

PERTURBATION THEORIES OF LIQUIDS

In the previous chapter we have studied the radial distribution function theory of liquids. This constitutes a rigorous statistical mechanical theory. Although we eventually had to introduce some sort of approximations into the formalism, we at least started from general principles. Because of this, however, the results are not particularly simple to use in practical calculations. There is an interesting and important result from the developments in Chapter 13 that we shall exploit in this chapter. Much evidence points to the fact that the structure of a liquid is primarily determined by the short-range repulsive forces and that the relatively longer-range attractive part of the potential provides a net force that gives a somewhat uniform attractive potential. Thus, in a sense we picture the repulsive part of the potential as determining the structure of the liquid and the attractive part as holding the molecules together at some specified density.

For example, except for the discontinuity at $r = \sigma$, the radial distribution function of a hard-sphere fluid is fairly similar to that of a real fluid. In particular, if this discontinuity is removed by multiplying $g(r)$ by $\exp[u(r)]$ to give $y(r)$, we find that this function is quite similar for hard spheres and real fluids. The function $y(r)$ is shown in Fig. 13-8 for hard spheres, but a similar result would be found for a Lennard-Jones potential.

Molecular dynamics calculations have also been used to show that the structure of a real fluid is similar to a hard-sphere fluid. Verlet* has carried out extensive molecular dynamics calculations on a system of molecules interacting with a Lennard-Jones 6-12 potential and has calculated the so-called structure factor $\hat{h}(k)$ of the fluid. The structure factor is related to the Fourier transform of $h(r) = g(r) - 1$, i.e., by

$$\hat{h}(k) = \rho \int e^{-ik \cdot r} h(r) dr \quad (14-1)$$

Verlet calculated $\hat{h}(k)$ since it is directly measured by X-ray scattering from the liquid.

* L. Verlet, *Phys. Rev.*, 165, p. 201, 1968.

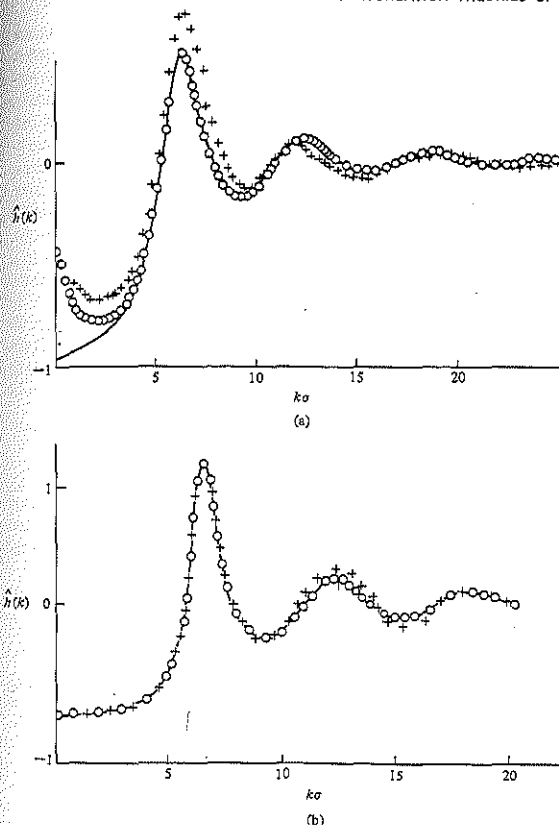


Figure 14-1. The structure factor, $\hat{h}(k)$, plotted as a function of the wave vector ka . The circles are the results from molecular dynamics calculations; the solid line is a hard-sphere model with an effective hard-sphere diameter; and the crosses represent neutron diffraction data. In (a) the reduced temperature is 1.326 and the reduced density is 0.5426. In (b), these values are 0.827 and 0.75, respectively. (From L. Verlet, *Phys. Rev.*, 165, p. 201, 1968.)

Figure 14-1 shows two graphs taken from Verlet's paper. The dots are the molecular dynamics results, and the solid lines in both Fig. 14-1(a) and (b) are the results for a hard-sphere fluid with an effective hard-sphere diameter that is a function of the temperature and the density. The important point is that at high densities the structure factor of the real (Lennard-Jones 6-12) fluid can be well represented by a hard-sphere structure factor.

This physical picture suggests that we attempt to treat a fluid as a system of molecules governed by a repulsive potential with an attractive potential that is treated as

a small perturbation. The unperturbed system, i.e., the system of repulsive molecules, is usually taken to be a system of hard spheres since this system is fairly well understood from Chapter 13. In Section 14-1 we shall introduce the basic statistical mechanical perturbation theory due to Zwanzig. Then in Section 14-2 we shall make a simple application of this perturbation theory formalism to derive the van der Waals equation. Remember that van der Waals in 1873 treated a liquid as a system of hard-sphere molecules with an attractive potential that gave a uniform background energy. Thus he was one of the earliest to use the perturbation theory ideas presented here. Van der Waals did not have the benefit of modern developments in the statistical mechanics of hard-sphere fluids and statistical mechanical theory of fluids in general, and we shall see how it is possible to improve upon the van der Waals equation in a very obvious and organized way. There were a number of developments along these lines in the late 1960s, and Section 14-3 will discuss some of these. We shall see in that section that the perturbation approach to liquids can be brought to the point of providing a simple, convenient theory of liquids that is numerically reliable well past the critical point and into the temperatures and densities of dense liquids. Recall that the integral equations of Chapter 13 gave poor numerical agreement near and below the critical region.

14-1 STATISTICAL MECHANICAL PERTURBATION THEORY

In this section we describe the statistical mechanical perturbation theory developed by Zwanzig in 1954.* The results are obtained by performing a perturbation expansion on the canonical partition function of the system and on the configuration integral in particular.

Let the total potential energy be separated into two parts,

$$U_N = U_N^{(0)} + U_N^{(1)} \quad (14-2)$$

where $U_N^{(0)}$ is the potential energy of an unperturbed (reference) system and $U_N^{(1)}$ is the perturbation. The reference system is usually taken to be a hard-sphere system, but this is, of course, not necessary. The perturbation potential is usually defined by the difference between the potential of the real system and the potential of the reference system, i.e., by $U_N^{(1)} = U_N - U_N^{(0)}$.

The configurational integral for this potential is

$$Z_N = \int \cdots \int e^{-\beta[U_N^{(0)} + U_N^{(1)}]} d\mathbf{r}_1 \cdots d\mathbf{r}_N$$

We now multiply and divide by

$$\int \cdots \int \exp(-\beta U_N^{(0)}) d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_N = Z_N^{(0)}$$

to get

$$Z_N = \int \cdots \int e^{-\beta U_N^{(0)}} d\mathbf{r}_1 \cdots d\mathbf{r}_N \frac{\int \cdots \int e^{-\beta[U_N^{(0)} + U_N^{(1)}]} d\mathbf{r}_1 \cdots d\mathbf{r}_N}{\int \cdots \int e^{-\beta U_N^{(0)}} d\mathbf{r}_1 \cdots d\mathbf{r}_N}$$

Note that the second factor here can be considered to be the average of $\exp(-\beta U_N^{(1)})$ over the unperturbed or reference system. Thus we can write

$$Z_N = Z_N^{(0)} \langle \exp(-\beta U_N^{(1)}) \rangle_0 \quad (14-3)$$

* R. W. Zwanzig, *J. Chem. Phys.*, 22, p. 1420, 1954.

where $Z_N^{(0)}$ is the configurational integral of the unperturbed system and $\langle \rangle_0$ indicates a canonical average in the unperturbed system. We assume that we know $Z_N^{(0)}$, and we shall consider $U_N^{(1)}$ to be small enough to expand the exponential in $U_N^{(1)}$. This gives an expansion in powers of β or $1/T$, according to

$$\langle \exp(-\beta U_N^{(1)}) \rangle_0 = 1 - \beta \langle U_N^{(1)} \rangle_0 + \frac{\beta^2}{2!} \langle (U_N^{(1)})^2 \rangle_0 + \cdots \quad (14-4)$$

We wish, however, to express the free energy and related thermodynamic functions as a power series in β . Since $A = -kT \ln Q$ and $Q = Z_N/N! \Lambda^{3N}$, we can write

$$\begin{aligned} -\beta A &= \ln \left(\frac{Z_N^{(0)}}{N! \Lambda^{3N}} \right) + \ln \langle \exp(-\beta U_N^{(1)}) \rangle_0 \\ &= -\beta A_0 - \beta A^{(1)} \end{aligned} \quad (14-5)$$

where clearly A_0 is the free energy of the reference system and $A^{(1)}$ is the perturbation free energy:

$$A^{(1)} = -kT \ln \langle \exp(-\beta U_N^{(1)}) \rangle_0 \quad (14-6)$$

It is this quantity that we wish to express as a power series in β . We write

$$A^{(1)} = \sum_{n=1}^{\infty} \frac{\omega_n}{n!} (-\beta)^n \quad (14-7)$$

where the ω_n are to be determined in terms of the $\langle (U_N^{(1)})^n \rangle_0$ of Eq. (14-4) by writing

$$\exp(-\beta A^{(1)}) = \exp \left(\sum_{n=1}^{\infty} \frac{\omega_n}{n!} (-\beta)^n \right)$$

We now expand the right-hand side in powers of β and compare like coefficients of β^n to

$$\begin{aligned} \exp(-\beta A^{(1)}) &= \langle \exp(-\beta U_N^{(1)}) \rangle_0 \\ &= \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \langle (U_N^{(1)})^k \rangle_0 \end{aligned}$$

Straightforward algebra gives the first few ω_n :

$$\begin{aligned} \omega_1 &= \langle U_N^{(1)} \rangle_0 \\ \omega_2 &= \langle (U_N^{(1)})^2 \rangle_0 - \langle U_N^{(1)} \rangle_0^2 \\ \omega_3 &= \langle (U_N^{(1)})^3 \rangle_0 - 3 \langle (U_N^{(1)})^2 \rangle_0 \langle U_N^{(1)} \rangle_0 + 2 \langle U_N^{(1)} \rangle_0^3 \end{aligned} \quad (14-8)$$

