MOLECULAR PHYSICS, 1972, VOL. 23, NO. 2, 393–406

Thermodynamic perturbation theory for simple polar fluids, I

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(*Received* 4 *November* 1971)

The application of thermodynamic perturbation theory to the computation of the properties of simple polar fluids is considered. The Helmholtz free energy of a fluid of molecules interacting via a Stockmayer potential v^{S} is computed through fourth order in μ, where μ is the dipole moment. Numerical results are obtained on the basis of both the 'exact' Monte-Carlo computations for a Lennard–Jones system and the Verlet–Weis perturbation-theoretic computations for that system. The results obtained on the latter basis are then compared with results for a fluid of molecules interacting via a central-force potential v^{ES} that is conformal with the Lennard–Jones 6–12 potential and equivalent to the Stockmayer potential through order μ^4. To facilitate the comparison the v^{ES} results are computed according to the Verlet–Weis method. The v^{ES} results and the fourth-order (in μ) v^{S} results constitute two different approximations to the thermodynamics of the Stockmayer potential; the compressibility factors as well as the free energies of the two approximations are compared.

It is concluded that the thermodynamic contribution of the dipole term of v^{S} is significant over the whole liquid region when $\mu^2=\epsilon\sigma^3$, where ϵ and σ are the usual Lennard–Jones parameters. For this μ, the two approximations we consider give results in close agreement.

1. INTRODUCTION AND GENERAL DISCUSSION

Recently a great deal of progress [1] has been made in applying thermodynamic perturbation theory (tpt) to a fluid consisting of particles interacting with a Lennard–Jones pair potential, which can be used to represent the molecular interaction in Argon and other monatomic fluids. Much earlier, the application of tpt to molecules that interact via non-central forces had been considered by several workers [2, 3] but the lack of accurate expressions for central-force reference systems severely limited their studies. The recent advances made in connection with Lennard–Jones molecules have led us to undertake a new investigation of the application of tpt to the case of non-central pair potentials, which we begin with this paper.

A simple way to represent orientation dependence of a potential is to add a multipole term or terms—a dipole–dipole term, a dipole–quadrupole term, a quadrupole–quadrupole term, etc.—to a contribution that depends solely upon the distance r between molecular centres, such as the Lennard–Jones potential. Such multipole terms cannot be expected to represent the lack of spherical symmetry associated with the highly repulsive core of a somewhat elongated or otherwise non-spherically-symmetric molecule, and for molecules in which such asymmetry of the core is a significant feature, one must also introduce the asymmetry explicitly in the core term. For cores that are not extremely orientation dependent, one can then perturb [4] off a hard-sphere core in an ' anisotropy parameter ' as well as in a softness parameter, absorbing the anisotropy as well as the softness into a judiciously chosen state-dependent sphere diameter. In the formal development of Part I of this work, however, we shall consider only the thermodynamic contribution of the multipole terms, and moreover we shall ignore all polarization effects. (A part of the polarization can be taken into account immediately albeit unsystematically by using actual multipole moments rather than the permanent moments in the multipole terms, but we shall not delve into this question in this paper.) In our numerical calculations of Part I we further restrict our attention to the well-known Stockmayer potential, which consists of a Lennard–Jones term plus an ideal dipole–dipole term.

The paper has three sections beyond this Introduction. In § 2 the formalism we use is developed. Our starting point is equation (2.4), a generalization to the case of non-central pair forces of an equation that has been previously introduced elsewhere [5] to relate the Helmholtz free energy and the pair-distribution function. When expanded in λ, a strength parameter associated with the perturbing potential, the equation immediately yields for polar systems an expansion originally obtained by Pople [2], and discussed in detail by Rowlinson [6]. The term of order λ is zero, the λ^2-term is well known. Here we also give the λ^3-term, which to our knowledge is a new result.

