

## Scaled Particle Theory of Fluids

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A statistical thermodynamic theory has been developed employing distance scaling as a coupling procedure. This is an extension to real fluids of the technique applied by Reiss, Frisch, and Lebowitz to rigid-sphere systems. One considers molecules interacting with pair potential  $u(r)$ , except for one particle which interacts with potential  $u(r/\lambda)$ . This single particle, essentially a scaled version of a normal molecule, is termed a  $\lambda$ -cule. It is convenient to restrict discussion to potentials with rigid cores at  $r=a$  and cutoffs at  $\gamma a$ . Attention is focused on a function,  $\Theta(\lambda, \rho, T)$ , which reduces to  $G$  of footnote reference 1 in the case of rigid spheres. The pressure, chemical potential, and work of expanding a  $\lambda$ -cule are simply related to  $\Theta$ . One can write  $\Theta$  exactly for  $\lambda < 1/2\gamma$  and simple connection conditions hold at  $\lambda = 1/2\gamma$ . An integral condition and  $\lambda = \infty$  condition on  $\Theta$  also exist. While  $\Theta$  is not completely specified, the foregoing conditions determine much of its behavior.

### 1. INTRODUCTION

RESEARCH in the statistical mechanics of classical fluids, including the liquid state, has centered around the free volume-cell theories and the radial distribution-function method. These theories have been moderately successful in predicting thermodynamic properties. Recently Reiss, Frisch, and Lebowitz<sup>1</sup> (hereinafter referred to as I) have taken a somewhat new approach to the theory of rigid sphere systems and have been able to make striking quantitative predictions of the thermodynamic properties of such fluids. Reiss, Frisch, Helfand, and Lebowitz<sup>2</sup> have employed that method to allow calculation of certain select properties of real fluids.

The present work is another effort to extend to the treatment of real fluids the technique of I which we shall show is essentially the use of distance scaling as a coupling parameter. We shall concentrate on a function,  $\Theta$ , which reduces in the rigid sphere limit to the  $G$  function of I. The  $\Theta$  function can be made to play a role of central importance in the statistical thermodynamics of fluids. It is also closely related to several microscopic, nonthermodynamic quantities.

In the following section the  $\Theta$  function will be defined and its relation to statistical thermodynamics and molecular processes will be elaborated. Under certain special, but no prohibitively restrictive conditions, it will be possible to display explicitly the expression for  $\Theta(\lambda)$  when the argument  $\lambda$ , the distance scaling parameter, is small. We will then wish to say a bit about the analytical properties of  $\Theta$  to aid in the extension of  $\Theta$  to higher  $\lambda$  values. For  $\lambda$  very large, some exact conditions which the function must satisfy can be developed. Finally, there exists an integral condition which may aid in extrapolation.

In Sec. 5 a relation between the  $\Theta$  function and the customary particle correlation functions will be developed.

### 2. DEFINITION OF THE $\Theta$ FUNCTION

Consider the statistical thermodynamics of a single component fluid in terms of the radial distribution function. Employing either the virial theorem<sup>3</sup> or the volume scaling method of Born and Green<sup>3,4</sup> the equation for the pressure may be written as

$$p/\rho kT = 1 - (\rho/6kT) \int_0^\infty r[du(r)/dr]g(r)4\pi r^2 dr, \quad (2.1)$$

where  $p$  is the pressure,  $\rho$  the particle number density,  $k$  the Boltzmann constant,  $T$  the temperature,  $u(r)$  the two-particle intermolecular potential, and  $g(r)$  the radial distribution function normalized to unity at infinite  $r$ .

There are several methods of determining the chemical potential. An interesting technique which we shall focus attention on is the reversible coupling of a single particle to an equilibrium system of  $(N-1)$  particles. Kirkwood<sup>5</sup> has employed the depth of the potential well as a coupling constant. This procedure has also been used partially by Reiss, Frisch, Helfand and Lebowitz<sup>2</sup> in the extension of I to the description of real fluids.

The rigid-sphere theory of I employs the sphere diameter as a coupling parameter. This is an example of a distance scaling coupling. Thus, the total potential energy of the fluid may be written as

$$U_N(\mathbf{r}_1, \dots, \mathbf{r}_N; \lambda) = U_{N-1}(\mathbf{r}_2, \dots, \mathbf{r}_N) + \sum_{i=2}^N u(\mathbf{r}_1/\lambda), \quad (2.2)$$

\* Supported by the Air Force Office of Scientific Research.

<sup>1</sup> H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959); *Proceedings of the 10th International Conference on Refrigeration, Copenhagen, August, 1959* (to be published).

<sup>2</sup> H. Reiss, H. L. Frisch, E. Helfand, and J. L. Lebowitz, *J. Chem. Phys.* **32**, 119 (1960).

<sup>3</sup> J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 134.

<sup>4</sup> M. Born and H. S. Green, *Proc. Roy. Soc. (London)* **A191**, 168 (1947).