It is possible to derive a general formula for this, but it is not necessary here.*

Thus we have shown that at high temperatures, the free energy is

$$A = A_0 + \omega_1 - \frac{\omega_2}{2kT} + O(\beta^2) \quad (14-9)$$

The first term in the expansion, $\omega_1 = \langle U_N^{(1)} \rangle_0$, simplifies considerably when $U_N^{(1)}$ can be written as a sum of pair potentials,

$$U_N^{(1)} = \sum_{i < j} u^{(1)}(r_{ij})$$

* R. W. Zwanzig, *J. Chem. Phys.*, 22, p. 1420, 1954.

since in this case

$$\begin{aligned}\langle U_N^{(1)} \rangle_0 &= \left\langle \sum_{i < j} u^{(1)}(r_{ij}) \right\rangle_0 = \frac{N(N-1)}{2} \langle u^{(1)}(r_{12}) \rangle_0 \\ &= \frac{N(N-1)/2}{Z_N^{(0)}} \int \cdots \int e^{-\beta U_N^{(0)}} u^{(1)}(r_{12}) d\mathbf{r}_1 \cdots d\mathbf{r}_N \\ &= \frac{1}{2} \int \int u^{(1)}(r_{12}) \rho_0^{(2)}(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{\rho^2 V}{2} \int u^{(1)}(r_{12}) g_0^{(2)}(r_{12}) d\mathbf{r}_{12} \quad (14-10)\end{aligned}$$

The zero subscript in the last two integrals indicates that the distribution function is that of the reference system.

On the other hand, terms like $\langle U_N^{(1)2} \rangle_0$ are awkward since they introduce higher-order density functions, namely, $P^{(3)}$ and $P^{(4)}$, which are due to terms like $u(r_{ij})u(r_{jk})$ and $u(r_{ij})u(r_{ki})$ which arise when $U_N^{(1)}$ is squared. We shall not require this second-order term in most of what we do here, and so we do not write it out.

Equations (14-3), (14-4), and (14-8) are the basic results of this section. In order to apply them, we must choose some reference fluid and hence $U_N^{(0)}$ and $U_N^{(1)}$. This is where the various applications, which we shall discuss in Section 14-3, differ from one another. Before going on to discuss these, however, we shall derive the van der Waals equation from a simple application of the equations of this section.

14-2 THE VAN DER WAALS EQUATION

We start with Eq. (14-3),

$$Z_N = Z_N^{(0)} \langle \exp(-\beta U_N^{(1)}) \rangle_0$$

and take the reference system to be a hard-sphere fluid. We furthermore assume that U_N is pair-wise additive and to be of the form $u(r) = u_{HS}(r) + u^{(1)}(r)$, where $u^{(1)}(r)$ is some arbitrary attractive part (and so is negative). We then assume that $\beta U_N^{(1)}$ is small enough that we can write

$$\begin{aligned}\langle \exp(-\beta U_N^{(1)}) \rangle_0 &\approx 1 - \beta \langle U_N^{(1)} \rangle_0 \\ &\approx \exp(-\beta \langle U_N^{(1)} \rangle_0) \quad \langle U_N^{(1)} \rangle_0 = \frac{\rho^2 V}{2} \int u^{(1)}(r) g_{HS}(r) 4\pi r^2 dr \quad (14-11)\end{aligned}$$

Equation (14-11) follows since we are assuming that terms in β^2 and higher can be neglected. From Eq. (14-10),

$$\langle U_N^{(1)} \rangle_0 = \frac{\rho^2 V}{2} \int_0^\infty u^{(1)}(r) g_{HS}(r) 4\pi r^2 dr$$

Certainly $g_{HS}(r)$ was not available to van der Waals, and he effectively approximated $g_{HS}(r)$ by

$$g_{HS}(r) = \begin{cases} 0 & r < \sigma \\ 1 & r > \sigma \end{cases} \quad (14-12)$$

This form is correct for hard spheres only in the limit $\rho \rightarrow 0$. Using this $g_{HS}(r)$, we have

$$\begin{aligned}\langle U_N^{(1)} \rangle_0 &= 2\pi\rho^2 V \int_\sigma^\infty u^{(1)}(r) r^2 dr \\ &= -aNp \quad (14-13)\end{aligned}$$

where

$$a = -2\pi \int_\sigma^\infty u^{(1)}(r) r^2 dr \quad (14-14)$$

The minus sign in the definition of a has been included to make a a positive number. Remember that $u^{(1)}(r)$ is negative. The specific form of $u^{(1)}(r)$ is not important here.

So far now, Eq. (14-3) has been reduced to

$$Z_N = Z_N^{(0)} e^{\beta a \rho N} \quad \ln Z_N = \ln Z_N^{(0)} + \beta a \rho N \quad (14-15)$$

and so we can write

$$\begin{aligned}\frac{p}{kT} &= \left(\frac{\partial \ln Z_N^{(0)}}{\partial V} \right)_{N,T} - \frac{a\rho^2}{kT} \\ &= \frac{p^{(0)}}{kT} - \frac{a\rho^2}{kT} \quad (14-16)\end{aligned}$$

where $p^{(0)}$ is the pressure of the unperturbed system.

The final approximation of the van der Waals theory is to assume that the hard-sphere configuration integral is of the form V_{eff}^N , where the effective volume is determined by assuming that the volume available to a molecule in the fluid has a volume $4\pi\sigma^3/3$ excluded to it by each other molecule of the system. However, we have to divide this quantity by 2 since this factor of $4\pi\sigma^3/3$ arises from a pair of molecules interacting, and only half the effect can be assigned to a given molecule. Therefore $V_{eff} = V - 2\pi N\sigma^3/3$, and we can write

$$Z_N^{(0)} = (V - Nb)^N \quad b = \frac{2\pi\sigma^3}{3} \quad (14-17)$$

Substituting Eq. (14-17) into Eq. (14-16), then, we get the famous van der Waals equation,

$$\frac{p}{kT} = \frac{\rho}{1 - b\rho} - \frac{a\rho^2}{kT} \quad (14-18)$$

Equation (14-18) is the van der Waals equation of state. Thus the constants a and b , defined in Eqs. (14-14) and (14-17), are the usual van der Waals constants, but here they are given in terms of the intermolecular potential function. We can calculate a and b for the square-well potential, for example, and compare the results to the empirically determined van der Waals parameters. The agreement is not particularly satisfactory, indicating that the van der Waals equation is not a good quantitative equation of state. Nevertheless, it does indicate a critical point and condensation by way of a simple model.

The perturbation theoretic derivation of the van der Waals equation suggests a number of obvious improvements. The most obvious ones are:

- (1) Use a better form for $g(r)$.
- (2) Use a better expression for $Z_N^{(0)}$.
- (3) Use a more realistic unperturbed system.
- (4) Consider higher terms in β .

The results of Chapter 13 allow us easily to consider points (1) and (2). We could use the analytic Percus-Yevick equations of state [Eqs. (13-91) and (13-92)], the Ree and Hoover Padé approximant [Eq. (13-3)], or the Carnahan-Starling equation of state (Problem 12-34). Furthermore, we could use the $g_{HS}(r)$ obtained from the Percus-Yevick or hypernetted-chain equations or even that calculated from molecular dynamics or Monte Carlo calculations. Points (3) and (4) are more difficult to incorporate since for point (3) we still must rely upon the results from the radial distribution theories of the previous chapter to give the unperturbed part and for (4)

because terms beyond the linear term in β require three- and four-body distribution functions. The recent advances in the statistical mechanical perturbation theory of fluids have considered points (3) and (4) above, and we discuss these in the next section.

14-3 SEVERAL PERTURBATION THEORIES OF LIQUIDS

In the late 1960s and early 1970s there was much activity in applying the statistical mechanical perturbation theory to dense fluids. In this section we shall discuss three of these theories. Each of these theories uses a fairly different approach and illustrates a particular manner in which the simple van der Waals theory of the preceding section can be improved.

THE BARKER-HENDERSON THEORY

The first generally successful approach was that due to Barker and Henderson.* For simplicity, we shall first discuss their theory for a square-well fluid and then extend their approach to real (6-12) fluids. Barker and Henderson were the first to consider the higher-order terms in the $1/T$ expansion in Eq. (14-9). The first-order term, i.e. ω_1 in Eq. (14-9), presents no difficulty [cf. Eq. (14-10)]. The second-order term involves three- and four-body distribution functions:

$$\omega_2 = \frac{N^2}{4} \iiint [P_0^{(4)}(1, 2, 3, 4) - P_0^{(2)}(1, 2)P_0^{(2)}(3, 4)] \times u^{(1)}(1, 2)u^{(1)}(3, 4) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 + N^3 \iiint P_0^{(3)}(1, 2, 3)u^{(1)}(1, 2)u^{(1)}(2, 3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 + \frac{N^2}{2} \iint P_0^{(2)}(1, 2)[u^{(1)}(1, 2)]^2 d\mathbf{r}_1 d\mathbf{r}_2 \quad (14-19)$$

where

$$P_0^{(n)}(1, 2, \dots, n) = \frac{1}{Z_N^{(0)}} \int \dots \int e^{-\beta U_N^{(0)}} d\mathbf{r}_{n+1} \dots d\mathbf{r}_N \quad (14-20)$$

We have left ω_2 in terms of the $P_0^{(n)}$ rather than the more commonly used $g_0^{(n)}(1, 2, \dots, n)$ because the conversion of Eq. (14-19) from integrals over the $P_0^{(n)}$ to integrals over $g_0^{(n)}$'s is somewhat subtle. This subtlety is due to the fact that $g(r) \rightarrow 1 + O(1/N)$ for large r ,† and so the integrand in Eq. (14-19) differs from zero by terms of order 1 in a region of molecular dimension and by terms of order $1/N$ in the whole volume; so the integral of these terms contribute the same order of magnitude to the final result. We shall not discuss this fine point any further, but refer the reader to a discussion by Henderson and Barker.‡

The important point about Eq. (14-19) is that it involves three- and four-body distribution functions, quantities that are not generally known. Barker and Henderson have approximated ω_2 in two different ways. The first method goes as follows.

