

in the times allotted for equilibrium, a direct calculation shows that if only Reactions (5) and (6) are effective, only 70% to 80% of the true equilibrium would be attained. This now leads to an extrapolated $K_{5,6}$, in good agreement with Eq. (20). The calculated times for attainment of 95% of true equilibrium are of the order of 70 h. Unfortunately, at 238.5°C, this is too long, since I_2 formation will become appreciable.

From Eq. (20) we can calculate $\Delta H_{5,6}=21.1$ kcal/mole and $\Delta S_{5,6}=33.0$ gibbs/mole. These can be compared to our original estimates¹³ of $\Delta H_{5,6}=21.3$ kcal/mole and $\Delta S_{5,6}=34.7$ gibbs/mole. However, these latter were based on an extrapolation⁵ from 25°C of $\Delta H_{5,6}^\circ=20.6$ kcal/mole, $\Delta S_{5,6}^\circ=34.1$ gibbs/mole, and $\langle\Delta C_P\rangle=1.6$ gibbs/mole. However, this last value for $\langle\Delta C_P\rangle$ is undoubtedly in error. If we correct the estimated value for $C_P^0(i\text{-PrI})$ to 21.7 gibbs/mole by comparison with the spectroscopically calculated value for $i\text{-PrCl}$ ¹⁴ and also allow for the proper temperature variation of ΔC_P , we find that $\langle\Delta C_P\rangle$ is about -1.0

gibbs/mole in the same temperature range. This leads to a new estimate of $\Delta H_{5,6}=20.4$ kcal/mole and $\Delta S_{5,6}=33.4$ gibbs/mole, in excellent agreement with the kinetic estimates.

Since the preparation of this article the original work of Holmes and Maccoll has been published.¹⁵ Although it is our intention to discuss their results in detail elsewhere, it should be mentioned here that they report new Arrhenius parameters for the homogeneous first-order pyrolysis of $i\text{-PrI}$ [Eq. (1)] of $10^{14.79} 10^{-48.0/l}$ sec⁻¹. These give rate constants about threefold larger than their previous results. Compared with the results reported here [$2k_5$ from Eq. (19)], these are 20% lower than ours at 357°C and about 40% lower at 290°C. We feel that there are a number of criticisms to be made of their experimental technique which make these differences obscure and favor our own values. The most important criticism is that they make no dead-space correction for their system, where we estimate it to be of the order of 20% to 30%.

¹⁴ K. E. Howlett, J. Chem. Soc. **1955**, 1784.

¹⁵ J. L. Holmes and A. Maccoll, J. Chem. Soc. **1963**, 5919.

Average Density Approximation for the Radial Distribution Function of a Fluid*

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(Received 30 December 1963)

The radial distribution function of a fluid, $g(r)$, is directly related to the difference between the work $W(r, \rho)$ necessary to introduce an extra particle at a distance r from the known position of a particle, and the work $W(\rho)$ of introducing a particle at an arbitrary point in the fluid. Now a system in which one particle is kept fixed can be thought of as a nonuniform system with density $\rho g(r)$. This suggests that $W(r, \rho)$ can be written as $W(\rho^*)$ where $\rho^*(r)$ is some appropriate effective local density. We have utilized this idea to approximate the radial distribution function using for ρ^* the average density $\bar{\rho}$, of the nonuniform system, with the Mayer f -function as a weighing factor. This leads to an integral equation for $g(r)$ which we have investigated in detail for a fluid of hard spheres. When this equation is solved in a virial expansion it yields reasonably good results for the first few terms. A linearization of this equation leads to an integral equation of the type considered by Kirkwood who was first to consider this type of approximation. We obtain the solution of this linearized equation. A different approximation for ρ^* , using the direct correlation function as the weighing factor is obtained by the use of functional Taylor expansion. It leads to an improvement in the virial coefficients and is shown to lead upon appropriate linearizations to either the hypernetted chain or the Percus-Yevick equations for $g(r)$. We also discuss the rigorous form of $\rho^*(r)$.

1. INTRODUCTION

THE purpose of this article is to obtain an approximation for the radial distribution function $g(r)$ in a fluid. The approximation method we shall develop is suggested by the analogy between the two-particle density in a uniform system and the single-particle density in a certain type of nonuniform system.

Consider a fluid confined to a volume V in contact with a reservoir at temperature T and chemical potential μ whose particles interact through a pair

potential $\phi(|\mathbf{r}_i - \mathbf{r}_j|)$. Let $\rho^{(k)}(\mathbf{r}_1, \dots, \mathbf{r}_k)$ be the joint probability density (the distribution function) of finding k particles at the positions $\mathbf{r}_1, \dots, \mathbf{r}_k$, when there are no external forces acting on the system. Let $n_k(\mathbf{r}_1, \dots, \mathbf{r}_k)$ be the same quantity when there is an external potential $U(\mathbf{r})$ acting on each particle. It is then clear from the definitions of these quantities¹ that the conditional probability density of finding l particles at Positions $\mathbf{r}_1, \dots, \mathbf{r}_l$ when k particles are known to be at Positions $\mathbf{x}_1, \dots, \mathbf{x}_k$, $\rho^{(l+k)}(\mathbf{x}_1, \dots, \mathbf{x}_k, \mathbf{r}_1, \dots, \mathbf{r}_l) / \rho^{(k)}(\mathbf{x}_1, \dots, \mathbf{x}_k)$ is equal to the l -particle

* Supported by the U.S. Air Force Office of Scientific Research under Grant No. 62-64 and by the U.S. Atomic Energy Commission under Contract AT(30-1)-1480.

¹ J. L. Lebowitz and J. K. Percus, J. Math. Phys. **4**, 116 (1963); J. K. Percus, Phys. Rev. Letters **8**, 462 (1962).

distribution function $n_i(\mathbf{r}_1, \dots, \mathbf{r}_i)$, with

$$U(\mathbf{r}_j) = \sum_{i=1}^k \phi(|\mathbf{r}_j - \mathbf{x}_i|), \quad (1.1)$$

i.e., the external potential is caused by keeping k particles fixed at positions $\mathbf{x}_1, \dots, \mathbf{x}_k$. In particular, when we go the limit of an infinite system, $V \rightarrow \infty$, $N/V \rightarrow \rho$, we have

$$\begin{aligned} \rho^{(1)}(\mathbf{r}_1) &= \rho, \\ \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) &= \rho^{(2)}(\mathbf{r}) = \rho^2 g(\mathbf{r}) = \rho n(\mathbf{r}), \end{aligned} \quad (1.2)$$

where $n(\mathbf{r})$ is the density in the nonuniform system created by keeping one particle fixed at the origin, $U(\mathbf{r}) = \phi(|\mathbf{r}|)$.