<sup>5</sup> J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

where  $r_{1i} = |\mathbf{r}_i - \mathbf{r}_1|$ . When  $\lambda=1$  particle 1 is fully coupled. When  $\lambda=0$  the potential  $u$  has argument  $\infty$  for all values of  $r_{1i}$ , so that  $u$  always is zero and particle 1 is fully decoupled. For other values of  $\lambda$  particle 1 is a scaled version of the other molecules. Such a scaled particle we shall term a  $\lambda$ -cule. The  $\lambda$ -cule may be regarded as a single solute particle and the remainder of the fluid as the solvent. Since the intermolecular potential has the functional form  $u(r) = \epsilon\phi(r/a)$  we see that  $u(r/\lambda) = \epsilon\phi(r/a\lambda)$ . The  $\lambda$ -cule is thus to be pictured as a particle with characteristic distance  $\lambda a$  rather than  $a$  but the same potential-well depth and  $\phi$  function.

The coupling procedures for determining the chemical potential,  $\mu$ , are based on the fact that

$$\begin{aligned} \mu &= (\partial A / \partial N)_{V, T} = A(N, V, T) - A(N-1, V, T) \\ &= kT \ln N \Lambda^3 - kT \ln(Z_N / Z_{N-1}), \end{aligned} \quad (2.3)$$

where  $A$  is the Helmholtz free energy,  $N$  the number of particles (assumed large),  $V$  the volume,  $\Lambda = h(2\pi mkT)^{-1/2}$ , and  $Z$  is the configuration integral

$$Z(\lambda) = \int_V \cdots \int_V \exp[-U_N(\lambda)/kT] d\mathbf{r}_1 \cdots d\mathbf{r}_N, \quad (2.4)$$

with  $Z(1) = Z_N$  and  $Z(0) = V Z_{N-1}$ . Equation (2.3) may be written as

$$\mu = kT \ln \rho \Lambda^3 - kT \int_0^1 \frac{\partial \ln Z(\lambda)}{\partial \lambda} d\lambda,$$

$$\begin{aligned} \frac{\partial \ln Z(\lambda)}{\partial \lambda} &= -[kT Z(\lambda)]^{-1} \sum_{i=2}^N \int \frac{\partial u(r_{1i}/\lambda)}{\partial \lambda} \\ &\times \left[ \int \cdots \int \exp[-U_N(\lambda)/kT] \cdot \prod_{j=2, j \neq i}^N d\mathbf{r}_j \right] d\mathbf{r}_1 d\mathbf{r}_i. \end{aligned} \quad (2.5)$$

We may write

$$\frac{\partial u(r/\lambda)}{\partial \lambda} = \frac{\partial(r/\lambda)}{\partial \lambda} \frac{\partial u(r/\lambda)}{\partial(r/\lambda)} = -(r/\lambda^2) u'(r/\lambda). \quad (2.6)$$

(N.B. The prime on  $u$  denotes differentiation with respect to the argument  $r/\lambda$ , not merely  $r$ .) The radial distribution function,  $g(r, \lambda)$ , defined by

$$\begin{aligned} \rho^2 g(r_{12}, \lambda) &= [N(N-1)/Z(\lambda)] \int \cdots \int \\ &\times \exp[-U_N(\lambda)/kT] d^3r_3 \cdots d^3r_N, \end{aligned} \quad (2.7)$$

has the physical significance that  $\rho g(r, \lambda)$  is the density of molecules at a distance  $r$  from a  $\lambda$ -cule. Combining these results we have for the chemical potential

$$\begin{aligned} \mu &= kT \ln \rho \Lambda^3 - \rho a^3 \int_0^1 \lambda^2 d\lambda \int_0^\infty (r/\lambda) u'(r/\lambda) g(r, \lambda) \\ &\quad (4\pi r^2 dr / \lambda^3 a^3). \end{aligned} \quad (2.8)$$

These results may be unified if we define a function  $\Theta(\lambda, \rho, T)$  by

$$\Theta(\lambda, \rho, T) = - \int_0^\infty (r/\lambda) \frac{u'(r/\lambda)}{kT} g(r, \lambda) \frac{r^2 dr}{\lambda^3 a^3}. \quad (2.9)$$

The  $\Theta$  function depends on the variable  $\lambda$  as well as the thermodynamic state specified by  $\rho$  and  $T$ . In this paper the  $T$  dependence will never explicitly be employed so that we shall not usually write it out. Frequently the  $\rho$  dependence will also be left implicit. The pressure and chemical potential may now be written in terms of  $\Theta$  as

$$p/\rho kT = 1 + \frac{2}{3} \pi \rho a^3 \Theta(1, \rho), \quad (2.10)$$

and

$$\mu = kT \ln \rho \Lambda^3 + 4\pi \rho a^3 kT \int_0^1 \lambda^2 \Theta(\lambda, \rho) d\lambda. \quad (2.11)$$

Equations (2.10) and (2.11) are identical in form with equations appropriate to rigid sphere systems<sup>1</sup> with the contact distribution function  $G(\lambda) = g(\lambda a^+, \lambda)$  of I replaced by  $\Theta$ .