* J. A. Barker and D. Henderson, *J. Chem. Phys.*, **47**, p. 2856, 1967; *Accounts of Chem. Res.*, **4**, p. 303, 1971; *Adv. Treatise of Phys. Chem.*, **8A** (in "Additional Reading"); *Ann. Rev. Phys. Chem.*, **23**, p. 439, 1972.

† See T. Hill, *Statistical Mechanics*, Appendix 7 (New York: McGraw-Hill, 1956), in "Additional Reading."

‡ See D. Henderson and J. A. Barker, in *Physical Chemistry*, Vol. 8A, edited by H. Eyring, D. Henderson, and W. Jost (New York: Academic Press, 1971) in "Additional Reading."

Imagine the range of intermolecular distances divided into intervals (r_0, r_1) , (r_1, r_2) , ..., (r_j, r_{j+1}) , ... Let $p(N_0, N_1, N_2, \dots) \equiv p(\{N_j\})$ be the probability that N_j molecules lie in the interval (r_j, r_{j+1}) in the unperturbed system. Also consider that the interval (r_j, r_{j+1}) is small enough that we can treat the perturbing potential $u^{(1)}(r)$ to have a constant value $u_j^{(1)}$ in the interval (r_j, r_{j+1}) . The configuration integral, Eq. (14-3), can then be written in the form

$$Z_N = Z_N^{(0)} \left\langle \exp \left(-\beta \sum_j N_j u_j^{(1)} \right) \right\rangle_0 = Z_N^{(0)} \sum_{\{N_j\}} p(\{N_j\}) \exp \left(-\beta \sum_j N_j u_j^{(1)} \right) \quad (14-21)$$

The quantity $p(\{N_j\})$ is as difficult to get as Z_N , but only the first two moments are necessary in order to calculate through terms of $O(\beta^2)$. To see this, expand the exponential in Eq. (14-21) to get

$$\frac{Z_N}{Z_N^{(0)}} = \sum_{\{N_j\}} p(\{N_j\}) \exp \left(-\beta \sum_j N_j u_j^{(1)} \right) = \sum_{\{N_j\}} p(\{N_j\}) - \beta \sum_j u_j^{(1)} \sum_{\{N_j\}} N_j p(\{N_j\}) + \frac{\beta^2}{2} \sum_i \sum_j u_i^{(1)} u_j^{(1)} \sum_{\{N_j\}} N_i N_j p(\{N_j\}) + \dots = 1 - \beta \sum_j u_j^{(1)} \langle N_j \rangle + \frac{\beta^2}{2} \sum_i \sum_j u_i^{(1)} u_j^{(1)} \langle N_i N_j \rangle + \dots$$

To get the expansion for the Helmholtz free energy, we take logarithms to get

$$\frac{A}{kT} = \frac{A_0}{kT} + \beta \sum_j \langle N_j \rangle u_j^{(1)} - \frac{1}{2} \beta^2 \sum_i \sum_j (\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle) u_i^{(1)} u_j^{(1)} + O(\beta^3) \quad (14-22)$$

The first moment is easy and is

$$\langle N_j \rangle = 2\pi N \rho \int_{r_j}^{r_{j+1}} r^2 g_0(r) dr = 2\pi N \rho r_j^2 g_0(r_j) (r_{j+1} - r_j) \quad (14-23)$$

The evaluation of the second-moment term in Eq. (14-22) must be done approximately. The N_j may be regarded as representing the numbers of molecules in spherical shells surrounding some central molecule. If these shells were large macroscopic volumes, the numbers of molecules in different shells would be uncorrelated, i.e.,

$$\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle = 0 \quad i \neq j \quad (14-24)$$

and the fluctuation of the number in a given shell would be given by [Eq. (3-53)]:

$$\langle N_j^2 \rangle - \langle N_j \rangle^2 = \langle N_j \rangle kT \left(\frac{\partial \rho}{\partial p} \right)_T \quad (14-25)$$

Thus the β^2 term in the expansion in Eq. (14-22) can be approximated by

$$- \frac{1}{2} \beta^2 \sum_j \langle N_j \rangle kT [u_j^{(1)}]^2 \left(\frac{\partial \rho}{\partial p} \right)_0$$

If we substitute Eq. (14-23) for $\langle N_j \rangle$ into this and then pass to the continuum limit, we get

$$\frac{A}{NkT} = \frac{A_0}{NkT} + \frac{\rho\beta}{2} \int u^{(1)}(r) g_0(r) 4\pi r^2 dr - \frac{\rho\beta^2}{4} \int [u^{(1)}(r)]^2 kT \left(\frac{\partial \rho}{\partial p} \right)_0 g_0(r) 4\pi r^2 dr + O(\beta^3) \quad (14-26)$$

This approximation for the β^2 term is called the *macroscopic compressibility approximation*. A more satisfactory approximation is obtained by arguing that one should use a "local" compressibility in Eq. (14-26), related to the pressure derivative of the density at a distance r from a given molecule; i.e., replace $(\partial \rho / \partial p)_0 g_0(r)$ in Eq. (14-26) by $(\partial \rho / \partial p)[\rho g(r)]_0$. This so-called *local compressibility approximation* gives

$$\frac{A}{NkT} = \frac{A_0}{NkT} + \frac{\rho\beta}{2} \int u^{(1)}(r) g_0(r) 4\pi r^2 dr - \frac{\rho\beta^2}{4} \int [u^{(1)}(r)]^2 kT \left[\frac{\partial (\rho g_0)}{\partial p} \right] 4\pi r^2 dr + O(\beta^3) \quad (14-27)$$

Note that the Helmholtz free energy A is expressed in terms of hard-sphere quantities and the perturbing potential $u^{(1)}(r)$.

In applying this equation to a square-well system; Barker and Henderson took the hard-sphere core as their unperturbed potential and the well as the perturbing potential. The comparison of the numerical results of this equation with the computer calculations of Alder and Wainwright* and Rotenberg† is shown in Fig. 14-2. In

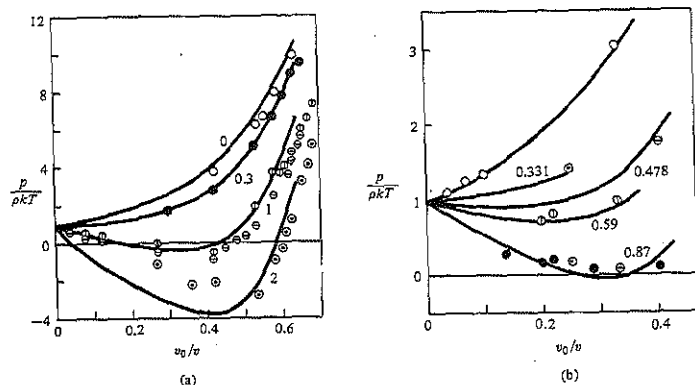


Figure 14-2. Equation of state for the square-well potential. The points are the results of various molecular dynamics and Monte Carlo calculations, and the curves are isotherms calculated from Eq. (14-27). The numbers labeling the curves give the values of ϵ/kT . (From J. A. Barker and D. Henderson, *J. Chem. Phys.*, 47, p. 2856, 1967.)

* B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* 33, p. 1439, 1960.

† A. Rotenberg, *J. Chem. Phys.*, 43, p. 1198, 1965.

obtaining these results, the Padé approximant of Hoover and Ree was used for the hard-sphere pressure $p^{(0)}$.

Smith *et al.** have also approximated ω_2 by using the superposition approximation on the three- and four-body distribution functions. This, of course, allows A to be written in terms of the two-body hard-sphere radial distribution function. The equations are too long to be given here, but the results are similar to the solid curves in Fig. 14-2. The agreement with the molecular dynamics results of Alder [Fig. 14-2(a)] is excellent. The agreement with the Monte Carlo results of Rotenberg is good except at the highest densities. Table 14-1 shows the first- and second-order terms for the Helmholtz free energy and the pressure. It can be seen that the perturbation series seems to converge rapidly. Table 14-2 compares the critical constants from the Barker-Henderson theory to the square-well molecular dynamics results of Alder. Again there is very good agreement.

Table 14-1. The first- and second-order terms in the Barker-Henderson perturbation series for the Helmholtz free energy and the pressure for a square-well fluid

$\rho\sigma^3$	A_2/NkT		$p_2 v_0/kT$	
	l.c.*	s.a.†	l.c.*	s.a.†
0.00	0.0000	0.000	0.0000	0.000
0.10	-0.5339	-0.188	-0.0403	-0.010
0.20	-1.1405	-0.282	-0.1816	-0.017
0.30	-1.8159	-0.310	-0.4502	-0.001
0.40	-2.5511	-0.295	-0.8501	+0.035
0.50	-3.3292	-0.253	-1.3993	0.088
0.60	-4.1234	-0.198	-2.0120	0.147
0.70	-4.8950	-0.140	-2.5787	0.196
0.80	-5.5933	-0.087	-2.9072	0.216
0.90	-6.1606	-0.045	-2.7701	0.194
1.00	-6.5484	-0.018	-2.0513	0.137

* Local compressibility approximation.

† Superposition approximation.

Source: J. A. Barker and D. Henderson, *J. Chem. Phys.*, 47, p. 2856, 1969; Symp. Thermophys. Properties, Papers, 4th, p. 30, 1968.