In order to utilize this analogy we consider the potential of mean force,² $w(\mathbf{r})$,

$$w(\mathbf{r}) \equiv -kT \ln g(\mathbf{r}), \quad (1.3)$$

where $w(\mathbf{r})$ is the work required to bring two particles from infinite separation to a distance r from each other. (This is done after passing to the limit $V \rightarrow \infty$.) This process can be split up into two steps, first we remove from the fluid a particle which was located an "infinite" distance away from a given fixed particle and then we introduce it again at distance r from the fixed particle. The work required for the first step is $-W(\rho)$, $W(\rho)$ being the chemical potential μ less the part associated with the translational motion, $W(\rho) = \mu - kT \ln \rho \Lambda^3$, $\Lambda = (h^2/2\pi m kT)^{1/2}$. $W(\mathbf{r}, \rho)$, the work required for the second step, is not a thermodynamic quantity. It will be our principal concern here. Using this division of w we have

$$\begin{aligned} -kT \ln g(\mathbf{r}) = w(\mathbf{r}) &= W(\mathbf{r}, \rho) - W(\rho) \\ &= \phi(\mathbf{r}) + \hat{W}[\mathbf{r}; n(\mathbf{y})] - W(\rho), \end{aligned} \quad (1.4)$$

where $\hat{W}[\mathbf{r}; n(\mathbf{y})]$ is analogous to $W(\rho)$ in that it is just the work of introducing a particle in a nonuniform fluid with a density $n(\mathbf{y}) = \rho g(\mathbf{y}, \rho)$ at each point \mathbf{y} .

The usual method for obtaining a formal expression for $w(\mathbf{r})$ is to use a coupling parameter λ . We mentally single out one particle of the system (call it Particle 1) and let its interaction with the remainder of the particles be described by a parameter λ so that, when $\lambda=0$ the particle is completely free of interaction with the system while $\lambda=1$ describes a complete coupling to the system. The actual form of this coupling can be chosen relatively freely. The simplest choice is a linear potential coupling so that the potential $\phi(\mathbf{r}_{1j}, \lambda)$ is simply $\lambda\phi(\mathbf{r}_{1j})$. This coupling was introduced by Kirkwood³ and applied by Kirkwood³ and Frisch.⁴ In the case of a fluid with hard cores, $\phi(\mathbf{r}) = +\infty$ for $r \leq a$, the diameter of the core, this scheme does not work. We can then

use a range coupling or scaling parameter,⁵ so that $\phi(\mathbf{r}_{1j}, \lambda) = \phi(\mathbf{r}_{1j}/\lambda)$. For a hard-sphere fluid this means

$$\phi(\mathbf{r}_{1j}, \lambda) = \begin{cases} 0, & r_{1j} > \lambda a. \\ +\infty, & r_{1j} \leq \lambda a. \end{cases} \quad (1.5)$$

The density of particles at a distance r from the "λ-cule" will be designated by $\rho g(\mathbf{r}, \lambda)$. This is clearly the same as the single-particle density $n(\mathbf{r}, \rho, \lambda)$ in the presence of an external potential¹ $U_\lambda(\mathbf{r}) = \phi(\mathbf{r}, \lambda)$. For $\lambda=1$, $g(\mathbf{r}, \lambda)$ equals $g(\mathbf{r})$, the radial distribution function in the fluid. We define then $w(\mathbf{r}, \lambda)$ in a manner similar to $w(\mathbf{r})$:

$$w(\mathbf{r}, \lambda) = -kT \ln g(\mathbf{r}, \lambda). \quad (1.6)$$

$w(\mathbf{r}, \lambda)$ is equal to the work of bringing a λ-cule and a regular particle from infinite separation to a separation r . This can be accomplished either by keeping the regular particle fixed and bringing the λ-cule to a distance r from it, or keeping the λ-cule fixed and moving the regular particle. Considering the first process we can again break the work up in two parts,⁶

$$w(\mathbf{r}, \lambda) = W(\mathbf{r}, \rho, \lambda) - W(\rho, \lambda). \quad (1.7)$$

Here $W(\mathbf{r}, \rho, \lambda)$ is the work of coupling a λ-cule a distance r from a fixed particle and $W(\rho, \lambda)$ is the same quantity at $r = \infty$, i.e., the work of coupling a λ-cule in a uniform system. The work $W(\mathbf{r}, \rho, \lambda)$ may again be written as the sum of the direct potential energy of the λ-cule, $\phi(\mathbf{r}, \lambda)$, and a remainder $\hat{W}[\mathbf{r}, \lambda, n(\mathbf{y})]$:

$$W(\mathbf{r}, \rho, \lambda) = \phi(\mathbf{r}, \lambda) + \hat{W}[\mathbf{r}, \lambda; n(\mathbf{y})]. \quad (1.8)$$

It seems reasonable to expect (and this will be verified for some cases) that for a given $n(\mathbf{y})$ and r there exists some effective density $\rho^*(\mathbf{r}, \lambda)$ which is a function of n , such that the work of coupling a λ-cule in the nonuniform system is the same as for coupling it in a uniform system having the density ρ^* ,

$$\hat{W}[\mathbf{r}, \lambda; n(\mathbf{y})] = W(\rho^*, \lambda). \quad (1.9)$$

This defines ρ^* .⁷ Now we expect on physical grounds that $\hat{W}[\mathbf{r}, \lambda; n(\mathbf{y})]$ should depend on the density $n(\mathbf{y})$ in the vicinity of \mathbf{r} only. The simplest approximation would then correspond to taking $\rho^*(\mathbf{r})$ equal to $n(\mathbf{r})$. This gives the equation

$$-kT \ln g(\mathbf{r}, \lambda) = \phi(\mathbf{r}, \lambda) + W[\rho g(\mathbf{r}), \lambda] - W(\rho, \lambda), \quad (1.10)$$

which is generally only correct to zeroth order in the density though it should be useful as a starting point for expansions in the gradient of the density.⁸ A more reasonable approximation would be to set ρ^* equal to

⁵ H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959); H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.* **32**, 119 (1960). E. Helfand, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **34**, 1037 (1961).

⁶ E. Helfand and F. H. Stillinger, Jr., *J. Chem. Phys.* **37**, 2646 (1962).

⁷ The concept of an effective local density is used by Helfand and Stillinger (Ref. 6) to obtain a generalized superposition approximation. The two average densities are identical for $\lambda \leq \frac{1}{2}$.

⁸ J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**, 248 (1963).

² T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956) Chap. 6.