Let us look further into the physical significance of the  $\Theta$  function. In Eq. (2.11) for  $\mu$  the ideal term  $kT \ln \rho \Lambda^3$  accounts for the translational free energy and the entropy of mixing. The integral term is the work of adding the molecule at a fixed position. More generally, the average work of adding a  $\lambda$ -cule at a given position is

$$W(\lambda, \rho) = 4\pi \rho a^3 kT \int_0^\lambda \lambda'^2 \Theta(\lambda', \rho) d\lambda' \quad (2.12)$$

so that the work of expanding the  $\lambda$ -cule's characteristic distance from  $\lambda a$  to  $(\lambda + d\lambda)a$  at constant density is

$$dW(\lambda, \rho) = 4\pi \rho a^3 kT \lambda^2 \Theta(\lambda, \rho) d\lambda. \quad (2.13)$$

This relates  $\Theta$  to the expansion work by

$$\Theta(\lambda, \rho) = (1/4\pi \rho a^3 kT \lambda^2) [\partial W(\lambda, \rho) / \partial \lambda]_\rho. \quad (2.14)$$

One reason for it being convenient to introduce the function  $W$  becomes clear upon examining the Mayer and Montroll<sup>6</sup> expression for this expansion work function. Referring again to Eqs. (2.2-4) it is seen that  $W$  may be written in terms of an activity coefficient  $\Gamma(\lambda)$  as

$$W(\lambda, \rho) = -kT \ln[Z(\lambda)/Z(0)] = -kT \ln \Gamma(\lambda), \quad (2.15)$$

and that  $Z(\lambda)/Z(0)$  may be expanded as

$$\begin{aligned} \Gamma(\lambda) &= Z(\lambda)/Z(0) \\ &= (V Z_{N-1})^{-1} \int \exp[-U_{N-1}(\mathbf{r}_2, \cdots, \mathbf{r}_N) kT] \\ &\quad \times \prod_{i=2}^N \exp[-u(r_{1i}/\lambda)/kT] d\mathbf{r}_1 \cdots d\mathbf{r}_N. \end{aligned} \quad (2.16)$$

<sup>6</sup> J. E. Mayer and E. Montroll, J. Chem. Phys. 9, 2 (1941).

If the Mayer  $f$  function

$$f(s) = \exp(-u(s)/kT) - 1 \quad (2.17)$$

is introduced and the product under the integral in Eq. (2.1) expanded in terms of the  $f$ 's, and one integration is performed, we find

$$\Gamma(\lambda) = 1 + \sum_{m=1}^N (\rho^m/m!) \Phi_m(\lambda) \quad (2.18)$$

$$\Phi_1 = \int f(r_{12}/\lambda) d\mathbf{r}_{12} \quad (2.19)$$

$$\Phi_m = \int \left[ \prod_{i=2}^{m+1} f(r_{1i}/\lambda) \right] g^{(m)}(\mathbf{r}_2, \dots, \mathbf{r}_{m+1}) d\mathbf{r}_{12} \dots d\mathbf{r}_{1,m+1} \quad (2.20)$$

where  $g^{(m)}$  is the  $m$  particle correlation function<sup>7</sup> defined in the absence of the  $\lambda$ -cule.

Performing a change of variables, we may express  $\Phi_1$  in terms of the second virial coefficient:

$$\Phi_1 = -2\lambda^3 B = -\left(\frac{4}{3}\right) \pi a^3 \lambda^3 B^*, \quad (2.21)$$

where

$$B = -\frac{1}{2} \int f(s) d\mathbf{s} = \frac{2}{3} \pi a^3 B^* \quad (2.22)$$

and  $B^*$  is the second virial coefficient reduced by the value of the second virial coefficient of a rigid sphere system.

To gather further insight into  $\Theta$  we shall consider its significance in the case of several types of molecular interactions.

### 3. MODEL POTENTIALS

#### Rigid Spheres

As previously stated the present development is a generalization of the rigid sphere theory of Reiss, Frisch, and Lebowitz.<sup>1</sup> In the rigid sphere case the potential has the form

$$u(r) = \begin{cases} \infty & r < a, \\ 0 & r > a. \end{cases} \quad (3.1)$$

Using the standard technique<sup>1,7</sup> for evaluating the integral involved in the definition of  $\Theta$ , Eq. (2.9), we find

$$\Theta(\lambda, \rho) = g(\lambda a+, \lambda) \equiv G(\lambda a, \rho) \quad (3.2)$$

where  $G$  is the symbol used in I. The derivations employed here therefore serve as an alternative to the probability arguments used there.

#### Square Wells

The square well is among the simplest potentials capable of qualitatively exhibiting real fluid behavior,

<sup>7</sup> T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Chap. 6.

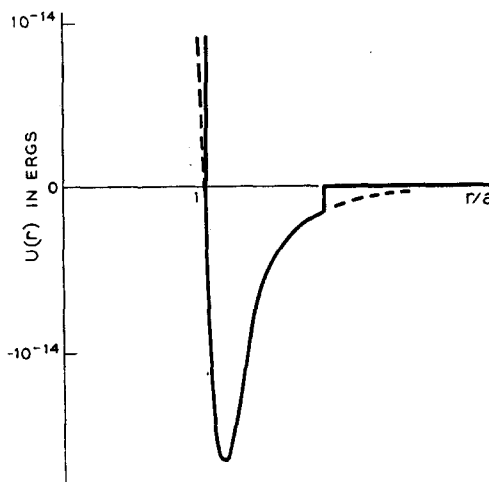


FIG. 1. Comparison of the finite range potential — with the Lennard-Jones 6-12 potential ---- for argon.

e.g., a vapor-liquid transition. Therefore, we shall frequently specialize to this case in order to avoid undue complications in illustrating techniques. For a potential of the form

$$u(r) = \begin{cases} \infty, & r < a, \\ -\epsilon, & a < r < \gamma a, \\ 0, & \gamma a < r, \end{cases} \quad (3.3)$$

we find that the  $\Theta$  function in terms of radial distribution functions is

$$\Theta(\lambda, \rho) = g(\lambda a+, \lambda) - \gamma^3 \omega g(\gamma \lambda a+, \lambda), \quad (3.4)$$

where  $\omega = [\exp(\epsilon/kT) - 1]$ .