In § 3, we consider some relations peculiar to the Stockmayer potential. In the special case presented by this potential, conformality arguments [3] enable one to express the results of lowest-order tpt (which is of fourth order in the dipole moment μ and which we label with the superscript S(4)) in terms of the thermodynamic properties of the Lennard–Jones fluid without the introduction of the Lennard–Jones radial distribution function. Alternatively one can exploit the existence [7] of an effective potential that is spherically symmetric and thermodynamically equivalent through terms of order μ^4 to the Stockmayer potential. When terms through order μ^4 are retained in this effective potential, the resulting expression (which we shall call the effective Stockmayer potential) is conformal with the Lennard–Jones potential. (We shall label the effective Stockmayer results with the superscript ES.) If one substitutes an arbitrary higher multipole term for the dipole–dipole term such conformality arguments are no longer of much use. Nevertheless the concept of effective potentials that reproduce the thermodynamics of the polar potentials through lowest order in the relevant multipole moments and depend only upon the distance r between molecular centers can be profitably retained. We exhibit the effective dipole–quadrupole, quadrupole–quadrupole and dipole–octupole potentials in § 3 for future reference.

In § 4 we give numerical results for the Stockmayer potential using the available Monte-Carlo results [1] for a Lennard–Jones system to assess the excess free energy per particle Δf for the Stockmayer system through order μ^4. We then compute the same quantity, $\Delta f^{S(4)}$, using the Verlet–Weis version [1] of tpt [15] to treat the Lennard–Jones system, and we compare the result with Δf^{ES}, the excess free energy per particle for v^{ES}, computed according to the same Verlet–Weis scheme. In addition we compute the S(4) and ES compressibility factors using the Verlet–Weis method. For sufficiently small $\mu^2/\epsilon\sigma^3$ (where ϵ and σ are the usual Lennard–Jones parameters) the S(4) and ES results must coincide, since they are identical through order $\mu^4/\epsilon^2\sigma^6$. For $\mu^2/\epsilon\sigma^3=1$, we still find excellent agreement between the two sets of results.

In Part II of this work we shall go on to consider the thermodynamic contributions associated with the higher multipole moments. In addition, we shall also continue our study of the thermodynamic properties of the Stockmayer potential.

2. Formal considerations

In the simplest model of a polar fluid, the pair interaction is approximated by a point dipole term v^D added to a non-polar term v^N. In this case the pair potential $v(\mathbf{r}_{ij}, \boldsymbol{\omega}_i, \boldsymbol{\omega}_j)$ between particles i and j with centres at $\mathbf{r}_i$ and $\mathbf{r}_j$ and angular orientations given by $\boldsymbol{\omega}_i$ and $\boldsymbol{\omega}_j$ can be written as

$$v(\mathbf{x}_i, \mathbf{x}_j) = v^N + \mu^2 v^D, \tag{2.1}$$

where $\mathbf{x}_i$ is the vector $(\mathbf{r}_i, \boldsymbol{\omega}_i)$ describing both the rotational and translational coordinates of the ith particle and v^D is given by

$$v^D(\mathbf{x}_1, \mathbf{x}_2) = \frac{-2\cos\theta_1 \cos\theta_2 + \sin\theta_1 \sin\theta_2 \cos(\phi_1-\phi_2)}{r_{12}^3}. \tag{2.2}$$

Here μ is the dipole moment, $r_{12}=|\mathbf{r}_{12}|$, θ_i is the angle made by the dipole of the ith particle with the line joining the particles, and ϕ_i is the azimuthal angle made ? by the dipole with any plane containing that line. We shall assume that $d\boldsymbol{\omega}$ is normalized so that $\int d\boldsymbol{\omega} = 4\pi$.