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

⁴ H. L. Frisch, *J. Chem. Phys.* **22**, 1713 (1954).

some weighted average of $n(\mathbf{y})$ in the vicinity of \mathbf{r} . A particularly simple situation occurs for a gas of hard spheres of diameter a . (We shall set $a=1$ from now on.) If we use scale coupling we will have that the potential $\phi(\mathbf{r}, \lambda)$ is $+\infty$ for $r \leq \lambda$ and zero for $r \geq \lambda$. Also the work of coupling a λ -cule is now identical to the work of creating a cavity of radius λ , as noted by Feiss, Frisch, and Lebowitz.⁵ It is therefore suggestive that we approximate ρ^* by the average density of the region of this cavity, $\bar{\rho}$:

$$\rho^* \simeq \bar{\rho} = (4/3\pi)^{-1} \rho \int_{|\mathbf{y}| < \lambda} g(|\mathbf{r} + \mathbf{y}|) d\mathbf{y}. \quad (1.11)$$

We shall show in the next section that setting $\rho^* = \bar{\rho}$ is exact when $\lambda \leq \frac{1}{2}$ (this was the reason for introducing λ).⁷ For $\lambda=1$ the approximation $\rho^* = \bar{\rho}$ together with some exact subsidiary conditions which determines $W(\rho)$ in terms of g leads to a closed equation for $g(\mathbf{r})$. Unfortunately the resulting equation is highly non-linear and has to be solved as a power series in ρ (Sec. II) or by linearization (Sec. III).

The approximation (1.11) for a hard sphere fluid may be written in a form that is immediately applicable to all potentials,

$$\rho^* \simeq \bar{\rho} = \frac{\rho \int g(|\mathbf{r} + \mathbf{y}|) f(\mathbf{y}) d\mathbf{y}}{\int f(\mathbf{y}) d\mathbf{y}}, \quad (1.12)$$

where $f(\mathbf{y})$ is the Mayer function,

$$f(\mathbf{y}) = \{\exp[-\beta\phi(\mathbf{y})] - 1\}, \quad \text{and} \quad \beta = (kT)^{-1}.$$

In Sec. IV we consider an "improved" approximation for $\rho^*(\mathbf{r})$. This consists in setting

$$\begin{aligned} \rho^*(\mathbf{r}) &= \tilde{\rho}(\mathbf{r}) = \rho \int g(\mathbf{r} + \mathbf{y}) C(\mathbf{y}) d\mathbf{y} / \int C(\mathbf{y}) d\mathbf{y} \\ &= \rho + [C(\mathbf{r}) - g(\mathbf{r}) + 1] / \beta W'(\rho), \end{aligned} \quad (1.13)$$

where $C(\mathbf{r})$ is the direct correlation function.

2. HARD-SPHERE FLUID

As mentioned previously the work of introducing a hard-sphere particle of size λ (i.e., one whose excluded volume is a sphere of radius λ) at some point \mathbf{r} in a fluid is equal to the direct (external) potential $U_\lambda(\mathbf{r})$ acting on the λ -cule plus the work of creating a spherical cavity of size λ with its center at \mathbf{r} . This work is in turn related to the probability of finding such a cavity at \mathbf{r} by the Einstein fluctuation formula⁹

$$p_0[\mathbf{r}, \lambda; n(\mathbf{y})] = \exp\{-\beta \hat{W}[\mathbf{r}, \lambda; n(\mathbf{y})]\}. \quad (2.1)$$

In a similar way we define $p_0(\rho, \lambda)$,

$$p_0(\rho, \lambda) = \exp[-\beta W(\rho, \lambda)]. \quad (2.2)$$

Defining p_l as the probability of finding exactly l particles inside the sphere of radius λ , we find⁵

$$p_0(\lambda) = 1 - \sum_{l=1}^{\infty} p_l(\lambda); = 1 + \sum_{l=1}^{\infty} (-)^l F_l, \quad (2.3)$$

where F_l is the average number of l -tuplets in the region of radius λ ,

$$F_l = \frac{1}{l!} \int_{|\mathbf{y}_i| < \lambda} n_l(\mathbf{r} + \mathbf{y}_1, \mathbf{r} + \mathbf{y}_2, \dots, \mathbf{r} + \mathbf{y}_l) d\mathbf{y}_1 \dots d\mathbf{y}_l. \quad (2.4)$$

Since n_l vanishes whenever $|\mathbf{y}_i - \mathbf{y}_j| < 1$, the summation in (2.2) will terminate after some $m(\lambda)$, $m(\lambda)$ being the maximum number of hard spheres of diameter 1 which can be put inside a sphere of radius λ . In particular, for $\lambda \leq \frac{1}{2}$, $m=1$ and we find

$$p_0[\mathbf{r}, \lambda; n(\mathbf{y})] = 1 - \int_{|\mathbf{x}| \leq \lambda} n(\mathbf{r} + \mathbf{x}) d\mathbf{x}, \quad (2.5)$$

which gives (cf. Ref. 6)

$$\begin{aligned} \hat{W}[\mathbf{r}, \lambda; n(\mathbf{y})] &= -kT \ln \left[1 - \int_{|\mathbf{x}| \leq \lambda} n(\mathbf{r} + \mathbf{x}) d\mathbf{x} \right] \\ &= -kT \ln \left[1 - \frac{4}{3} \pi \lambda^3 \bar{\rho} \right] = W(\bar{\rho}, \lambda), \quad \lambda \leq \frac{1}{2}, \end{aligned} \quad (2.6)$$

where the average density $\bar{\rho}$ is defined in Eq. (1.11). We thus see that our ansatz (1.11) is true for $\lambda \leq \frac{1}{2}$. According to Eq. (2.3), (1.11) is equivalent to the assumption that the average number of l -tuplets in a spherical region of radius λ in a nonuniform system is equal to the same average in a uniform system with a density equal to the average density in this region.

We are interested in the case $\lambda=1$. The equation for $g(\mathbf{r})$ is, using (1.12),

$$g(\mathbf{r}, \rho) = \begin{cases} \exp\{\beta W(\rho) - \beta W(\bar{\rho})\}, & r \geq 1; \\ 0, & r < 1. \end{cases} \quad (2.7)$$

In order to make (2.7) a complete equation we have to be able to express $W(\rho)$ in terms of $g(\mathbf{r})$. This may be done by noting that $W(\rho)$ is related to the pressure through the equations

$$W(\rho) = \mu - kT \ln(\rho \Lambda^3) \quad (2.8)$$

and

$$\frac{\partial p}{\partial \rho} = \rho \frac{\partial \mu}{\partial \rho} = \rho \frac{\partial W}{\partial \rho} + kT. \quad (2.9)$$

The pressure may in turn be related to the radial distribution function either through the virial theorem,¹⁰

$$\begin{aligned} \beta p &= \rho - \frac{2}{3} \pi \rho^2 \int_0^\infty \frac{d\phi(r)}{dr} g(r) r^3 dr \\ &= \rho + \frac{2}{3} \pi \rho^2 g(1), \quad \text{for hard spheres,} \end{aligned} \quad (2.10)$$

or through the compressibility relation¹¹

$$kT \left(\frac{\partial p}{\partial \rho} \right)^{-1} = 1 + 4\pi \rho \int_0^\infty [g(r) - 1] r^2 dr. \quad (2.10')$$

⁹ R. C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, London, 1938), Sec. 141.

¹⁰ Reference 2, Sec. 30.

¹¹ Reference 2, Sec. 37.