#### Finite Range Potential

While we are discussing potential models, let us introduce one which will be quite useful in the subsequent discussion, and which is capable of quantitatively emulating real fluids. This potential has the form (cf., Fig. 1)

$$u(r) = \begin{cases} \infty, & r < a, \\ v(r), & a < r < \gamma a, \\ 0, & \gamma a < r, \end{cases} \quad (3.5)$$

where  $v(r)$  is any suitable function, e.g., the Lennard-Jones 6-12. In such a case the rigid core cutoff might be chosen where  $v(r) = 0$ . It will not strain matters too severely if we restrict  $\gamma$  to be less than 2. More general conditions are tractable but in places lead to a slightly more complicated formalism.

Hitherto we have discussed  $\Theta$  primarily in terms of radial distribution functions. Our aim was to develop a physical description in terms of a quantity which has long been familiar. We will now proceed to a considera-

tion of the properties of  $\Theta$  itself, namely, to the development of certain conditions which describe it.

#### 4. CONDITIONS ON $\Theta$

##### Integral Condition

In view of the fact that Eqs. (2.10) and (2.11) for  $p$  and  $\mu$  are formally identical with Eqs. (1.1) and (2.9) of I from the theory of rigid-sphere fluids, the integral condition (2.22) of I will apply, with the replacement of  $G$  by  $\Theta$ . Briefly stated we employ the thermodynamic equation

$$p = \int_0^{\rho} \rho (\partial \mu / \partial \rho) \tau d\rho \quad (4.1)$$

with Eq. (2.10) on the right-hand side and (2.11) on the left. We find

$$\frac{2}{3} \pi \rho^2 \Theta(1, \rho) = \rho^2 \int_0^1 4\pi \lambda^2 \Theta(\lambda, \rho) d\lambda - \int_0^{\rho} \rho' d\rho' \int_0^1 4\pi \lambda^2 \Theta(\lambda, \rho') d\lambda \quad (4.2)$$

as an exact condition. This equation does not have a unique solution. Nevertheless it is evident that Eq. (4.2) strongly restricts the possible shape of the  $\Theta$  function. In addition it is capable of telling us quite a bit about the density dependence of  $\Theta$  when its dependence on  $\lambda$  is known. (Note the indefinite limit on the  $\rho$  integration as opposed to the definite limit on the  $\lambda$  integration.)

As in I it is possible to derive an integral equation for  $\Theta$  with definite  $\lambda$  limits by considering the statistical mechanics of mixtures. Development of this point will be postponed until Sec. 5.

##### Value for Small $\lambda$

The exact expression for the  $\Theta$  function may be determined for a range of small values of  $\lambda$ . This possibility arises as a consequence of the finite upper cutoff possessed by the intermolecular potential function [ $u(r) = 0$  for  $r > \gamma a$ ]. There are several approaches to this calculation and we shall present two of them. The first is based on Eqs. (2.14)–(2.20).

According to the definition of the Mayer  $f$  function,  $f$  vanishes when  $u$  vanishes; i.e.,  $f(r/\lambda) = 0$  for  $r \geq \gamma \lambda a$ . On the other hand it is a property of the radial distribution function that  $g(r_{12}) = 0$  for  $r_{12} < a$ . Examining Eq. (2.20) for  $\Phi_2$  we see that for values of  $\lambda < 1/(2\gamma)$  there is no configuration of particles 1 and 2 such that the radial distribution function or one or the other of the  $f$  functions in the product does not vanish. The same argument applies to all higher order  $\Phi_m$ , so that

$$\Phi_m(r, \lambda < 1/2\gamma) = 0 \quad \text{for } m \geq 2. \quad (4.3)$$

$\Theta(\lambda < 1/2\gamma, \rho)$  may thus be expressed in terms of  $\Phi_1$  (i.e., the second virial coefficient) only, and by Eqs.

(2.14), (2.15), (2.18), and (2.21), one finds

$$\Gamma(\lambda < 1/2\gamma) = 1 - \left(\frac{4}{3}\right) \pi \rho a^3 \lambda^3 B^*, \quad (4.4)$$

$$\Theta(\lambda < 1/2\gamma) = B^* / [1 - \left(\frac{4}{3}\right) \pi \rho a^3 \lambda^3 B^*]. \quad (4.5)$$

Equation (4.5) may also be obtained directly from the definition of the  $\Theta$  function, Eq. (2.9), by studying the radial distribution function  $g(r, \lambda)$ . The effective range of integration in (2.9) is  $r < \gamma \lambda a$  where the potential does not vanish. For values of  $\lambda < 1/2\gamma$  the  $\lambda$ -cule may be in interaction with but one molecule at a time. This is brought out in Fig. 2 where a molecule and  $\lambda$ -cule (with  $\lambda < 1/2\gamma$ ) are pictured as being in interaction. One notes that when the center of molecule 2 is inside the potential range of the  $\lambda$ -cule no other molecule can approach within  $(\gamma \lambda a)$  of the  $\lambda$ -cule because of the rigid core sphere of exclusion of molecule 2. Thus the radial distribution function between molecules and  $\lambda$ -cules has the  $r$  dependence of a Boltzmann factor,  $\exp[-u(r/\lambda)/kT]$ . The prefactor, however, is not unity and to determine it, it is necessary to discuss the problem in a quantitative fashion.