Table 14-2. Critical constants for the square-well potential ($\lambda = 1.5$)

	Barker-Henderson theory	molecular dynamics
kT_c/ϵ	1.32	1.28
V_0/V_c	~0.22	0.235
$P_c V_0/NkT_c$	0.076	0.072

Barker and Henderson have applied their perturbation theory to a Lennard-Jones potential as well.† They actually develop the Helmholtz free energy as a double perturbation series. One variable, γ , is a measure of the depth of the attractive well, and the other variable, α , is a measure of the inverse steepness of the repulsive part of the

* W. R. Smith, D. Henderson, and J. A. Barker, *J. Chem. Phys.*, 53, p. 508, 1970.

† J. A. Barker and D. Henderson, *J. Chem. Phys.*, 47, p. 4714, 1967.

potential, i.e., the smaller α , the steeper the repulsive part. They do this by defining a modified potential function $v(\alpha, \gamma, d; r)$ corresponding to $u(r)$ by

$$v(\alpha, \gamma, d; r) = \begin{cases} u\left(d + \frac{r-d}{\alpha}\right) & d + \frac{r-d}{\alpha} < \sigma \\ 0 & \sigma < d + \frac{r-d}{\alpha} < d + \frac{\sigma-d}{\alpha} \\ \gamma u(r) & \sigma < r \end{cases} \quad (14-28)$$

The quantity d is a distance parameter which is as yet unspecified, and σ is customarily taken to be that point at which the potential $u(r)$ passes through zero. This appears to be complicated at first, but notice that $v(\alpha, \gamma, d; r)$ is independent of d and reduces to $u(r)$ when $\alpha = \gamma = 1$. When $\alpha = \gamma = 0$, on the other hand, v becomes a hard-sphere potential of diameter d , which is still arbitrary (Problem 14-10). Thus by varying γ and α , we can go from our original potential $u(r)$ to a hard-sphere potential.

The idea now is to express the Helmholtz free energy A in terms of this modified potential as a double power series about $\alpha = \gamma = 0$ according to

$$A = A_0 + \alpha \left(\frac{\partial A}{\partial \alpha} \right)_{\alpha=\gamma=0} + \gamma \left(\frac{\partial A}{\partial \gamma} \right)_{\alpha=\gamma=0} + \frac{\alpha^2}{2} \left(\frac{\partial^2 A}{\partial \alpha^2} \right)_{\alpha=\gamma=0} + \cdots \quad (14-29)$$

Note that the coefficients of α , γ , α^2 , etc., here are evaluated at $\alpha = \gamma = 0$ or, in other words, are hard-sphere quantities. The differentiations indicated in Eq. (14-29) involve lengthy algebra,* but the final result is quite simple:

$$A = A_0 + \alpha 2\pi N k T \rho \int_0^\infty g_0(d) \left[d + \int_0^\sigma f(z) dz \right] + \gamma 2\pi N \rho \int_0^\infty g_0(r) u(r) r^2 dr - \gamma^2 \pi N \rho \left(\frac{\partial \rho}{\partial p} \right)_0 \frac{\partial}{\partial \rho} \left[\rho \int_0^\infty g_0(r) u^2(r) r^2 dr \right] + O(\alpha^2) + O(\alpha\gamma) + \cdots \quad (14-30)$$

In this result A_0 , g_0 , and $(\partial \rho / \partial p)_0$ are the free energy, radial distribution function, and compressibility of a system of hard spheres of diameter d (as yet unspecified). The first-order terms in Eq. (14-30) are exact, but the γ^2 term has been approximated by the local compressibility approximation.

The value of d is still at our disposal. We choose for d the value

$$d = - \int_0^\sigma f(z) dz \quad (14-31)$$

so that the linear term in α vanishes. This gives d as a well-defined temperature-dependent effective hard-sphere diameter. Barker and Henderson argue that with this choice of d , the terms in α^2 and $\alpha\gamma$ in Eq. (14-30) are considerably smaller than the γ^2 term.

For $\alpha = \gamma = 1$, Eq. (14-30) is just the Helmholtz free energy for a system with potential $u(r)$, and so we finally write

$$A = A_0 + 2\pi N \rho \int_0^\infty g_0(r) u(r) r^2 dr - \pi \rho \beta \left(\frac{\partial \rho}{\partial p} \right)_0 \left[\rho \int_0^\infty g_0(r) u^2(r) r^2 dr \right] \quad (14-32)$$

where A_0 , $g_0(r)$, and $(\partial \rho / \partial p)_0$ are the free energy, radial distribution function, and compressibility of a system of hard spheres of diameter d , given by Eq. (14-31).

* See the reference to Barker and Henderson in "Additional Reading" for complete details.

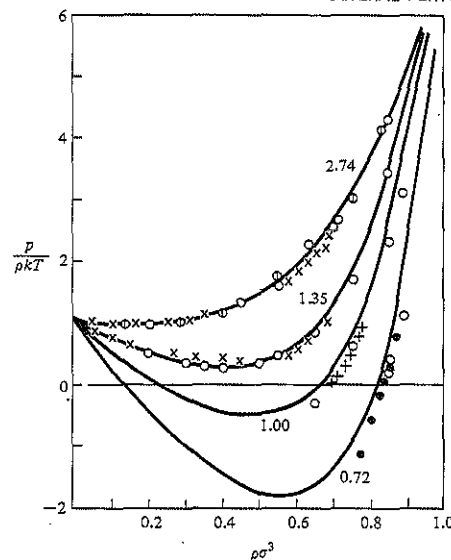


Figure 14-3. The equation of state for the 6-12 potential according to Barker and Henderson. The curves are labeled by the value of T^* . The points are a mixture of machine calculations and actual experimental data. (From J. A. Barker and D. Henderson, *J. Chem. Phys.*, 47, p. 4714, 1967.)

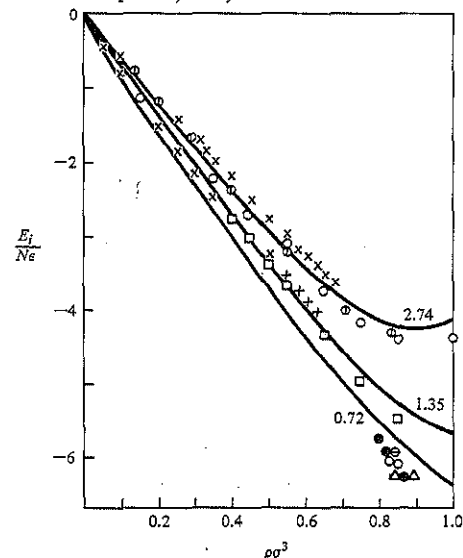


Figure 14-4. Internal energy for the 6-12 potential according to Barker and Henderson. The curves are labeled with the values of T^* . The points are a mixture of machine calculations and actual experimental data. (From J. A. Barker and D. Henderson, *J. Chem. Phys.*, 47, p. 4714, 1967.)

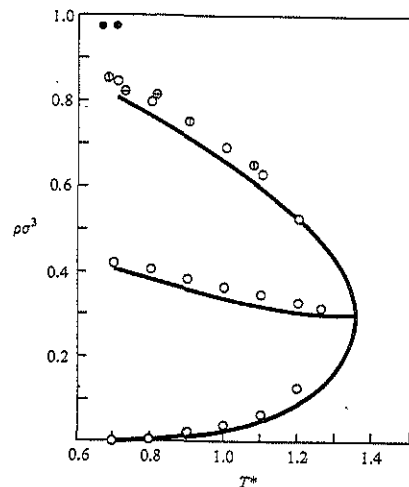


Figure 14-5. Densities of coexisting phases for the 6-12 potential according to Barker and Henderson. The points are a mixture of machine calculations and actual experimental data. (From J. A. Barker and D. Henderson, *J. Chem. Phys.*, 47, p. 4714, 1967.)

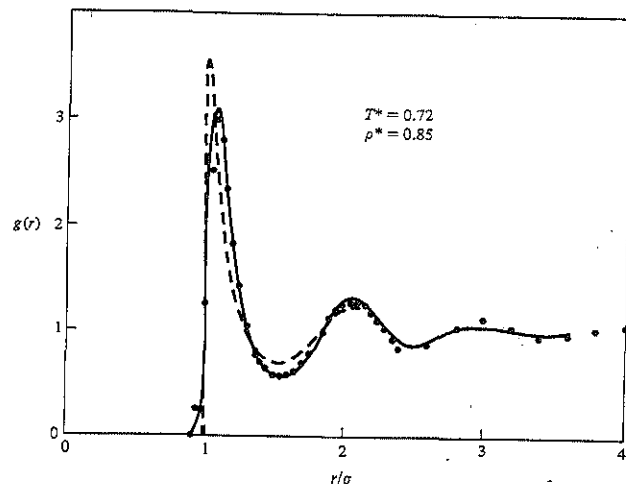


Figure 14-6. Radial distribution function of the 6-12 liquid near its triple point. The points give the results of molecular dynamics calculations, and the curves give the results of the Barker-Henderson perturbation theory. The quantities ρ^* and T^* are $\rho\sigma^3$ and kT/ϵ , respectively. (From J. A. Barker and D. Henderson, *Ann. Rev. Phys. Chem.*, 23, p. 439, 1972.)