Equations (2.7), (2.9), and either (2.10) or (2.10') then constitute a set of equations for $g(r)$.

We now solve for $g(r)$ by means of power series expansions in ρ . We can write $g(r)$ as

$$\begin{aligned} g(r) &= g_0(r) + \rho g_1(r) + \rho^2 g_2(r) + \dots, & r \geq 1 \\ g_l(r) &\equiv 0, & r < 1 \\ g_0(r) &= 1, & r \geq 1 \end{aligned} \quad (2.11)$$

and expand $\bar{\rho}$ in powers of ρ :

$$\bar{\rho} = \alpha_1 \rho + \alpha_2 \rho^2 + \alpha_3 \rho^3 + \dots, \quad (2.12)$$

with α_n given by

$$\alpha_n = \left(\frac{4}{3}\pi\right)^{-1} \int_{|\mathbf{y}| < 1} g_{n-1}(|\mathbf{r} + \mathbf{y}|) d\mathbf{y}. \quad (2.13)$$

The expansion for W in powers of ρ will have the form

$$\begin{aligned} \beta W(\rho) &= \sum_{l=1}^{\infty} W_l \rho^l, \\ W(\bar{\rho}) &= \sum W_l \bar{\rho}^l = \sum c_{kl} \rho^k, \end{aligned} \quad (2.14)$$

The coefficients W_l are given in terms of the virial coefficients B_l via Relation (2.9),

$$W_l = [(l+1)/l] B_{l+1}, \quad (2.15)$$

and are thus given in terms of $g(r)$ by either (2.10) or (2.10').

$$W_n = [(n+1)/n] \frac{4}{3}\pi g_{n-1}(1), \quad (2.16)$$

or

$$\begin{aligned} &(1 + W_1 \rho + 2W_2 \rho^2 + \dots + nW_n \rho^n + \dots)^{-1} \\ &= 1 + \frac{4}{3}\pi \rho + 4\pi \sum_{n=1}^{\infty} \rho^{n+1} \int_1^{\infty} g_n(r) r^2 dr. \end{aligned} \quad (2.16')$$

Substituting the above expansions into (2.7) and equating terms in equal powers of ρ , we get the following expressions for the first few terms in Equation (2.11):

$$g_1(r) = W_1(1 - \alpha_1), \quad (2.17)$$

$$g_2(r) = W_2(1 - \alpha_1^2) - W_1 \alpha_2 + \frac{1}{2} W_1^2 (1 - \alpha_1)^2, \quad (2.18)$$

$$\begin{aligned} g_3(r) &= W_3(1 - \alpha_1^3) - W_1 \alpha_3 - 2W_2 \alpha_1 \alpha_2 - W_1^2 (1 - \alpha_1) \alpha_2 \\ &+ \frac{1}{6} W_1^3 (1 - \alpha_1)^3 + W_1 W_2 (1 - \alpha_1) (1 - \alpha_1^2), \end{aligned} \quad (2.19)$$

These equations can be solved by iteration. Starting with $g_0=1$, we obtain α_1 from (2.13) and W_1 from either (2.10) or (2.10'), both yielding the same result. Substitution of these values in (2.17) then yields $g_1(r)$. Knowing $g_1(r)$ we proceed to calculate α_2 and W_2 and again (2.10) and (2.10') yield identical results. We thus find

$$W_1 = 2b, \quad (2.20)$$

$$g_1(r) = \begin{cases} \frac{4}{3}\pi(1 - 3/4r + 1/16r^3), & 1 \leq r \leq 2 \\ 0, & r > 2 \end{cases} \quad (2.21)$$

$$W_2 = \frac{1}{16} b^2, \quad (2.22)$$

$$g_2(r) = \begin{cases} \pi^2 \left(\frac{9}{70} r^{-1} + \frac{5}{6} - \frac{23}{20} r + \frac{17}{84} r^2 + \frac{1}{9} r^3 - \frac{17}{384} r^4 \right. \\ \quad \left. + \frac{1}{9} \frac{1}{2} \frac{1}{16} r^6 \right), & 1 \leq r \leq 2 \\ \pi^2 \left(\frac{27}{70} r^{-1} - \frac{9}{4} + \frac{9}{5} r - \frac{1}{4} r^2 - \frac{1}{6} r^3 + \frac{1}{20} r^4 - \frac{1}{1280} r^6 \right), & 2 \leq r \leq 3 \\ 0, & r > 3 \end{cases} \quad (2.23)$$

where b is the second virial coefficient B_2 , $b=2/3\pi$. If we compare (2.20)–(2.23) with the exact calculation of Nijboer and Van Hove¹² we note that W_1 , $g_1(r)$, and W_2 are given exactly by our approximation and $g_2(r)$ is exact for $r \geq 2$.

The reason that $g_2(r)$ is exact for $r > 2$ is easily explained, the expression for $g_2(r_{12})$, (2.18), reduces to $-W_1 \alpha_2$ in this interval, and this is seen to be the integral $\int f(r_{1j_1}) f(r_{j_1 j_2}) f(r_{j_2 2}) d\mathbf{r}_{j_1} d\mathbf{r}_{j_2}$ which is the correct expression for $r > 2$. In general $g_n(r_{12})$ will be given in the n th shell by the expression

$$g_n(r) = -W_1 \alpha_n, \quad n \leq r \leq n+1 \quad (2.25)$$

and since this is the contribution from the chain diagrams

$$\int f(r_{1j_1}) f(r_{j_1 j_2}) \dots f(r_{j_{n-2} j_{n-1}}) d\mathbf{r}_{j_1} \dots d\mathbf{r}_{j_{n-2}}$$

this means that $g_n(r)$ will be exact in the n th shell and will be zero for $r \geq n+1$. Now since our $g_3(r)$ is not exact in the range, $1 \leq r < 2$, the value of W_3 will depend on whether the virial theorem (2.10) or the compressibility relation (2.10') is used in computing it,

$$W_3^v = 0.4388b^3, \quad W_3^c = 0.2880b^3, \quad W_3^e = 0.3860b^3,$$

where W_3^e is the exact value of W_3 . The different W_3 's will lead to different values for $g_3(r)$ or $r < 3$. We have used W_3^e to compute $g_3(r)$. This corresponds essentially to using (2.7) as an approximation for the radial distribution function assuming that the thermodynamic parameters of the system, given by $W(\rho)$, are known. We find

$$W_4^v = 0.180b^4, \quad W_4^e = 0.149b^4. \quad (2.26)$$

W_4^e is taken from the recent calculations by Ree and Hoover.¹³

3. LINEARIZED INTEGRAL EQUATION

The equation for $g(r)$ developed in Sec. 2 is so highly nonlinear that despite its intuitive basis there seems little chance of solving it in a form other than a virial series. We shall therefore consider a linearized version of this equation, which turns out to be of interest in itself.

Assuming that $\bar{\rho}(r)$ is close to ρ we expand the

¹² B. R. A. Nijboer and L. Van Hove, Phys. Rev. **85**, 777 (1952).