The radial distribution function is defined to order  $1/N$  by [cf. Eqs. (2.2), (2.4), and (2.7)]

$$g(r_{12}, \lambda) = [V^2/Z(\lambda)] \int \exp[-U_{N-1}(\mathbf{r}_2, \dots, \mathbf{r}_N)/kT] \times \prod_{i=2}^N \exp[-u(r_{1i}/\lambda)/kT] d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (4.6)$$

For the given range of  $r$  and  $\lambda$  particle 1 (the  $\lambda$ -cule) can interact only with particle 2, as was just explained, so that in the product which appears in the integrand only the  $i=2$  term differs from unity. By expressing all distances relative to  $\mathbf{r}_2$  we may write

$$g(r_{12}, \lambda) = \{ \exp[-u(r_{12}/\lambda)/kT] \} / \Gamma(\lambda). \quad (4.7)$$

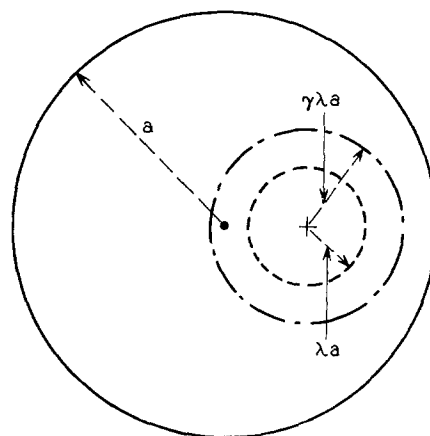


FIG. 2. A  $\lambda$ -cule with  $\lambda < 1/2\gamma$  in interaction with a molecule. Note that no other molecule can enter sphere of interaction of the  $\lambda$ -cule. + center of the  $\lambda$ -cule, • center of the molecule, ——— sphere of exclusion of molecule, ——— range of interaction of  $\lambda$ -cule, — — — sphere of exclusion of  $\lambda$ -cule.

Using Eq. (4.4) for  $\Gamma(\lambda)$  and inserting  $g$  into Eq. (2.9), we obtain

$$\Theta(\lambda < 1/2\gamma) = - (a^3 kT)^{-1} [1 - (\frac{4}{3}) \pi \rho a^3 \lambda^3 B^*] \times \int_0^\infty s u'(s) e^{-u(s)/kT} s^2 ds. \quad (4.8)$$

The integral on the right-hand side may be written as

$$-kT \int_0^\infty s^3 \{d[e^{-u(s)/kT} - 1]/ds\} ds,$$

so that an integration by parts yields Eq. (4.5) for  $\Theta(\lambda < 1/2\gamma)$ .

### Continuity Conditions

It is possible to study the analytic properties of  $\Theta$  as a function of  $\lambda$  at  $\lambda = 1/2\gamma$ , and in particular the continuity of  $\Theta$  and its derivatives. The chain of reasoning we shall use will be to show that the first discontinuous derivative of  $\mathbf{y}(\lambda)$  at  $1/2\gamma$  is the third, which implies, by Eq. (2.15), that  $W(\lambda)$  and its first two derivatives are continuous. This, in turn, leads one, by Eq. (2.14), to the conclusion that  $\Theta$  and its first derivative are continuous at  $\lambda = 1/2\gamma$ .

As seen previously, up to  $\lambda = 1/2\gamma$  the function  $\mathbf{y}(\lambda)$  is given in terms of  $\Phi_1(\lambda)$  which has been evaluated in Eq. (2.21) and which is continuous. At  $\lambda = 1/2\gamma$  the function  $\Phi_2$  enters  $\Gamma$  since now two  $f$ 's can be simultaneously nonzero ( $\Phi_m, m \geq 3$  still vanishes). Thus we may concentrate on a study of the continuity properties of  $\Phi_2$ .

To simplify the discussion let us restrict consideration, at first, to the square well model. For such a potential it is possible to greatly simplify  $\Phi_2$ ; viz., all but one of the sixfold integrations may be performed. One finds that<sup>8</sup>

$$\Phi_2 = -8\pi^2 \{ (\omega + 1)^2 L(\lambda, \lambda) - 2(\omega + 1)\omega [L(\gamma, \gamma\lambda) - L(-\gamma, \gamma\lambda)] + \omega^2 L(\gamma\lambda, \gamma\lambda) \}, \quad (4.9)$$

where  $\omega = \exp(\epsilon/kT) - 1$ ,  $\epsilon$  is the depth of the well, and  $L$  is the integral

$$L(u, v) = -(\frac{1}{2}\gamma) a^6 \int_0^{u+v} s g(sa) \times [s^4 - 6s^2(u^2 + v^2) + 8s(u^3 + v^3) - 3(u^2 - v^2)^2] ds. \quad (4.10)$$

