} \frac{v_0}{v} g_1 \right], \\ y &= v/v_0, \end{aligned} \quad (40)$$

since the excess internal energy E^E vanishes. The excess entropy in the Born-Green approximation has been calculated by numerical integration, with the use of the second of Eqs. (40) and the values of $g_1(\lambda)$ as a function of v/v_0 presented in Table II. In the Kirkwood approximation, Eq. (5) and the first of Eqs. (40) yield the expression,

$$\frac{S^E}{R} = -\frac{\lambda}{3} + \frac{2\pi\sqrt{2}}{3} \frac{v_0}{v} g_1 + \log \left[1 + \frac{2\pi\sqrt{2}}{3} \frac{v_0}{v} g_1 \right], \quad (41)$$

from which the excess entropy has been calculated with

the aid of the data of Table II. The results of the two calculations are presented in Table IV.

It will be remarked that the agreement between the Kirkwood and the Born-Green approximations is moderately good both for the equation of state and for the entropy. In the case of the equation of state, the free volume theory yields a result which does not deviate greatly from either the Kirkwood or the Born-Green results, the departures becoming smaller as the density increases toward close-packing.

APPENDIX

1. The relation between the density $N a^3/v$ and the parameter λ may be derived for the Kirkwood theory with the following thermodynamic equation, the equation of state, Eq. (37), and the expression for the chemical potential Eq. (34c) given by Kirkwood and Boggs,⁷

$$\frac{1}{RT} \left(\frac{\partial \mu}{\partial v} \right)_T = \frac{v}{RT} \left(\frac{\partial p}{\partial v} \right)_T, \quad (42)$$

$$\frac{\mu}{RT} = -\log v + \frac{\lambda}{3} + \frac{\mu^*(T)}{RT} \quad (34c)$$

$$\frac{p}{RT} = \frac{1}{v} + \frac{2\pi\sqrt{2}}{3} \frac{v_0}{v^2} g_1(\lambda), \quad (37)$$

where $g_1(\lambda)$ is $g(1+\epsilon)$ as $\epsilon \rightarrow +0$. By differentiating the last two equations with respect to v and equating their derivatives by the first expression, we get

$$-\frac{1}{v} + \frac{1}{3} \frac{d\lambda}{dv} = -\frac{1}{v} + \frac{2\pi\sqrt{2}}{3} \frac{v_0}{v^3} \left[\frac{d}{dv} \left(\frac{g_1(\lambda)}{v^2} \right) \right]; \quad (43)$$

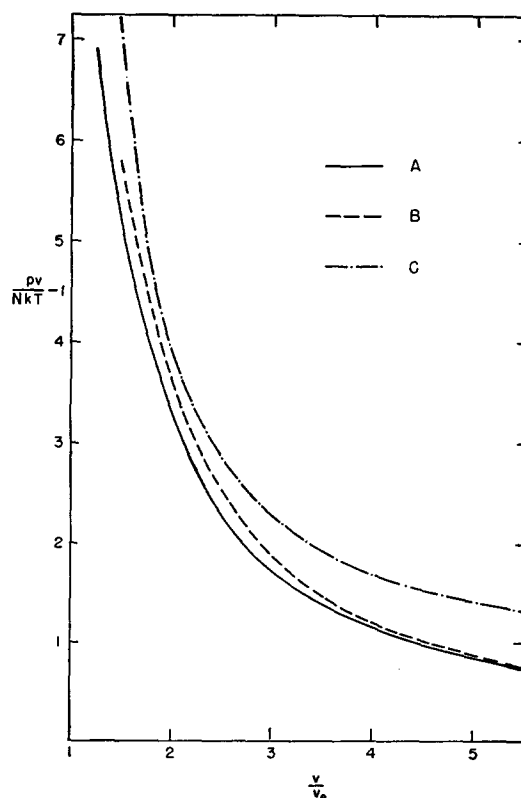


FIG. 3. Equation of state: $p v/RT - 1$ as function of v/v_0 . A, Kirkwood basis, B, Born and Green, C, free-volume theory. v = volume per mole, v_0 = volume per mole in close-packed arrangement.

¹² H. Eyring and J. O. Hirschfelder, J. Phys. Chem. 41, 249 (1937).