¹³ F. H. Ree and W. G. Hoover, UCRL Report No. 7372, Radiation Laboratory.

exponent of (2.8) to get

$$g(r) - 1 = \beta \rho W'(\rho) \left(\frac{4}{3}\pi\right)^{-1} \int [g(|\mathbf{r} + \mathbf{y}|) - 1] f(\mathbf{y}) d\mathbf{y},$$

$$r > 1,$$

$$g(r) = 0, \quad r < 1. \quad (3.1)$$

Changed to bipolar coordinates¹⁴ this equation can be written in a one-dimensional form:

$$\sigma(r) = Ar - \lambda \int_1^\infty \sigma(r') K(r-r') dr', \quad r > 1 \quad (3.2)$$

where

$$\sigma(r) = \begin{cases} 0, & r < 1 \\ rg(r), & r > 1, \end{cases}$$

$$\lambda = \frac{3}{2}\beta\rho W'(\rho), \quad (3.3)$$

$$A = 1 + \frac{2}{3}\lambda,$$

and

$$K(t) = \begin{cases} \frac{1}{2}(1-t^2), & |t| < 1 \\ 0, & |t| > 1. \end{cases} \quad (3.4)$$

Equation (3.2) is of the form considered by Kirkwood and Boggs¹⁵ and Abe.¹⁶ It is most readily solved by satisfying the requirement on the value of $\sigma(r)$ for $r < 1$ through the introduction of a suitable new function $\sigma_1(r)$ that vanishes for $r > 1$, and is otherwise determined by the requirement that $\sigma(r)$ vanish for $r < 1$. With the help of this new function, (3.2) may be written as

$$\sigma(r) = Ar - \sigma_1(r) - \lambda \int_1^\infty \sigma(r') K(r-r') dr', \quad r > 0. \quad (3.5)$$

Kirkwood and Boggs¹⁵ have obtained an expression for $\sigma(r)$. Their solution, however, involved coefficients that were not determined explicitly. We shall utilize a method developed by Wertheim¹⁷ for a different problem to find an essentially explicit solution of (3.5). Let us differentiate equation (3.5) with respect to r and take the Laplace transform of the resulting equation. This yields

$$sG(s) = (A/s) - sF_1(s) + G(s) \{F_2(s) - F_2(-s)\}, \quad (3.6)$$

where,

$$G(s) = \int_1^\infty e^{-rs} \sigma(r) dr, \quad (3.7)$$

$$F_1(s) = \int_0^1 e^{-rs} \sigma_1(r) dr, \quad (3.8)$$

$$F_2(s) = \lambda \int_0^1 e^{-rs} r dr = \lambda \left[\frac{1}{s^2} - \frac{e^{-s}}{s} \left(1 + \frac{1}{s}\right) \right]. \quad (3.9)$$

¹⁴ See Ref. 2.

¹⁵ J. G. Kirkwood and E. M. Boggs, *J. Chem. Phys.* **10**, 394 (1942). They obtained an equation of the same form as (3.2) by using the Kirkwood equation with a kernel proportional to the Mayer f function.

¹⁶ R. Abe, *Progr. Theoret. Phys.* **19**, 57 (1958).

¹⁷ M. Wertheim, *J. Math. Phys.* (to be published).

Solving (3.6) for $G(s)$ yields

$$G(s) = \frac{1 - s^2 F_1(s)/A}{\{s^2 + s[F_2(-s) - F_2(s)]\}/A} = \frac{C(s)s^{-2}}{D(s)}$$

$$= \frac{C(s)s^{-2}}{\{1 + \lambda s^{-3}[e^s(1-s) - e^{-s}(1+s)]\}/A},$$

$$C(0) = 1, \quad D(0) = 1. \quad (3.10)$$

The behavior of $G(s)$ will be determined by the requirement that $g(r) \rightarrow 1$ as $r \rightarrow \infty$. Let us rewrite (3.7) as

$$G(s) = \frac{e^{-s}}{s^2} (1+s) + \int_1^\infty e^{-sr} r [g(r) - 1] dr. \quad (3.11)$$

We look for solutions such that

$$\int_1^\infty r |g(r) - 1| dr < \infty. \quad (3.12)$$

This implies that $G(s) - s^{-2}$ will have no singularities in the closed right half of the s plane. Hence, the zeros of $D(s)$ in the closed rhp must be canceled by zeros of $C(s)$. [This can only happen, as we see later, when $D(s)$ has no zeros on the imaginary axis, which will be¹⁵ true for $\lambda < 17.4$. We assume this to be the case and discuss it further at the end of this section.] Replacing s by $-s$ in (3.10) yields

$$G(-s) = C(-s)s^{-2}/D(s). \quad (3.13)$$

Combining (3.10) and (3.13) gives

$$L(s) = G(s)C(-s) - s^{-2} = [C(s)C(-s)s^{-2}]/D(s) - s^{-2}$$

$$= G(-s)C(s) - s^{-2} = L(-s). \quad (3.14)$$

Since $C(s)$ is an entire function and $C(0) = 1$, $L(s)$ has to be regular both in the closed rhp and the closed lhp. It is therefore an entire function. Furthermore, from (3.5) and (3.8) as $s \rightarrow \infty$ along a ray in the rhp.,

$$|C(s)| \rightarrow |\sigma_1^{(2)}(0)| |s^{-3}| A^{-1} = |\lambda| |\sigma_1(1)| |s^{-3}| A^{-1},$$

$$|C_1(-s)| \rightarrow |\sigma_1(1)| |s^{-1}| |e^s| A^{-1} = |g(1)| |s^{-1}| |e^s| A^{-1},$$

$$|D(s)| \rightarrow \lambda |s^{-2}| |e^s| A^{-1}, \quad (3.15)$$

where superscripts denote differentiation with respect to r , and we have made use of Eq. (3.5) to show that $\sigma_1(r) + \sigma(r)$ is continuous at $r = 1$ and that

$$\sigma_1(0) = 0, \quad \sigma_1^{(1)}(0) = A, \quad \sigma_1^{(2)}(0) = -\lambda g(1). \quad (3.16)$$

It follows from (3.15) that $|L(s)| \rightarrow |g^2(1)/A|$ along every ray. (This may also be verified for the imaginary axis.) Since $L(s)$ is an entire function this implies that $L(s)$ is constant everywhere. By considering the behavior of $L(s)$ along the real axis we find

$$L(s) = -g^2(1)/A \equiv -\gamma^{-2}. \quad (3.17)$$

Equation (3.14) may now be written as

$$s^2 G(s) = \frac{C(s)}{D(s)} = \frac{(1-s/\gamma)(1+s/\gamma)}{C(-s)}. \quad (3.18)$$

Thus,

$$C(s)C(-s) = (1-s/\gamma)(1+s/\gamma)D(s) \quad (3.19)$$

will have zeros whenever $D(s)$ has zeros and also at $s = \pm\gamma$. Now for $\lambda=0$, $\sigma(r) + \sigma_1(r) = A = D(s) = \gamma = 1$, and $C(s) = e^{-s}(1+s)$. Hence $C(s)$ has a zero at $-\gamma$ and $C(-s)$ at γ . We may assume that this will be the case also for $\lambda > 0$. Using now again our assumption that $s^2G(s)$ is regular in the rhp we have that $C(s)/(1+s/\gamma)$ is an entire function all of whose zeros coincide with the zeros of $D(s)$ in the rhp. Similarly all the zeros of $C(-s)/(1-s/\gamma)$ coincide with the zeros of $D(s)$ in lhp.