In this form the derivatives may be explicitly taken and examined. One finds that  $\Phi_2, d\Phi_2/d\lambda$ , and  $d^2\Phi_2/d\lambda^2$  are continuous for all values of  $\lambda$ . The third derivative  $d^3\Phi_2/d\lambda^3$  has a discontinuity at  $\lambda = 1/2\gamma$  (recall that this is the first point for which  $\Phi_2 \neq 0$ ) as well as at many

<sup>8</sup> The calculation is quite extensive, although for the most part straightforward. Converting to bipolar coordinates renders three of the variables of integration redundant. Two more of the variables appear only in the limits of integration. One proceeds further by inverting the order of integration to make the  $s=r_{23}$  integration the last. Extensive use may be made of symmetry if one defines  $g(-s) = g(+s)$ .

greater values of  $\lambda$ . Explicitly the third derivative is given for any  $\lambda$  by

$$d^3\Phi_2/d\lambda^3 = 8\pi^2 \lambda^3 a^6 [8(\omega + 1)^2 g(2\lambda a) - \gamma(\gamma + 1)^4 (\omega + 1)\omega g(\lambda a + \gamma\lambda a) + 8\gamma^6 \omega^2 g(2\gamma\lambda a)] + \text{continuous part}, \quad (4.11)$$

so that the points of discontinuity are determined by those of the radial distribution function. We shall return to this point shortly.

Following the chain of reasoning outlined earlier we conclude that  $\Theta$  and its first derivative are continuous at  $\lambda = 1/2\gamma$ . In the case of a hard sphere system it can be shown<sup>1</sup> that the first discontinuities in  $\Phi_m$  appear in the  $(2m - 1)$  derivative.<sup>9</sup> Because of the similarity in the type of integral which appears for square well and hard sphere one is tempted to conjecture that this result applies also to the more general potential. If this is the case then one would have that  $\Theta$  and its first derivative are continuous for all  $\lambda$ .

By means of a change of variables in Eq. (2.20) for  $\Phi_m$  one can shift points of view on this continuity problem. Thus, write

$$\Phi_m = \lambda^m \int \left[ \prod_{i=2}^{m+1} f(z_{1i}) \right] \times g^{(m)}(\lambda z_{12}, \dots, \lambda z_{1,m+1}) dz_{12} \dots dz_{1,m+1}, \quad (4.12)$$

from which it is seen that the analytic properties of  $\Phi_m$  are totally related to the analytic properties of  $g^{(m)}$ .

While attention has been confined to the square well in this section the results are actually quite general. The discontinuities in the  $f$  function are what lead to discontinuous  $\Theta$  derivatives. Whether  $f$  is flat between discontinuities or not is unimportant. As a matter of fact if  $f$  were completely analytic  $\Theta$  would be analytic. However, if  $f$  undergoes drastic changes in short, but finite distance, as it is known to do physically,  $\Theta$  would also change drastically in nature with a small, but finite, increment of  $\lambda$ .

### Infinity Condition

When the  $\lambda$ -cule becomes very large it is possible to consider its effects from the point of view of macroscopic thermodynamics. In the case of a rigid-sphere potential (footnote reference 1) the  $\lambda$ -cule behaves like a rigid wall.  $\Theta$  for hard spheres is related to the density of molecules at the wall, while this density, in turn, is directly proportional to the pressure. The infinity condition for a more general potential is not as simple, but one still can be found. Once again the salient features of the derivation are brought out most clearly when discussion is restricted to the square well potential. Let us consider a system with a very large  $\lambda$ -cule in its interior. The volume of the system,  $V$ , may be

<sup>9</sup>  $\Phi_m$  corresponds to the function  $(-1)^m F_m$  of I.

divided into three regions. Part 1, of volume  $V_1 = V - (\frac{4}{3})\pi\lambda^3 a^3$ , is outside the sphere of interaction of the  $\lambda$ -cule. Volume 2,  $V_2 = \frac{4}{3}\pi(\gamma^3 - 1)\lambda^3 a^3$ , is within the well of the  $\lambda$ -cule. Region 3 is the exclusion sphere of the  $\lambda$ -cule. For the present discussion we will consider the total system to be infinite. The  $\lambda$ -cule is now also taken as approaching infinity but with  $(V_2 + V_3)/V \rightarrow 0$ . In this way the over-all density is unaffected by its presence. The work of expanding the  $\lambda$ -cule is related to the Helmholtz free energy of the system  $A$  by

$$dW = dA = - \sum_{i=1}^3 p_i dV_i + \sum_{i=1}^3 \tilde{\mu}_i dN_i + \text{surface of } \lambda\text{-cule terms.} \quad (4.13)$$

The summations are over the three regions. The surface terms are of higher order in  $1/\lambda$  and may be neglected here. The pressure  $p_3$  is zero since no particles can get inside 3. The important volume changes may be related to  $d\lambda$  by the expressions in the earlier part of this paragraph. The total chemical potentials,  $\tilde{\mu}_i$ , include the effect of the  $\lambda$ -cule's field, and must be equal in the equilibrium condition. There are no molecules in region 3 so  $dN_3 = 0$ , and therefore  $dN_1 = -dN_2$ . On using these facts with Eq. (2.13) we may write

$$dW = 4\pi\lambda^2 \rho_1 a^3 kT \Theta(\infty, \rho_1) d\lambda, \\ = 4\pi\lambda^2 a^3 \rho_1 d\lambda - 4\pi\lambda^2 a^3 (\gamma^3 - 1) \rho_2 d\lambda. \quad (4.14)$$