In applying thermodynamic perturbation theory to any system one begins by writing the pair potential as a sum of two parts, the choice of which is dictated by the particular problem at hand,

$$v(\mathbf{x}_1, \mathbf{x}_2) = v_0(\mathbf{x}_1, \mathbf{x}_2) + \lambda w(\mathbf{x}_1, \mathbf{x}_2). \tag{2.3}$$

Then if F is the Helmholtz free energy, F_0 the free energy of the reference system in which $\lambda=0$, and $n(\mathbf{x}_1, \mathbf{x}_2)$ the two-particle probability distribution function (such that $n(\mathbf{x}_1, \mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2$ gives the probability of finding a particle with $\mathbf{x}_1$ in the element $d\mathbf{x}_1$ and some other particle with $\mathbf{x}_2$ in $d\mathbf{x}_2$),

$$F = F_0 + \tfrac{1}{2}\int_0^\lambda d\tilde{\lambda} \int d\mathbf{x}_1 d\mathbf{x}_2 n(\mathbf{x}_1, \mathbf{x}_2; \tilde{\lambda}) w(\mathbf{x}_1, \mathbf{x}_2). \tag{2.4}$$

(Our notation differs here from our previous [8] use of F as a free energy density.) The $n(\mathbf{x}_1, \mathbf{x}_2; \lambda)$ is the $n(\mathbf{x}_1, \mathbf{x}_2)$ for the particular value of λ being considered in (2.3) and F, F_0 and $n(\mathbf{x}_1, \mathbf{x}_2; \lambda)$ are all to be evaluated at the same number density ρ and temperature $T=(\beta k)^{-1}$. By expanding $n(\mathbf{x}_1, \mathbf{x}_2; \lambda)$ in powers of λ,

$$n(\mathbf{x}_1, \mathbf{x}_2; \lambda) = n^{(0)}(\mathbf{x}_1, \mathbf{x}_2) + \lambda n^{(1)}(\mathbf{x}_1, \mathbf{x}_2) + \dots, \tag{2.5}$$

and inserting this expression into (2.4), one generates a corresponding λ-expansion of F

$$F=F_0+\lambda F_1+\lambda^2F_2+\dots, \qquad (2.6)$$

where

$$F_1=\tfrac{1}{2}\int d\mathbf{x}_1 d\mathbf{x}_2 n^{(0)}(\mathbf{x}_1, \mathbf{x}_2)w(\mathbf{x}_1, \mathbf{x}_2). \qquad (2.7)$$

In general, the higher-order terms are of a somewhat complex form when expressed in terms of s-particle distribution functions, but for certain potentials, such as the one given by (2.1), a remarkable simplification takes place. Identifying v^{N} as the reference potential v_0, v^{D} as w, and μ^2 as λ, one finds that if v^{N} depends only upon r_{12}, then F_1 vanishes and F_2 simplifies, because the spherical-harmonic expansion of v^{D} is free of terms of the type $X^{000}(r)$ that give rise to non-zero contributions [6] upon integration over $\boldsymbol{\omega}_1$ and $\boldsymbol{\omega}_2$. (See [6] for details.) Thus the free energy per particle $f=F/N$ reduces to

$$f=f_0+\mu^4f_2+\mu^6f_3+\mathrm{O}(\mu^8) \qquad (2.8)$$

with

$$f_2=-\frac{\beta\rho}{4(4\pi)^2}\int g_0(r_{12})[v^{\mathrm{D}}(\mathbf{x}_1, \mathbf{x}_2)]^2\, d\mathbf{r}_{12}d\omega_1 d\omega_2, \qquad (2.9)$$

where $g_0(r)$ is the radial distribution function of the reference fluid. In the next term we have

$$f_3=\frac{\beta^2\rho^2}{6(4\pi)^3}\int g_{123}{}^{(0)}(r_{12}, r_{13}, r_{23})v^{\mathrm{D}}(\mathbf{x}_1\mathbf{x}_2)v^{\mathrm{D}}(\mathbf{x}_1, \mathbf{x}_3)v^{\mathrm{D}}(\mathbf{x}_2, \mathbf{x}_3)\, d\mathbf{r}_2 d\mathbf{r}_3 d\omega_1 d\omega_2 d\omega_3, \qquad (2.10)$$

where $g_{123}{}^{(0)}(r_{12}, r_{13}, r_{23})$ is the three-particle distribution function of the reference fluid. The expression for f_2 can be further simplified to read