We shall denote the zeros of $D(s)$, an even function, by $\pm s_i, \pm \bar{s}_i$ where $s_i = x_i + iy_i, \bar{s}_i = x_i - iy_i, x_i > 0, y_i > 0$. Using Hadamard's¹⁸ factorization theorem for $D(s)$, which is an entire function of order 1, we may write

$$D(s) = \exp P_1(s) \prod_i \left[\left(1 - \frac{s}{s_i}\right) \exp\left(\frac{s}{s_i}\right) \left(1 - \frac{s}{\bar{s}_i}\right) \exp\left(\frac{s}{\bar{s}_i}\right) \right] \times \prod_i \left[\left(1 + \frac{s}{s_i}\right) \exp\left(-\frac{s}{s_i}\right) \left(1 + \frac{s}{\bar{s}_i}\right) \exp\left(-\frac{s}{\bar{s}_i}\right) \right], \quad (3.20)$$

where $P_1(s)$ is a polynomial of degree 1. When s_i is real the square bracket should contain only one term. Since there are, however, only a finite number of real roots we shall not consider them explicitly. Now since $D(s)$ is even and $D(0) = 1, P_1(s) = 0$, and we have

$$D(s) = \prod_i \left\{ \left[1 + \frac{s^2 - 2x_i s}{x_i^2 + y_i^2} \right] \exp\left[\frac{2x_i s}{x_i^2 + y_i^2} \right] \right\} \times \prod_i \left\{ \left[1 + \frac{s^2 + 2x_i s}{x_i^2 + y_i^2} \right] \exp\left[\frac{-2x_i s}{x_i^2 + y_i^2} \right] \right\}. \quad (3.21)$$

A careful examination of $D(s)$ shows that asymptotically $x_i \sim 2 \ln y_i$ and $y_i \sim N\pi + l\pi$ where N is an integer. Hence,

$$2 \sum_i [x_i / (x_i^2 + y_i^2)] \equiv b \quad (3.22)$$

is convergent and we may write

$$D(s) = \prod_i \left\{ 1 + \frac{s^2 - 2x_i s}{x_i^2 + y_i^2} \right\} \prod_i \left\{ 1 + \frac{s^2 + 2x_i s}{x_i^2 + y_i^2} \right\} = d(s)d(-s),$$

where $d(s)$ has zeros only in the rhp and $d(-s)$ only in the lhp. Substituting (3.23) into (3.19) gives

$$\frac{C(s)}{(1+s/\gamma)d(s)} = \frac{(1-s/\gamma)d(-s)}{C(-s)} = \xi(s). \quad (3.24)$$

By our previous considerations $\xi(s)$ has no zeros anywhere and is an entire function of order one (or zero). Since $\xi(0) = 1$, it is by Hadamard's¹⁸ factorization theorem equal to e^{-as} where a is a constant. In order to find the value of a we expand (3.24) in powers of s ,

$$1 + s(b - \gamma^{-1}) + O(s^2) = 1 - as + O(s^2), \quad (3.25)$$

obtaining, $a = \gamma^{-1} - b$. Substituting (3.24) into (3.18) yields

$$G(s) = \frac{(1+s/\gamma)}{s^2} \exp[(b-\gamma^{-1})s] / \prod_i \left[\left(1 + \frac{s}{s_i}\right) \left(1 + \frac{s}{\bar{s}_i}\right) \right]. \quad (3.26)$$

We may now take the inverse Laplace transform of the right side of (3.26) to obtain $\sigma(r) = rg(r)$ "explicitly" in terms of $g(1) = [1 + \frac{2}{3}\lambda]^{1/2}/\gamma$ and λ .

$$rg(r) = r + \sum \left\{ \frac{[(1/s_i) - (1/\gamma)] \exp[-(b-\gamma^{-1})s_i] \exp(-s_i r)}{\prod' [1 - (s_i/s_n)] [1 - (s_i/\bar{s}_n)]} + \frac{[(1/\bar{s}_i) - (1/\gamma)] \exp[-(b-\gamma^{-1})\bar{s}_i] \exp(-\bar{s}_i r)}{\prod' [1 - (\bar{s}_i/s_n)] [1 - (\bar{s}_i/\bar{s}_n)]} \right\}. \quad (3.27)$$

Eliminating $g(1)$ from (3.27) leaves us g as a function of $\lambda, \lambda = \frac{3}{2}\beta\rho W'(\rho)$. We can obtain λ in a "self-consistent" way by using either the compressibility relation (2.10') or the virial equation (2.10). Alternatively, we may adopt the attitude (cf. end of Sec. 2) that we somehow know the thermodynamics properties of our system and use (3.28) as an approximation to the radial distribution function for a system of known compressibility, i.e., $W'(\rho)$. Adopting this approach we can use for hard spheres the $W'(\rho)$ obtained by Reiss, Frisch, and Lebowitz from considerations of the cavity creation work in a uniform system, discussed in Sec. 2, and by Wertheim¹⁹ and Thiele²⁰ from solutions of the Percus-Yevick integral equation for $g(r)$. They found

$$\beta p(\rho) = \rho [1 + \eta + \eta^2] / (1 - \eta)^3, \quad (3.28)$$

$$\lambda = \frac{3}{2}\beta\rho W'(\rho) = \frac{3}{2}\eta(8 - 2\eta + 4\eta^2 - \eta^3) / (1 - \eta)^4, \quad (3.29)$$

$$\eta = (\pi/6)\rho.$$

The equation of state (3.28) is in very good agreement with the results of machine computations over the whole range of "fluid" densities $\rho \leq 0.8$. The machine computations²¹ indicate a fluid-solid phase transition at $\rho \simeq 0.8$.

We return now to the question of what happens when $\lambda \rightarrow 17.4$, at which value $D(s)$ has a root on the imaginary axis. An inspection of (3.18) shows that in this case $G(s)$ will have a singularity on the imaginary axis and (3.12) will not be satisfied. Hence our approximation breaks down completely for $\lambda = 17.4$.

The breakdown of our integral equation for some value of λ (or ρ) occurs also for a one-dimensional fluid of hard rods and cannot thus be identified with the phase transition at $\rho \simeq 0.8$.

¹⁸ See, e.g., E. C. Titchmarsh, *The Theory of Functions* (Oxford University Press, London, 1939).