The pressures may be expressed in terms of  $\Theta$  functions by Eq. (2.10) so that one obtains as a condition relating  $\Theta(\infty)$  to  $\Theta(1)$

$$\rho_1 \Theta(\infty, \rho_1) = \gamma^3 [\rho_1 + \frac{2}{3}\pi a^3 \rho_1^2 \Theta(1, \rho_1)] \\ = (\gamma^3 - 1) [\rho_2 + \frac{2}{3}\pi a^3 \rho_2^2 \Theta(1, \rho_2)]. \quad (4.15)$$

This equation is actually somewhat complex in that  $\rho_2$  is a function of  $\rho_1$ . A relation between these two densities arises from the condition

$$0 = \tilde{\mu}_2 - \tilde{\mu}_1 = (\mu_2 - \epsilon) - \mu_1, \quad (4.16)$$

which yields, by Eq. (2.11),

$$\epsilon/kT = \ln(\rho_2/\rho_1) + 4\pi a^3 \int_0^1 \lambda^2 [\rho_2 \Theta(\lambda, \rho_2) - \rho_1 \Theta(\lambda, \rho_1)] d\lambda, \quad (4.17)$$

to be considered simultaneously with Eq. (4.15).

The case of hard spheres may be obtained by specializing to  $\gamma = 1$  with finite  $\epsilon$ , or by letting  $\epsilon = 0$ . In either limit Eq. (3.14) reduces to

$$\Theta_{HS}(\infty, \rho) = G(\infty, \rho) = p/\rho kT,$$

where  $G$  is the notation of I.

**5. A MORE GENERAL INTEGRAL EQUATION FROM THE MIXTURE VIEWPOINT**

In footnote reference 1 the possibility of writing a determinate integral equation for  $G$  by considering

dilute mixtures of  $\lambda$ -cules in molecules was exploited. It is easily shown that the parallelism between  $\Theta$  and  $G$  applies here and one may write the same equation for real fluids; viz.,

$$Q(\lambda, \rho) = -\rho a^3 (\partial/\partial \rho) \left\{ \rho \int_0^\lambda 4\pi\lambda^2 \Theta(\lambda, \rho) d\lambda \right. \\ \left. + \frac{4}{3}\pi\rho a^3 \lambda^3 \Theta(\lambda, \rho) \right\}, \quad (5.1)$$

where

$$Q(\lambda, \rho) = -\frac{2}{3}\pi a^3 \rho^2 [\partial \Theta(1, \rho) / \partial \rho_\lambda]_{\rho_\lambda \rightarrow 0}. \quad (5.2)$$

With the definition of  $\Theta$ , Eq. (2.9), we obtain

$$Q(\lambda, \rho) = \frac{2}{3}\pi\rho^2 \int_0^\infty r u'(r) [\partial g_{mm}(r, \rho, \rho_\lambda) / \partial \rho_\lambda]_{\rho_\lambda \rightarrow 0} r^2 dr, \quad (5.3)$$

where  $g_{mm}(r, \rho, \rho_\lambda)$  is the molecule-molecule radial distribution function in a mixture with molecule density  $\rho$  and  $\lambda$ -cule density  $\rho_\lambda$ .

In order to develop further insight into the  $Q$  function it is of interest to find another expression for it in terms of correlation functions. The  $\rho_\lambda$  derivative of  $g_{mm}$  may be written as

$$V^{-1} [\partial g_{mm} / \partial \rho_\lambda]_{\rho_\lambda \rightarrow 0} = [\partial g_{mm} / \partial N_\lambda]_{N_\lambda \rightarrow 0} \\ = g_{mm}(N_\lambda = 1) - g_{mm}(N_\lambda = 0), \quad (5.4)$$

where  $N_\lambda$  is the number of  $\lambda$ -cules. Now if the presence of a single  $\lambda$ -cule is reflected in  $g_{mm}$  by specification of the value of  $\lambda$ , i.e.,  $g_{mm}(\lambda)$ , then

$$V^{-1} [\partial g_{mm} / \partial \rho_\lambda]_{\rho_\lambda \rightarrow 0} = g_{mm}(\lambda) - g_{mm}(0) \\ = \int_0^\lambda [\partial g_{mm}(\lambda') / \partial \lambda'] d\lambda'. \quad (5.5)$$