Figures 14-3 through 14-5 show the results from Eq. (14-32) and other thermodynamic functions. These comparisons indicate that the Barker-Henderson perturbation theory gives excellent results at temperatures that are not too low. Figures 14-6 and 14-7 compare the radial distribution function of the Barker-Henderson theory

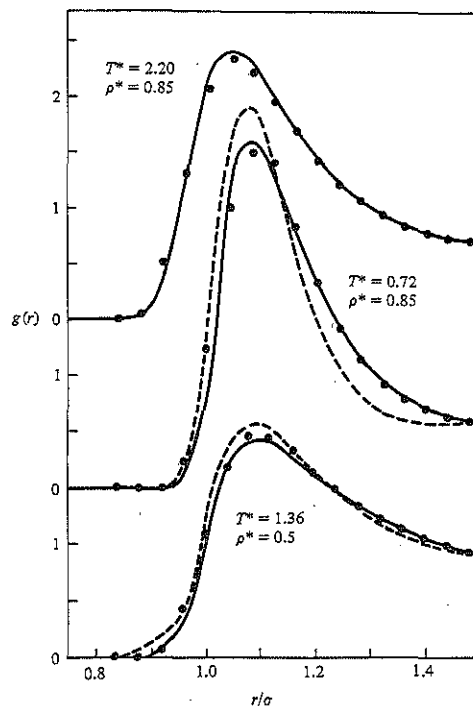


Figure 14-7. Radial distribution function of the 6-12 fluid. The points give the results of molecular dynamics calculations, and the broken and solid curves give the result of the Percus-Yevick and Barker-Henderson theories, respectively. The quantities ρ^* and T^* are $\rho\sigma^3$ and kT/ϵ , respectively. (From J. A. Barker and D. Henderson, *Ann. Rev. Phys. Chem.*, 23, p. 439, 1972.)

to that from the Percus-Yevick equation and molecular dynamics. Note that the conditions of Fig. 14-6 are near the critical point and so this serves as a fairly severe test. Figure 14-7 compares the radial distribution function around the first maximum. Again one can see that the agreement is excellent.

Table 14-3 compares values of A/NkT for a 6-12 fluid for a number of theories. The column headed by PY(E) indicates the Percus-Yevick results starting from the energy equation. We saw in Fig. 13-12 and the discussion surrounding it that this seems to be the most reliable treatment of the Percus-Yevick theory. The columns headed BH1(PY), BH1, and BH2 are the results of the Barker-Henderson theory calculated from first-order perturbation theory using the PY hard sphere $g(r)$, from first-order perturbation theory using the Monte Carlo values of the hard sphere $g(r)$, and from second-order perturbation theory using the Monte Carlo $g_0(r)$. The agreement of the BH2 results with those of the molecular dynamics is excellent. The other columns in Table 14-3 will be discussed shortly. Table 14-4 compares values of p/pkT in a similar way. Table 14-5 compares the critical constants obtained from this theory to the molecular dynamics calculations of Verlet and experimental data of argon.

Table 14-3. Values of A/NkT for the 6-12 potential

kT/ϵ	$\rho\sigma^3$	molecular dynamics*	PY(E)	BH1-(PY)	BH1	BH2	CWA (PY)	CWA
2.74	0.60	-0.34	-0.33	-0.31	-0.31	-0.33	-0.32	-0.33
	0.70	+0.01	+0.01	+0.04	+0.02	+0.01	+0.02	+0.01
	0.80	0.43	0.43	0.45	0.46	0.42	0.43	0.41
	0.90	0.93	0.95	0.97	0.99	0.95	0.97	0.92
	1.00	1.59	1.61	1.65	1.66	1.62	1.65	1.56
1.35	0.60	-1.77	-1.75	-1.67	-1.65	-1.75	-1.73	-1.74
	0.70	-1.65	-1.62	-1.54	-1.51	-1.63	-1.62	-1.63
	0.80	-1.41	-1.37	-1.30	-1.26	-1.41	-1.39	-1.41
	0.90	-1.02	-0.99	-0.90	-0.84	-1.01	-0.98	-1.02
	0.95	-0.72	-0.72	-0.62	-0.55	-0.72	(-0.67)	(-0.74)
1.15	0.60	-2.29	-2.28	-2.16	-2.15	-2.30	-2.25	-2.26
	0.70	-2.25	-2.23	-2.11	-2.10	-2.26	-2.23	-2.24
	0.80	-2.06	-2.06	-1.95	-1.92	-2.10	-2.08	-2.09
	0.90	-1.79	-1.74	-1.61	-1.56	-1.76	-1.73	-1.77
0.75	0.60	-4.24		-3.99	-3.99	-4.29	-4.17	-4.18
	0.70	-4.53	-4.50	-4.26	-4.26	-4.51	-4.51	-4.51
	0.80	-4.69	-4.63	-4.38	-4.37	-4.74	-4.69	-4.69
	0.90		-4.55	-4.29	-4.26	(-4.60)	(-4.62)	

* Verlet et al., *Phys. Rev.*, 182, p. 307, 1969; 159, p. 98, 1967.Source: J. A. Barker and D. Henderson, *Ann. Rev. Phys. Chem.*, 23, p. 439, 1972.Table 14-4. Values of p/pkT for the 6-12 potential

kT/ϵ	$\rho\sigma^3$	molecular dynamics*	Monte Carlo†	PY(E)	BH1-(PY)	BH1	BH2	CWA (PY)	CWA
2.74	0.65	2.22		2.23	2.23	2.24	2.22	2.21	2.18
	0.75	3.05		3.11	3.11	3.14	3.10	3.11	3.04
	0.85	4.38		4.42	4.42	4.48	4.44	4.50	4.30
	0.95	6.15		6.31	6.37	6.41	6.40	6.57	6.10
1.35	0.10	0.72		0.72	0.77	0.77	0.74	0.77	0.77
	0.20	0.50		0.51	0.54	0.55	0.52	0.53	0.53
	0.30	0.35		0.36	0.35	0.39	0.36	0.32	0.31
	0.40	0.27		0.29	0.25	0.26	0.26	0.17	0.17
	0.50	0.30		0.33	0.29	0.31	0.27	0.18	0.18
	0.55	0.41		0.43	0.40	0.43	0.35	0.27	0.27
	0.65	0.80		0.85	0.85	0.91	0.74	0.72	0.71
	0.75	1.73		1.72	1.77	1.87	1.64	1.70	1.64
	0.85	3.37		3.24	3.36	3.54	3.36	3.51	3.28
	0.95	6.32		5.65	5.96	6.21	6.32	(6.58)	(5.90)
1.00	0.65	-0.25		-0.22	-0.25	-0.21	-0.36	-0.51	-0.50
	0.75	+0.58	0.48	+0.57	+0.62	+0.71	+0.53	+0.43	+0.40
	0.85	2.27	2.23	2.14	2.30	2.48	2.25	2.41	2.20
	0.90	~3.50		3.33	3.57	3.79	3.53	(3.96)	(3.55)
0.72	0.85	0.40	0.25	0.33	0.50	0.70	0.25	0.43	0.26
	0.90		~1.60	1.59	1.90	2.15	1.63	(2.24)	(1.83)

* Verlet et al., *Phys. Rev.*, 182, p. 307, 1969; 159, p. 98, 1967.† McDonald and Singer, *J. Chem. Phys.*, 50, p. 2308, 1969.Source: J. A. Barker and D. Henderson, *Ann. Rev. Phys. Chem.*, 23, p. 439, 1972.

Table 14-5. Critical constants for the 6-12 potential

	Barker-Henderson	Verlet*	Exp. (argon)†
T_c^*	1.35	1.32-1.36	1.26
ρ_c^*	0.30	0.32-0.36	0.316
p_c^*	0.14	0.13-0.17	0.117
$\rho_c V_c/NkT_c$	0.34	0.30-0.36	0.293

* L. Verlet, *Phys. Rev.*, 159, p. 98, 1967.† J. S. Rowlinson, *Liquids and Liquid Mixtures* (London: Butterworths, 1959).

The Barker-Henderson theory was the first generally successful perturbation theory and showed that perturbation theory is probably the most appealing approach to the liquid state. Barker and Henderson have extended and summarized their approach in a number of later papers.* Two important extensions are the generation of tables that allow one to use Monte Carlo values of A_2 and the inclusion of three-body forces. These are discussed in the most recent reference given below.

THE CHANDLER-WEEKS-ANDERSEN THEORY

In 1971 a new perturbation theory of liquids was formulated by Chandler, Weeks, and Andersen.† The primary difference between their approach and the Barker-Henderson approach is the way in which the intermolecular potential is divided into an unperturbed and a perturbed part. Chandler, Weeks, and Andersen argue that it is physically significant to separate the potential into a part containing all the repulsive forces and a part containing all the attractive forces. As they point out, "As far as the motion of a molecule in a liquid is concerned, the molecules do not 'know' the sign of their mutual potential energy, but do 'know' the sign of the derivative of the potential, i.e., the sign of the force." Notice that this separation is distinctly different from separating the potential into positive and negative parts as in the Barker-Henderson theory.

Thus the CWA theory separates the intermolecular potential according to

$$u(r) = u_0(r) + u^{(1)}(r)$$

where for a Lennard-Jones 6-12 potential:

$$\begin{aligned} u_0(r) &= u(r) + \epsilon & r < 2^{1/6}\sigma \\ &= 0 & r \geq 2^{1/6}\sigma \\ u^{(1)}(r) &= -\epsilon & r < 2^{1/6}\sigma \\ &= u(r) & r \geq 2^{1/6}\sigma \end{aligned} \quad (14-33)$$

In Eq. (14-33), ϵ represents the depth of the potential well of $u(r)$, and the term $2^{1/6}\sigma$ is the same as r_{\min} for a 6-12 potential. This division is shown in Fig. 14-8.

The separation utilized in the CWA theory has two advantages over other separations. Equation (14-8) shows that the higher-order terms $\omega_2, \omega_3, \dots$ are like central moments about some distribution, and so are smaller the more smoothly $u^{(1)}(r)$ varies. As Fig. 14-8 shows, the perturbing part of the potential chosen in the CWA theory

* J. A. Barker and D. Henderson, *J. Chem. Educ.*, 45, p. 2, 1968; W. R. Smith, D. Henderson, and J. A. Barker, *J. Chem. Phys.*, 53, p. 508, 1970; *ibid.*, 55, p. 4027, 1971; J. A. Barker and D. Henderson, *Accs. Chem. Res.*, 4, p. 303, 1971; *Ann. Rev. Phys. Chem.*, 23, p. 439, 1972.† D. Chandler and J. D. Weeks, *Phys. Rev. Lett.*, 25, p. 149, 1970; J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.*, 54, p. 5237, 1971.