¹⁹ M. Wertheim, *Phys. Rev. Letters* **8**, 321 (1963).

²⁰ E. Thiele, *J. Chem. Phys.* **39**, 474 (1963).

²¹ B. Alder and T. Wainwright, *J. Chem. Phys.* **33**, 1349 (1960).

4. OTHER INTEGRAL EQUATIONS FOR $g(r)$

In the last two sections we investigated the consequences, for a fluid of hard spheres, of our assumption that the effective density $\rho^*(r)$ "defined" by the equation

$$g(r) = \exp[-\beta\phi(r)] \exp\{-\beta[W(\rho^*) - W(\rho)]\} \quad (4.1)$$

may be approximated by an average density $\bar{\rho}$. $\bar{\rho}(\mathbf{r})$ is the actual density in the vicinity of \mathbf{r} , $\rho g(r)$, weighted by the Mayer function $f(r)$:

$$\begin{aligned} \rho^*(r) \simeq \bar{\rho}(r) &= \int \rho g(\mathbf{r}-\mathbf{r}') f(r') d\mathbf{r}' / \int f(r') d\mathbf{r}' \\ &= \rho + \rho \int [g(\mathbf{r}-\mathbf{r}') - 1] f(r') d\mathbf{r}' / \int f(r') d\mathbf{r}'. \end{aligned} \quad (4.2)$$

It is interesting to consider also other approximations to ρ^* using weighting factors which may themselves depend on g . A particularly suggestive weighting factor is the direct correlation function $C(r)$ which measures essentially the effect of a nonuniform density on the potential felt by a particle at \mathbf{r} .²² $C(r)$ satisfies the equation

$$g(r) - 1 \equiv u(r) = C(r) + \rho \int u(\mathbf{r}-\mathbf{r}') C(r') d\mathbf{r}'. \quad (4.3)$$

Using C as a weighting factor yields,

$$\rho^*(r) \simeq \tilde{\rho}(r) = \int \rho g(\mathbf{r}-\mathbf{r}') C(r') d\mathbf{r}' / \int C(r') d\mathbf{r}'. \quad (4.4)$$

When (4.4) is substituted into (4.1) and use is made of Eq. (4.3) and the compressibility relation (2.10), we obtain

$$g(r) = \exp\left\{-\beta\left[\phi(r) + W\left(\rho + \frac{C(r) - u(r)}{\beta W'(\rho)}\right) - W(\rho)\right]\right\}. \quad (4.5)$$

Expanding $W(\bar{\rho})$ in (4.5) and keeping only the first two terms yields

$$g(r) = \exp\{-\beta\phi(r) + [g(r) - 1 - C(r)]\}. \quad (4.6)$$

This is the hypernetted chain approximation²³ for the radial distribution. Expanding the exponent yields,

$$g(r) = \exp[-\beta\phi(r)] \{1 + [g(r) - 1] - C(r) + \dots\}, \quad (4.7)$$

which cut off after the first term gives the Percus-Yevick²⁴ (PY) equation

$$f(r)g(r) = C(r) \exp[-\beta\phi(r)]. \quad (4.8)$$

The above results can be readily understood by considering the functional Taylor expansion¹ of $\rho^*(\mathbf{r})$, which is a functional of the density at each point \mathbf{y} , $\rho^*(\mathbf{r}) = \rho^*[\mathbf{r}; n(\mathbf{y})]$, from some initial reference

²² L. S. Ornstein and F. Zernike, Proc. Amsterdam Acad. Sci. 17, 793 (1914).

²³ See, e.g., G. Stell, Physica 29, 517 (1963).

²⁴ J. K. Percus and G. F. Yevick, Phys. Rev. 110, 7 (1957).

density $n_0(\mathbf{y})$. [In our case $n(\mathbf{y}) = \rho g(y)$, $n_0(\mathbf{y}) = \rho$.] This change in the density is accomplished by "turning on" an external potential from $U_0(\mathbf{y})$ to $U(\mathbf{y})$ while the chemical potential μ or the fugacity z remains constant. The effective density $\rho^*[\mathbf{r}; n(\mathbf{y})]$ is defined by the relation [cf. Eqs. (1.4)]

$$\beta W(\rho^*) = \beta \hat{W}[\mathbf{r}; n(\mathbf{y})] \equiv \ln\{n(\mathbf{y}) \exp[\beta U(\mathbf{y})]/z\}, \quad (4.9)$$

while the symbols $\hat{W}[\mathbf{r}; n(\mathbf{y})]$ and $W(\rho)$ have the same meanings as before. We then have [see Lebowitz and Percus Ref. 8, Eq. (2.5)]

$$\begin{aligned} [\delta\beta W(\rho^*)/\delta n(\mathbf{x})] &= \beta W'(\rho^*) [\delta\rho^*/\delta n(\mathbf{x})] \\ &= C[\mathbf{r}, \mathbf{x}; n(\mathbf{y})], \end{aligned} \quad (4.10)$$

where C is the direct correlation function in the system whose density is $n(\mathbf{y})$. The functional Taylor expansion for ρ^* will therefore have the form

$$\begin{aligned} \rho^*[\mathbf{r}; n(\mathbf{y})] &= \rho^*[\mathbf{r}; n_0(\mathbf{y})] \\ &+ \int \frac{\delta\rho^*[\mathbf{r}; n(\mathbf{y})]}{\delta n(\mathbf{x})} \Big|_{n_0} [n(\mathbf{x}) - n_0(\mathbf{x})] d\mathbf{x} + \dots \\ &= \rho^*[\mathbf{r}; n_0(\mathbf{y})] + (\beta W'[\rho^*[\mathbf{r}; n_0(\mathbf{y})]])^{-1} \\ &\times \int C[\mathbf{r}_1\mathbf{x}; n_0(\mathbf{y})] [n(\mathbf{x}) - n_0(\mathbf{x})] d\mathbf{x} + \dots \end{aligned} \quad (4.11)$$

Setting now $n(\mathbf{y}) = \rho g(y)$, $n_0(\mathbf{y}) = \rho$, and dropping all the remainder terms in (4.11) we obtain

$$\begin{aligned} \rho^*[\mathbf{r}; \rho g(y)] &= \rho + [\beta W'(\rho)]^{-1} \rho \int C(\mathbf{r}-\mathbf{x}) [g(\mathbf{x}-\mathbf{y}) - 1] d\mathbf{x} \\ &= \rho + [\beta W'(\rho)]^{-1} \rho [u(\mathbf{r}-\mathbf{y}) - C(\mathbf{r}-\mathbf{y})] \\ &= \tilde{\rho}(\mathbf{r}-\mathbf{y}). \end{aligned} \quad (4.12)$$

which is our approximation in Eq. (4.4). The similarity with the PY and the hypernetted chain equations is now clear for as pointed out by Percus¹ these approximations are obtained by carrying out a functional Taylor expansion and dropping higher order terms for the quantities $n(\mathbf{r}) \exp\beta U(\mathbf{r})$ and $\ln[n(\mathbf{r}) \exp\beta U(\mathbf{r})]$, respectively.