The molecule correlation function  $g_{k_1, \dots, k_n}^{(n)}(\mathbf{r}_{k_1}, \dots, \mathbf{r}_{k_n}, \lambda)$  ( $g_{mm}^{(2)}$ ) is the radial distribution function ( $g_{mm}$ ) may be expressed to order  $1/(N-n)$  as

$$g_{k_1, \dots, k_n}^{(n)}(\lambda) = [V^n / Z(\lambda)] \int_V \dots \int_V \\ \times \exp[-U_N(\lambda)/kT] \prod_{j=1, \dots, k_1, \dots, k_n} d\mathbf{r}_j, \quad (5.6)$$

where the  $\lambda$ -cule is particle 1. Differentiating  $\ln g_{23}^{(2)}(\mathbf{r}_{23}, \lambda)$  with respect to  $\lambda$ , multiplying by  $g_{23}^{(2)}(\lambda)$ , and introducing higher-order correlation functions yields, after some manipulations,

$$\frac{\partial g_{23}^{(2)}(\lambda)}{\partial \lambda} = \frac{(N-3)}{kTV^2} \iint \frac{\partial u(\mathbf{r}_{14}/\lambda)}{\partial \lambda} \\ \times [g_{14}^{(2)}(\lambda) g_{23}^{(2)}(\lambda) - g_{1234}^{(4)}(\lambda)] d\mathbf{r}_1 d\mathbf{r}_4 \\ + \frac{2}{kTV} \int \frac{\partial u(\mathbf{r}_{12}/\lambda)}{\partial \lambda} \\ \times [g_{12}^{(2)}(\lambda) g_{23}^{(2)}(\lambda) - g_{123}^{(3)}(\lambda)] d\mathbf{r}_1. \quad (5.7)$$

Employing (5.4), (5.5), and (2.6), we arrive at

$$\begin{aligned}
 [\partial g_{23}^{(2)}/\partial \rho_\lambda]_{\rho_{\lambda=0}} &= [(N-3)/kT] \int_0^\lambda \lambda'^2 d\lambda' \iint (r_{14}/\lambda') u'(r_{14}/\lambda') [g_{1234}^{(4)}(\lambda') - g_{14}^{(2)}(\lambda') g_{23}^{(2)}(\lambda')] (d\mathbf{r}_1 d\mathbf{r}_4/\lambda'^3) \\
 &+ (2/kT) \int_0^\lambda \lambda'^2 d\lambda' \int (r_{12}/\lambda') u'(r_{12}/\lambda') [g_{123}^{(3)}(\lambda') - g_{12}^{(2)}(\lambda') g_{23}^{(2)}(\lambda')] (d\mathbf{r}_1/\lambda'^3), \quad (5.8)
 \end{aligned}$$

which may be substituted immediately into Eq. (5.3) for  $Q$ . It is to be noted that important contributions to both integrals of Eq. (5.8) come only from the region where the  $\lambda$ -cule, particle 1, is near the pair 2,3. In the second integral this is evident from the short range nature of  $u(r_{12}/\lambda)$ . In the first integral the potential  $u(r_{14}/\lambda)$  requires that 1 be near 4. Thus when 1 is far

from 2, 3, so is 4. The particles are then correlated only in pairs so that  $g_{1234}^{(4)} = g_{14}^{(2)} g_{23}^{(2)}$  and the integrand vanishes.

It will be convenient to examine certain properties of  $Q$  by referring to the hard sphere case. In this instance Eq. (5.3) becomes

$$Q_{HS}(\lambda, \rho) = -\frac{2}{3} a^3 \rho^2 \left[ \frac{\partial g_{23}^{(2)}(r_{23}=a, \lambda)}{\partial \rho_\lambda} \right]_{\rho_{\lambda=0}}. \quad (5.9)$$

Let us consider the value of  $Q$  for  $\lambda \leq \frac{1}{2}$ . In the first integral of Eq. (5.8), because of the  $\delta(r_{14}-\lambda a)$  nature of  $u'(r_{14}/\lambda)$ , the  $\lambda$ -cule must be wholly inside of particle 4 for a nonvanishing integrand. In this case the  $\lambda$ -cule cannot be in contact with, or in any way influence, any particle except 4, so that

$$g_{1234}^{(4)}(\lambda) = g_{14}^{(2)}(\lambda) g_{234}^{(3)}(\lambda), \quad \lambda < \frac{1}{2}. \quad (5.10)$$

The first integral may be written, for  $\lambda < \frac{1}{2}$ , as

$$[(N-3)/kT] \int_0^\lambda (d\lambda'/\lambda'^2) \int r_{14} u'(r_{14}/\lambda') g_{14}^{(2)}(\lambda') d\mathbf{r}_{14} \{ \int [g_{234}^{(3)}(\lambda') - g_{23}^{(2)}(\lambda')] d\mathbf{r}_4 \}. \quad (5.11)$$

By definition of the correlation function, Eq. (5.6), the expression in { } vanishes. In the second integral on the right-hand side of (5.8) the  $\lambda$ -cule must be totally inside of particle 2 so that

$$g_{123}^{(3)}(\lambda) = g_{12}^{(2)}(\lambda) g_{23}^{(2)}(\lambda), \quad \lambda < \frac{1}{2}, \quad (5.12)$$

and this term also vanishes. Thus, for  $\lambda < \frac{1}{2}$  in the hard sphere case we have  $Q_{HS}(\lambda < \frac{1}{2}, \rho) = 0$ , a result already obtained in I in a different manner.

Similar results may be demonstrated for the general case of a potential with core at  $a$  and cutoff at  $\gamma a$ . In this instance we have

$$Q(\lambda, \rho) = 0, \quad \lambda \leq 1/2\gamma. \quad (5.13)$$

It is easily shown that the  $\Theta(\lambda < 1/2\gamma)$  of Eq. (4.5) is a solution of Eq. (4.1) when  $Q=0$ .