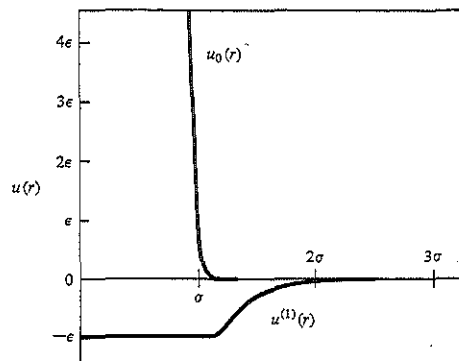


Figure 14-8. The CWA separation of the Lennard-Jones potential, $u(r)$, into a part containing all the repulsive forces, $u_0(r)$, and a part containing all the attractive forces, $u^{(1)}(r)$. (From J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.*, **54**, p. 5237, 1971.)

does indeed vary slowly for all r . This is to be contrasted with Barker and Henderson's separation of $u(r)$, in which $u_0(r)$ is that part of $u(r)$ greater than zero and $u^{(1)}(r)$ is that part less than zero. Their $u^{(1)}(r)$ varies quite rapidly with r , particularly between $r = \sigma$ and $r = 2^{1/6}\sigma$. Secondly, the reference system chosen by Chandler, Weeks, and Andersen is more realistic than a hard-sphere system. In fact, we shall see below that at high densities the radial distribution function of the Lennard-Jones systems can be very well approximated by the radial distribution function of a system with the potential $u_0(r)$ in Fig. 14-8, i.e., the reference system of CWA.

Using Eq. (14-33) in Eqs. (14-9) and (14-10), then we have

$$A = A_0 + \frac{1}{2}\rho^2 V \int g_0(r) u^{(1)}(r) dr + \dots \quad (14-34)$$

where, of course, the zero subscripts indicate the reference system with potential $u_0(r)$ given in Eq. (14-33). For the purpose of comparison with experimental data and other theories, it is convenient to calculate not A itself, but the *excess* free energy with respect to the ideal gas at the same volume, temperature, and density. If we denote this excess free energy by ΔA , we can write Eq. (14-34) in the form

$$\frac{\beta \Delta A}{N} = \frac{\beta \Delta A_0}{N} + \frac{1}{2}\beta \rho \int dr g_0(r) u^{(1)}(r) + \dots \quad (14-35)$$

Chandler, Weeks, and Andersen argue on physical grounds and then show numerically (see below) that for low as well as high temperatures this equation will be approximately valid, i.e., errors 10 percent when the density is low, but will become much more accurate as the density increases.

The principal disadvantage of the CWA theory is that the properties of the reference state are not well known as they are for a hard-sphere system. In order to avoid having to perform expensive machine calculations to obtain this information, they present an approximate treatment of the reference system. The essence of their approximation goes back to Fig. 13-8, which shows the function $y(r) = g(r)\exp[\beta u(r)]$ versus r . It was stated there that the shape of $y(r)$ is not too sensitive to the intermolecular potential. Chandler, Weeks, and Andersen approximate $y(r)$ for the reference fluid, i.e.,

$y_0(r)$, by the similar function appropriate to a hard-sphere system of diameter d , $y_d(r)$. For $g_0(r)$, then, we have*

$$g_0(r) \approx y_d(r) \exp[-\beta u_0(r)] \quad (14-36)$$

They choose the value of d by requiring the thermodynamic properties of the reference system to equal those of a hard-sphere system through the equation [Eq. (13-54)]

$$\frac{1}{\beta} \left(\frac{\partial \rho}{\partial p} \right)_\beta = 1 + \rho \int [g(r) - 1] dr$$

Thus if we equate the compressibility of the reference system to the compressibility of a hard-sphere system, we have

$$\int dr (y_d e^{-\beta u_0} - 1) = \int dr (y_d e^{-\beta u_d} - 1) \quad (14-37)$$

where u_d denotes as hard-core repulsion of diameter d . This equation gives a unique value of d as a function of both temperature and density. Verlet and Weis† have presented a simple algorithm for $d(\beta, \rho)$. Once a value of d is obtained for a particular ρ and β , the free energy of the reference system is taken to be the free energy of a hard-sphere system with diameter d and density ρ . Figure 14-9 shows the behavior

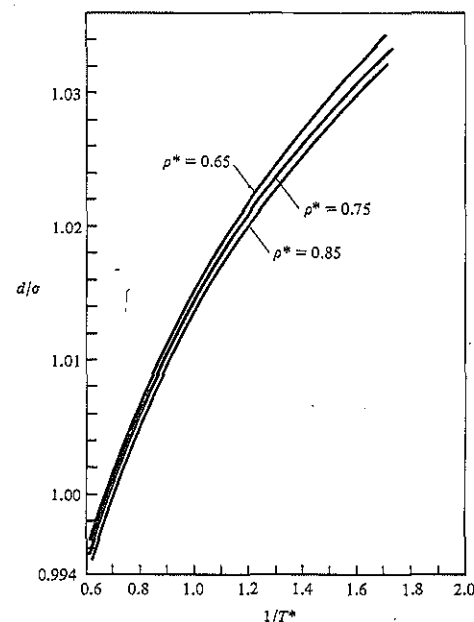


Figure 14-9. The effective hard-sphere diameter according to the CWA theory [Eq. (14-37)]. (From J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.*, **54**, p. 5237, 1971.)

* Such an approximation had been used previously, e.g., By M. Orentlicher and J. M. Prausnitz, *Can. J. Chem.*, **45**, p. 595, 1967.

† L. Verlet and J. Weis, *Phys. Rev.*, **5A**, p. 939, 1972.

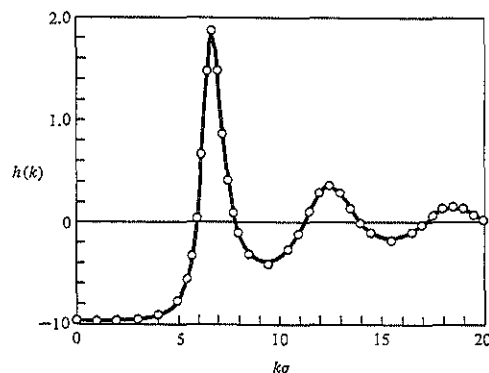


Figure 14-10. Plot of $h(k)$ for $\rho^* = 0.844$, $T^* = 0.723$. The line represents the use of Eq. (14-36); the circles are the molecular dynamics results of Verlet. (From J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.* 54, p. 5237, 1971.)

Table 14-6. Perturbation theory and Monte Carlo results for the excess free energy on the $T^* = 0.75$, 1.15, and 1.35 isotherms

T^*	ρ^*	$-\beta\Delta A/N$		
		CWA	Monte Carlo	Barker-Henderson
0.75	0.1	0.55	0.81	0.57
	0.2 ^a	1.15	1.48	1.16
	0.3 ^a	1.78	2.11	1.77
	0.4 ^a	2.42	2.68	2.38
	0.5 ^a	3.06	3.23	2.96
	0.6 ^a	3.65	3.74	3.48
	0.7 ^a	4.14	4.17	3.90
	0.8 ^a	4.46	4.47	4.16
	0.84	4.51	4.54	4.20
1.15	0.1	0.29	0.39	0.30
	0.2	0.60	0.73	0.61
	0.3	0.92	1.05	0.92
	0.4 ^a	1.23	1.33	1.20
	0.5 ^a	1.51	1.59	1.46
	0.55 ^a	1.63	1.69	1.56
	0.6 ^a	1.74	1.79	1.65
	0.65	1.82	1.84	1.72
	0.75	1.88	1.88	1.76
1.35	0.85	1.77	1.78	1.63
	0.1	0.22	0.30	0.23
	0.2	0.45	0.56	0.46
	0.3	0.68	0.80	0.69
	0.4	0.90	1.00	0.89
	0.5	1.09	1.16	1.05
	0.6	1.22	1.26	1.16
	0.7	1.26	1.29	1.18
	0.8	1.16	1.19	1.07

^a Corresponds to one-phase metastable states in the liquid-gas two-phase region.

Source: J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.*, 54, p. 5237, 1971.

of d obtained numerically from Eq. (14-37) versus ρ and β . It is interesting to note that the curves of $d(\rho, \beta)$ obtained here are very similar to the empirical curves for an effective hard-sphere diameter determined empirically by Verlet* in the discussion surrounding Fig. 14-1. Figure 14-10 shows $h(k)$ [Eq. (14-1)] obtained from the ap-

Table 14-7. Approximate results for the excess free energy on the $\rho^* = 0.88$, 0.85, 0.75, and 0.65 isochores

ρ^*	T^*	$-\beta\Delta A/N$		
		CWA	computer results	Barker-Henderson
0.88	1.095	1.94	1.99	1.80
	0.94	2.84	2.88	2.65
	0.591	6.80	6.86	6.30
	2.889	-0.93	-0.86	-0.94
0.85	2.202	-0.44	-0.37	-0.47
	1.214	1.51	1.55	1.39
	1.128	1.86	1.91	1.73
	0.880	3.32	3.35	3.10
	0.782	4.18	4.21	3.90
	0.786	4.14	4.17	3.86
	0.760	4.41	4.44	4.10
	0.719	4.87	4.90	4.53
	0.658	5.66	5.71	5.26
	0.591	6.74	6.81	6.25
0.75	2.849	-0.56	-0.50	-0.58
	1.304	1.36	1.41	1.27
	1.069	2.22	2.26	2.08
	1.071	2.21	2.25	2.07
	0.881	3.27	3.30	3.06
	0.827	3.66	3.69	3.43
0.65	2.557	-0.18	-0.20	-0.11
	1.585	0.79	0.85	0.73
	1.036	2.24	2.30	2.12
	0.900	2.90	2.96	2.74

Source: D. Chandler, and H. C. Andersen, *J. Chem. Phys.*, 54, p. 5237, 1971.