Carrying out a virial expansion of (4.5) combined with Eq. (4.3) yields

$$\tilde{g}(r) = \exp[-\beta\phi(r)] [1 + \rho\tilde{g}_1(r) + \rho^2\tilde{g}_2(r) + \dots], \quad (4.13)$$

where $\tilde{g}_1(r)$ is exact and $\tilde{g}_2(r)$ is related to the exact $g_2(r)$ by the equation

$$\begin{aligned} \tilde{g}_2(r_{12}) &= g_2(r_{12}) - \frac{1}{2} \int d\mathbf{r}_3 d\mathbf{r}_4 f(r_{13}) f(r_{14}) f(r_{23}) f(r_{24}) \\ &\times [f(r_{34}) + (2W_2/W_1^2)], \end{aligned} \quad (4.14)$$

where W_1 and W_2 are again given exactly by our approximation. $\tilde{g}_2(r_{12})$ may be written in terms of the usual graphical symbols as

$$\tilde{g}_2(r_{12}) = \frac{1}{2} \int d\mathbf{r}_3 d\mathbf{r}_4 \left[\left(1 - \frac{2W_2}{W_1^2}\right) \begin{array}{c} \diagdown \\ \diagup \end{array} + 4 \begin{array}{c} \diagdown \\ \diagup \end{array} + 2 \begin{array}{c} \diagdown \\ \diagup \end{array} \right] \quad (4.15)$$

Using \tilde{g}_2 and (2.10) and (2.10') to find \tilde{W}_3^c and \tilde{W}_3^v for a fluid of hard spheres we obtain

$$W_3^c = 0.3336b^3, \quad W_3^v = 0.4784b^3.$$

For the Gaussian model, $f(r) = -e^{-\alpha r^2}$, α being a constant, our results are²⁵

$$\tilde{W}_3^c = -0.144b^3, \quad \tilde{W}_3^v = -0.167b^3.$$

ACKNOWLEDGMENTS

We would like to thank O. Penrose, G. Stell, M. Wertheim, and J. Percus for many valuable discussions, and Jim Steadman for help with some of the computations.

APPENDIX A. EXISTENCE OF $\rho^*(r)$

The effective density ρ^* is defined by the relation

$$W(\rho^*) = -\beta^{-1} \ln \{ g(r) \exp[\beta\phi(r)] \exp[-\beta W(\rho)] \} \\ = \beta^{-1} \ln [z(\rho^*)/\rho^*]. \quad (\text{A.1})$$

The inversion of $W(\rho^*)$ to obtain $\rho^*(W)$ and thus $\rho^*(r)$ as a function of $g(r)$ will be unique for all values of the density if and only if $W(\rho)$ is a monotonic function. Now $\rho W'(\rho) = \beta^{-1} [(d\phi/d\rho) - 1]$ which will in

²⁵ G. E. Uhlenbeck and G. W. Ford, *Theory of Linear Graphs in Studies in Statistical Mechanics* (North Holland Publishing Company, Amsterdam, The Netherlands, 1962), Vol. 1.

general change sign. [If the particles have hard cores or the potential is repulsive, $\phi'(r) \geq 0$, $W(\rho) \rightarrow \infty$ for $z \rightarrow \infty$ while if the system undergoes a phase transition; or if the second virial coefficient is negative $W'(\rho)$ will be negative for some values of ρ .] Hence, Eq. (A.1) may be satisfied by more than one value of $\rho^*(r)$ for some values of r . If we chose then $\rho^*(r)$ to be the smallest density which will satisfy (A.1), $\rho^*(r)$ may be a discontinuous function of r . However, it may be shown by the methods used by Lebowitz and Penrose²⁶ to prove the existence of a lower bound for the radius of convergence of the virial expansion of the pressure that there exists a finite range of W for which $\rho(W)$ is analytic. This proves the existence of a virial expansion in powers of ρ for $\rho^*(r)$ for sufficiently small values of ρ . The coefficients in this expansion may be obtained explicitly by expanding both sides of (A.1) in powers of ρ . We thus find

$$\rho^*(r) = \left[1 - \frac{g_1(r)}{W_1} \right] \rho + \left[\frac{1}{2} \frac{g_1^2(r)}{W_2} - \frac{g_1^2(r)}{W_1^2} \right. \\ \left. + \frac{2g_1(r)}{W_1} - \frac{g_2(r)}{W_2} \right] \rho^2 + \dots \quad (\text{A2})$$

²⁶ J. L. Lebowitz and O. Penrose, *J. Math. Phys.* (to be published).

Electrical Properties of the Cerium and Gadolinium Hydrogen Systems*

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(Received 20 December 1963)

Conductivities of polycrystalline solid samples of cerium hydride and gadolinium hydride were measured over the composition ranges H/Ce=0-2.5 and H/Gd=0-2.13 at room temperature and at elevated temperatures (400°-750°C). Conduction is metallic and the results for the two systems are very similar. The conductivity in the variable composition dihydride phase of each system decreases with increasing hydrogen content and is explained assuming that the hydrogen is anionic, taking its extra electron from the system's conduction band. Measurements of absolute Seebeck coefficients (CeH_{2.37}, -17 μ V/°C; GdH_{2.12}, -6 μ V/°C) support this model. The measured conductivity curves extrapolate to zero at CeH_{2.7} and GdH_{2.3}. For the dihydride phases the composition dependencies of the conductivities are used to calculate carrier mobilities. The values obtained are in the range 1 to 10 cm²/V-sec. The conductivities of compositions H/M=0 to 2 show that the dihydrides can exist with hydrogen-to-metal ratios much less than 2.0. Ionic conduction has been found not to be important to the conduction mechanism from the results of a concentration cell measurement.

INTRODUCTION

THE rare-earth hydrogen systems have been the center of increasing attention, due largely to the extensive nonstoichiometry which they exhibit. There has been speculation, supported by some experimental evidence, that their electrical properties are directly and significantly related to their hydrogen content. It is the purpose of this paper to present and to discuss results of conductivity and related measurements on two representative rare-earth hydrogen systems, those

* This work supported by the U. S. Atomic Energy Commission.

of cerium and gadolinium. The measurements cover the compositions CeH₀ to CeH_{2.5} and GdH₀ to GdH_{2.13}. In contrast with most previous work, the present measurements were made with samples in the form of solid slabs.

Previously, conductivities of rare-earth hydrides have been given for powdered samples by Daou¹ (CeH₀ to CeH_{2.0}) and by Stalinsky² for a number of Ce-H and

¹ J. N. Daou, *Compt. Rend.* **247**, 1595 (1958).

² B. Stalinsky, *Bull. Acad. Polon. Sci.* **7**, 269 (1959); **5**, 1001 (1957).