TABLE III. Equation of state of the fluid of rigid spheres.

| v/v_0^a | $pv/RT-1$ (K) | $pv/RT-1$ (BG) |
|-----------|---------------|----------------|
| 8.38 | 0.44 | 0.44 |
| 4.74 | 0.91 | 0.93 |
| 3.48 | 1.39 | 1.46 |
| 2.83 | 1.89 | 2.04 |
| 2.42 | 2.40 | 2.65 |
| 2.15 | 2.91 | 3.21 |
| 1.94 | 3.43 | 3.75 |
| 1.78 | 3.93 | 4.33 |
| 1.64 | 4.44 | 4.96 |
| 1.53 | 4.95 | 5.54 |
| 1.44 | 5.46 | |
| 1.37 | 5.99 | |
| 1.30 | 6.50 | |
| 1.24 | 6.93 | |

^a For values of the Kirkwood parameter $\lambda=2.5, 5.0, \dots$, except for the last point, $\lambda=34.8$.

hence, introducing $z=v/[g_1(\lambda)]^{1/2}$,

$$\frac{d\lambda}{[g_1(\lambda)]^{1/2}} = -4\pi N a^3 \frac{dz}{z^2}; \quad N a^3 = \sqrt{2} v_0, \quad (44)$$

and integration with the limits (λ, v) and $(\lambda=0, v=\infty)$ yields Eq. (16, K).

2. The divergence of a direct iteration attempt to solve Eq. (23) may be seen by considering

$$\begin{aligned} f(x) &= \sigma(x) + \int_a^b k(x, s) f(s) ds, \\ f^{(n)}(x) &= \sigma(x) + \int_a^b k(x, s) f^{(n-1)}(s) ds; \end{aligned} \quad (45)$$

hence, by subtraction,

$$\Delta f^{(n)} = f - f^{(n)} = \int_a^b k(x, s) \Delta f^{(n-1)}(s) ds, \quad (46)$$

where $f(x)$ is the exact solution of the linear integral equation whose inhomogeneous part is $\sigma(x)$, $f^{(n-1)}(x)$ is a trial solution, and $f^{(n)}(x)$ the iterate of the trial solution. Using a representation for

TABLE IV. Excess entropy of the fluid of rigid spheres as a function of density.

| v/v_0 | S^E/R (K) | S^E/R (BG) |
|---------|-------------|--------------|
| 8.38 | -0.03 | -0.03 |
| 4.74 | -0.12 | -0.11 |
| 3.48 | -0.24 | -0.23 |
| 2.83 | -0.39 | -0.37 |
| 2.42 | -0.55 | -0.56 |
| 2.15 | -0.73 | -0.76 |
| 1.94 | -0.92 | -1.00 |
| 1.78 | -1.14 | -1.23 |
| 1.64 | -1.37 | -1.49 |
| 1.53 | -1.60 | -1.77 |
| 1.44 | -1.84 | |
| 1.37 | -2.07 | |
| 1.30 | -2.32 | |
| 1.24 | -2.60 | |

the real symmetric kernel $k(x, s)$ in terms of its orthonormal set of eigenfunctions χ_i and its eigenvalues λ_i , and expanding $\Delta f^{(n-1)}$ in the form,

$$\begin{aligned} k(x, s) &= \sum_i \frac{\chi_i(x) \chi_i(s)}{\lambda_i}, \\ \Delta f^{(n-1)}(s) &= \sum_j a_j^{(n-1)} \chi_j(s), \end{aligned} \quad (47)$$

leads by substitution into Eq. (46) to

$$\begin{aligned} \Delta f^{(n)}(x) &= \sum_j \frac{a_j^{(n-1)} \chi_j(x)}{\lambda_j} = \sum_j a_j^{(n)} \chi_j(x), \\ a_j^{(n)} &= \frac{a_j^{(n-1)}}{\lambda_j}. \end{aligned} \quad (48)$$

Thus $a_j^{(n-1)}$ is increased by $1/\lambda_j$ after each iteration, hence divergence occurs if for any $|\lambda_j| < 1$ $a_j^{(n-1)} \neq 0$, because then

$$\left| \frac{a_j^{(n)}}{a_j^{(n-1)}} \right| > 1$$

and $\Delta f^{(n)}$ increases in magnitude with each iteration.