Table 14-8. Approximate and molecular dynamics results for the pressure and internal energy as obtained from Eqs. (14-38) and (14-39), respectively*

ρ^*	T^*	$\beta p/\rho$			$-\beta\Delta E/N$		
		CWA	MD	PY	CWA	MD	PY
0.85	1.128	2.82	2.78	3.57	5.08	5.05	4.98
	0.88	1.82	1.64	3.17	6.77	6.75	6.61
	0.786	1.23	0.99	2.97	7.70	7.70	7.51
	0.719	0.69	0.36	2.82	8.52	8.51	8.28

* Columns 3 and 6 give the values obtained by applying the approximation $g(r) \cong g_0(r)$. Columns 4 and 7 give the molecular dynamics results. The results obtained by using the solution of the Percus-Yevick equation for $g(r)$ are given in columns 5 and 8.

Source: J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.*, 54, p. 5237, 1971.

proximate radial distribution function in Eq. (14-36) for $\rho^* = \rho\sigma^3 = 0.844$ and $T^* = 0.723$. It can be seen from this just how much the repulsive part of the potential determines the structure of a liquid at high densities. A similar result is found for the radial distribution function itself.

* L. Verlet, *Phys. Rev.*, 165, p. 201, 1968.

Tables 14-6 through 14-8 show some thermodynamic results calculated from the CWA theory. Table 14-6 shows the excess free energy calculated according to Eq. (14-35). One sees that the excess free energy does converge at high densities ($\rho^* \geq 0.65$) to the values predicted by computer calculations. Table 14-7 shows some more detailed results for $\beta\Delta A/N$. The CWA theory does seem to improve as the density increases. Table 14-8 gives some results for the pressure and the excess internal energy. Although these quantities could be calculated from A , they were actually calculated from the equations

$$\beta p = \rho - \frac{1}{2}\beta\rho^2 \int ru'(r)g(r) dr \quad (14-38)$$

and

$$\frac{\Delta E}{N} = \frac{1}{2}\rho \int u(r)g(r) dr \quad (14-39)$$

with $g(r)$ replaced by simply $g_0(r)$. It can be seen that the results are far superior to a solution of the Percus-Yevick equation for a 6-12 potential. The poorer results for the pressure found at the lowest temperatures in Table 14-8 are attributed to approximating the reference system by an effective hard-sphere system rather than in any inadequacy of the CWA approach.

Tables 14-3 and 14-4 include values of A/NkT and p/pkT calculated from the CWA theory. The column headed CWA(PY) indicates that the Percus-Yevick $g_0(r)$ was used, and the column headed by CWA indicates that Monte Carlo values of $g_0(r)$ were used. The numbers in parentheses were calculated using a hard-sphere system which was so dense that these results are of uncertain accuracy. As one would expect from a satisfactory theory, the results calculated from the more accurate $g_0(r)$ are in better agreement with the molecular dynamics and Monte Carlo results. The agreement is seen to be excellent.

There is at present some discussion* concerning the relative merits of the BH and CWA theories, but it can be said that the two theories are complementary rather than competitive. They are based on differing compromises, and each has its merits and drawbacks.† The Barker-Henderson theory uses a well-known reference state, but must include terms second order in β . The Chandler-Weeks-Andersen theory, on the other hand, is rapidly enough convergent that it does not require second-order terms, but the reference state is not universal, as in the case with perturbation theories based on hard spheres. Regardless, both theories are very successful and show that the perturbation theory approach to the liquid state is not only physically appealing but numerically very satisfactory.

ADDITIONAL READING

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* See e.g., J. A. Barker and D. Henderson, *Phys. Rev.*, **A4**, p. 806, 1971.

† D. Henderson, *Mol. Phys.*, **21**, p. 841, 1971; see also J. A. Barker and D. Henderson, *Ann. Rev. Phys. Chem.*, **23**, p. 477, 1972.

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PROBLEMS

14-1. By using the van der Waals equation and the fact that $(\partial p/\partial V)_T$ and $(\partial^2 p/\partial V^2)_T$ equal zero at the critical point, show that

$$T_c = \frac{8a}{27bR}, \quad V_c = 3b, \quad p_c = \frac{a}{27b^2}$$

and

$$\frac{p_c V_c}{T_c} = \frac{3R}{8}$$

Show also that the van der Waals equation can be written in reduced form as

$$\left(p^* + \frac{3}{V^{*2}}\right)\left(V^* - \frac{1}{3}\right) = \frac{8}{3}T^*$$

where $p^* = 27b^2p/a$, $V^* = V/3b$, and $T^* = 27RbT/8a$.

14-2. Determine the virial coefficients associated with the van der Waals equation. How do they compare to the exact ones?

14-3. The critical constants of nitrogen are $p_c = 33.6$ atm, $V_c = 0.090$ liters/mole, and $T_c = 126^\circ\text{K}$. Calculate the van der Waals constants and determine the molar volume of nitrogen at 300°K and 1 atm; 10 atm; 100 atm. Compare these values to those calculated from the ideal gas equation of state.

14-4. Show that the van der Waals equation is a special case of the more general equation

$$p = \frac{NRT}{V} \beta(\rho) - \alpha(\rho) \quad \text{where} \quad \beta(\rho) = \frac{1}{V} \left(\frac{\partial \ln Z}{\partial \ln V} \right)_T = \frac{1}{V} \left(\frac{\partial \ln Z}{\partial \ln V} \right)_T = \frac{1}{V} \left(\frac{\partial \ln Z}{\partial \ln V} \right)_T = \frac{1}{V} \left(\frac{\partial \ln Z}{\partial \ln V} \right)_T$$

where α and β are functions of the density ρ , but independent of temperature. Rigby* calls this a generalized van der Waals equation. Show that two thermodynamic consequences of this equation are that $(\partial p/\partial T)_V$ is a function only of the molar volume and that the entropy is determined solely by the $\beta(\rho)$ term.

14-5. Using Eqs. (14-14) and (14-17), calculate the van der Waals constants a and b for nitrogen. For $u(r)$, assume a Lennard-Jones 6-12 potential with ϵ and σ given in Table 12-3. Compare these calculated values to the experimentally determined values, $a = 1.39 \times 10^6$ cm⁶ · atm/mole² and $b = 39.1$ cm³/mole. Such poor agreement is quite typical, simply indicating the inadequacy of the van der Waals equation.

14-6. Show how terms in $(1/T)^2$ involve $g^{(3)}$ and $g^{(4)}$ as well as $g^{(2)}$ when part of the intermolecular potential is treated as a perturbation. Write out this term.

14-7. Show that the expression for the Helmholtz free energy of a square-well fluid to second order in the Barker-Henderson perturbation theory is

$$\frac{A - A_0}{NkT} = -2\pi\rho \left(\frac{\epsilon}{kT} \right) \int_0^{\lambda\sigma} r^2 g_0(r) dr - \pi\rho \left(\frac{\epsilon}{kT} \right)^2 \frac{(1-\eta)^4}{1+4\eta+4\eta^2} \frac{\partial}{\partial \rho} \left[\rho \int_0^{\lambda\sigma} r^2 g_0(r) dr \right]$$

* *Quart. Rev.*, **24**, p. 416, 1970.

where $\eta = \pi\rho\sigma^3/6$ and the Percus-Yevick compressibility equation of state has been used for $(\partial\rho/\partial p)_0$.*

14-8. Evaluate the square-well second and third virial coefficients from the Barker-Henderson theory and compare them to the exact expression as a function of $T^* = kT/\epsilon$.

14-9. Using the Grundke-Henderson program for the hard-sphere radial distribution function given in Appendix D, evaluate the integrals in Problem 14-7 and compare your final results for A to those of Barker and Henderson in their original paper.†

14-10. Show that Eq. (14-28) reduces to the hard-sphere case when $\alpha = \gamma = 1$.

14-11. In the second paper in the Barker-Henderson series,‡ the double Taylor expansion of the Helmholtz free energy, Eq. (14-30), is derived. Following the first few pages of their paper, derive Eq. (14-30).

14-12. Show that the Barker-Henderson effective hard-sphere diameter is always less than or equal to σ .

14-13. Evaluate the Barker-Henderson effective hard-sphere diameter $d(T)$ for a hard-sphere, square-well, and r^{-12} potential.

14-14. Evaluate the Barker-Henderson effective hard-sphere diameter $d(T)$ for the Lennard-Jones 6-12 potential and compare your result to Fig. 1 of Barker and Henderson's second paper.§

14-15. Show that if three-body forces are included in the intermolecular potential, then the Barker-Henderson theory gives

$$A = A_0 + 2\pi N\rho \int_0^\infty g_0(r)u(r)r^2 dr \\ - \pi N\beta\rho \frac{(1-\eta)^4}{1+4\eta+4\eta^2} \frac{\partial}{\partial\rho} \left[\rho \int_0^\infty g_0(r)u(r)r^2 dr \right] \\ + \frac{N\rho^2}{6} \iint g_0(123)u(123) d\mathbf{r}_2 d\mathbf{r}_3$$

where the Percus-Yevick compressibility equation has been used for $(\partial\rho/\partial p)_0$.||

14-16. Using the Grundke-Henderson program for the radial distribution function given in Appendix D, evaluate Eq. (14-32) for the Lennard-Jones 6-12 potential and compare the results to those given in Table 14-3.

14-17. The first step in the Chandler-Weeks-Andersen perturbation theory is the calculation of the effective hard-sphere diameter $d(\rho, T)$. This is defined through Eq. (14-37), but Verlet and Weis¶ have presented a simple algorithm from this defining equation. Define a quantity d_R^* by

$$d_R^*(T) = \int_0^\infty [1 - e^{-\beta v_0(x)}] dx \quad (14-40)$$

where $x = r/\sigma$ and $v_0(x)$ is the CWA reference potential. Verlet and Weis show that this is well represented by the empirical expression:

$$d_R^* = \frac{0.3837 + 1.068\beta^*}{0.4293 + \beta^*} \quad (14-41)$$

* See J. A. Barker and D. Henderson, *J. Chem. Phys.*, **47**, p. 2856, 1967.

† *J. Chem. Phys.*, **47**, p. 2856, 1967.

‡ *J. Chem. Phys.*, **47**, p. 4714, 1967.

§ *J. Chem. Phys.*, **47**, p. 4714, 1967.

|| See J. A. Barker, D. Henderson, and W. R. Smith, *Phys. Rev. Lett.*, **21**, p. 134, 1968, for a discussion of the effect of the inclusion of three-body forces into perturbation theory.

¶ *Phys. Rev.*, **5A**, p. 939, 1972.

where $\beta^* = 1/T^* = \epsilon/kT$. For $0.7 < T^* < 1.6$, the error here is less than 2×10^{-4} , and for $1.6 < T^* < 4.5$, the error may reach 8×10^{-4} . The error also decreases rapidly with density. In addition, Verlet and Weis show that the density dependence of the CWA value of d^* , to first order, is given by

$$d^* = d_R^*(1 + A\delta) \quad (14-42)$$

where

$$\delta = \frac{1}{210.21 + 404.6\beta^*} \quad (14-43)$$

is a function of temperature only, and

$$A = \frac{1 - 4.25\eta_w + 1.362\eta_w^2 - 0.8751\eta_w^3}{(1 - \eta_w)^2} \quad (14-44)$$

with

$$\eta_w = \eta - \frac{1}{16}\eta^2 \quad (14-45)$$

where $\eta = (\pi/6)\rho d^3$ is the packing fraction. This procedure gives the CWA values of d^* to within 1 percent. Before Eq. (14-45) can be used, however, d must be known. An iterative procedure will, however, suffice. As a first choice, set $d^* = d_R^*$, then evaluate the quantities appearing in Eqs. (14-43), (14-44), and (14-45). Thus d^* can be found from (14-42) and will yield the second choice for d^* . Three iterations will yield ample convergence. Use this Verlet-Weis algorithm to reproduce the curves in Fig. 14-9.

14-18. Using the Verlet-Weis algorithm represented in Problem 14-17 and the Grundke-Henderson program for the hard-sphere radial distribution function given in Appendix D, calculate the CWA reference system radial distribution function according to Eq. (14-36), namely,

$$g_0(r) \approx y_A(r) \exp[-\beta u_0(r)]$$

and compare this to the molecular dynamics results of Hansen and Weis,* and to the molecular dynamics calculations of Verlet.†

14-19. The CWA expression for the excess free energy is given by Eq. (14-35):

$$\frac{\beta\Delta A}{N} = \frac{\beta\Delta A_0}{N} + \frac{1}{2}\beta\rho \int d\mathbf{r} g_0(r)u(r)$$

Using the results from Problems 14-17 and 14-18, reproduce Tables I and II from the paper of Weeks, Chandler, and Andersen.‡

14-20. Using Eqs. (14-38) and (14-39) with $g(r)$ replaced by

$$g_0(r) \approx y_A(r) \exp[-\beta u_0(r)]$$

calculate the pressure and excess internal energy and reproduce Table III in the paper of Weeks, Chandler, and Andersen.§

14-21. According to the approximation discussed in Problem 14-18 show that the structure factor of the reference fluid may be written as

$$h_0(k) = h_A(k) + \rho \int d\mathbf{r} y_A(r) [\exp(-\beta u_0) - \exp(-\beta u_2)] \exp(-ik \cdot r)$$

Using this, reproduce Figs. 3 and 4 in the paper of Weeks, Chandler, and Andersen.¶

* *Mol. Phys.*, **23**, p. 853, 1972.

† *Phys. Rev.*, **165**, p. 201, 1968.

‡ *J. Chem. Phys.*, **54**, p. 5237, 1971. See also *J. Chem. Phys.*, **55**, p. 5422, 1971.

§ *J. Chem. Phys.*, **54**, p. 5237, 1971. See also *J. Chem. Phys.*, **55**, p. 5422, 1971.

¶ *J. Chem. Phys.*, **54**, p. 5237, 1971.

14-22. Can the Barker-Henderson theory or the Chandler-Weeks-Andersen theory be applied to fused salts? Why or why not? Does the requirement of electroneutrality help?

14-23. The Barker-Henderson theory has been applied to mixtures of real fluids.* Assume that the pair potential is of the form

$$u_{\lambda\mu}(r) = 4\epsilon_{\lambda\mu} \left\{ \left(\frac{\sigma_{\lambda\mu}}{r} \right)^{12} - \left(\frac{\sigma_{\lambda\mu}}{r} \right)^6 \right\}$$

along with the combining rules

$$\epsilon_{12} = \xi_{12}(\epsilon_{11}\epsilon_{22})^{1/2}$$

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$$

Show that to first order

$$\frac{A - A_0}{NkT} = -4\pi\rho x_1 x_2 d_{12}^2 g_0^{12}(d_{12})[d_{12} - \delta_{12}] + 2\pi\beta\rho \sum_{\lambda,\mu} x_\lambda x_\mu \int_{\sigma_{\lambda\mu}}^{\infty} u_{\lambda\mu}(r) g_0^{\lambda\mu}(r) r^2 dr$$

where A_0 and $g_0^{\lambda\mu}(r)$ are the Helmholtz free energy and radial distribution functions of a hard-sphere mixture with

$$d_{\lambda\mu} = \frac{1}{2}(d_{\lambda\lambda} + d_{\mu\mu})$$

$$d_{\lambda\lambda} = \sigma_{\lambda\lambda}$$

and

$$\delta_{\lambda\mu} = \int_0^{\sigma_{\lambda\mu}} [1 - e^{-\beta u_{\lambda\mu}(x)}] dx$$

Grundke *et al.* show that very good agreement with various experimental data can be obtained with this equation.

14-24. Neff and McQuarrie† have applied perturbation theory to the calculation of the Henry's law constant. Recall that this is defined by

$$K_H = \lim_{x_2 \rightarrow 0} \left(\frac{p_2}{x_2} \right)$$

where p_2 is the partial pressure of the solute above the solution and x_2 is the mole fraction of solute in solution.

From K_H , the molar heat of solution ΔH_s and the partial molar volume solute \bar{V}_2 can be obtained from

$$\frac{\Delta H_s}{RT} = \left(\frac{1}{T} \right) \left[\frac{\partial \ln K_H}{\partial T^{-1}} \right]_p$$

$$\bar{V}_2 = RT \left(\frac{\partial \ln K_H}{\partial p} \right)_T$$

Consider a liquid solution of some solute (denoted by a subscript 2) in some solvent (subscript 1) which is in equilibrium with gaseous solute at partial pressure p_2 .

$$\mu_2^{\text{gas}} = \mu_2^{\text{soln}}$$

If we assume the gas phase to be ideal, $\mu_2^{\text{gas}} = \mu_2^*(T) + kT \ln(p_2/kT)$. The chemical potential of solute in the solution can be obtained from

$$\mu_2^{\text{soln}} = \left(\frac{\partial A}{\partial N_2} \right)_{T, V, N_1}$$

* Cf. e.g., E. W. Grundke, D. Henderson, J. A. Barker, and P. J. Leonard, *Mol. Phys.*, **25**, p. 883, 1973.
† *J. Phys. Chem.*, **77**, p. 413, 1973.

From Problem 14-23, we have that

$$\beta A = \beta A_0 - 4\pi\rho_1 N_2 d_{12}^2 g_0(d_{12})[d_{12} - \delta_{12}] + 2\pi\beta \sum_{i,j} \rho_i N_j \int_{\sigma_{ij}}^{\infty} dr r^2 u_{ij}(r) g_0^{ij}(r)$$

where all the symbols are defined in Problem 14-23.

Following Neff and McQuarrie, show that $\ln K_H$ can be written in the form

$$\ln K_H = \ln \frac{RT}{\bar{V}_1} + \left(\frac{\mu_2^{\text{HS}}}{kT} \right) + \left(\frac{\mu_2^{\text{corr}}}{kT} \right)$$

where

$$\frac{\mu_2^{\text{HS}}}{kT} = -\ln(1-y) + y\chi(y)R^2 + \left(\frac{1}{2} \right) \left[\frac{3y}{(1-y)} \right]^2 R^2 + \left[\frac{3y}{(1-y)} \right] (R^2 + R)$$

$$y = \frac{\pi\rho_1 d_{11}^3}{6}$$

$$R = \frac{d_{22}}{d_{11}}$$

$$\chi(y) = \frac{(1+y+y^2)}{(1-y)^3}$$

$$\frac{\mu_2^{\text{corr}}}{kT} = \left(\frac{-2\rho_1 a_{12}}{kT} \right) + \left(\frac{2\rho_1 I_{11}}{kT} \right) - 4\pi\rho_1 d_{12}^2 (d_{12} - \delta_{12}) g_0^{12}(d_{12})$$

$$a_{12} = -2\pi \int_{\sigma_{12}}^{\infty} dr r^2 u_{12}(r) g_0^{12}(r)$$

$$I_{11} = \pi N_1 \int_{\sigma_{11}}^{\infty} dr r^2 u_{11}(r) \left[\frac{\partial g_0^{11}(r)}{\partial N_2} \right]_{T, V, N_1}$$

Neff and McQuarrie compare this equation and its derivatives to experimental data.