$$f_2=-\frac{\beta\rho}{6}\int g_0(r)r^{-6}\, d\mathbf{r} \qquad (2.11)$$

or

$$f_2=-\frac{2\pi\beta\rho}{3}\int_0^\infty g_0(r)r^{-4}\, dr. \qquad (2.12)$$

More general polar potentials than that given by (2.1) can also be treated in the same way. For example one can include a point dipole–quadrupole term v^{DQ}, a point quadrupole–quadrupole term v^{QQ}, and a point dipole–octupole term, v^{DO}, and do a multiple perturbation expansion in $\lambda_1=\mu^2$, $\lambda_2=\Theta^2$, and $\lambda_3=\Phi^2$ where Θ is the quadrupole moment and Φ the octupole moment. The generalization of (2.3)–(2.6) to such an expansion is obvious. One finds, after simplification

$$f=f_0+\mu^4f_2{}^{\mu}+\mu^2\Theta^2f_{1,1}{}^{\mu\Theta}+\Theta^4f_2{}^{\Theta}+\mu^2\Phi^2f_{1,1}{}^{\mu\Phi}+\dots, \qquad (2.13)$$

where $f_2{}^{\mu}$ is the f_2 of equation (2.9),

$$f_{1,1}{}^{\mu\Theta}=-\frac{\beta\rho}{2}\int g_0(r)r^{-8}\, d\mathbf{r}, \qquad (2.14)$$

$$f_2^{\Theta}=-\frac{7\beta\rho}{10}\int g_0(r)r^{-10}\,dr, \tag{2.15}$$

$$f_{1,1}^{\mu\Theta}=-\frac{4\beta\rho}{3}\int g_0(r)r^{-10}\,dr. \tag{2.16}$$

Still higher multipole terms—for example, a quadrupole-octupole term—can easily be included, but we shall have no occasion to consider such terms here or in Part II.

The expansion for f given by (2.13) was derived by Pople [3] and has been discussed in detail by Rowlinson [4]. (We know of no previous treatment of polar fluids in which the explicit form of f_3 given by (2.10) has appeared, although Pople [9] derived some time ago a special case of (2.10) in connection with a lattice system of dipoles.)

3. Specific perturbation schemes for simple polar potentials

The potential given by (2.1) for the choice in which v^{D} is given by (2.2) and v^{N} is the Lennard-Jones potential

$$v^{\mathrm{LJ}}=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right] \tag{3.1}$$

was first studied by Stockmayer [10] and bears his name. We shall denote it by v^{S} and use the superscript S to refer to it. It follows from (2.11) and (2.8) that, through order μ^4, the thermodynamics of a Stockmayer system is exactly equivalent to the thermodynamics of a temperature-dependent potential v^{ES}, where

$$v^{\mathrm{ES}}=v^{\mathrm{LJ}}+v^{\mathrm{ED}}, \tag{3.2}$$

with

$$v^{\mathrm{ED}}=-(\mu^4/3kT)r^{-6}, \tag{3.3}$$

so that

$$v^{\mathrm{ES}}=4\epsilon\left\{\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}(1+2\chi)\right\}, \tag{3.4}$$

where $\chi(T)=\mu^{*4}/24T^*$ in which the reduced dipole moment $\mu^*=(\mu^2/\epsilon\sigma^3)^{1/2}$ and the reduced temperature $T^*=kT/\epsilon$. The v^{ES} is conformal with the Lennard-Jones potential since (3.4) may be written in the form

$$v^{\mathrm{ES}}=4\epsilon'\left\{\left(\frac{\sigma'}{r}\right)^{12}-\left(\frac{\sigma'}{r}\right)^{6}\right\}, \tag{3.5}$$

with $\epsilon'=\epsilon(1+2\chi)^2$ and $\sigma'=\sigma/(1+2\chi)^{1/6}$. From the law of corresponding states it follows that if F^{ES} is the free energy of the system with potential v^{ES} then

$$\frac{F^{\mathrm{ES}}(\rho,T)}{NkT}=\frac{F^{\mathrm{LJ}}(\rho',T')}{NkT'}+\tfrac{1}{2}\ln(1+2\chi), \tag{3.6}$$

where $\rho'=\rho/(1+2\chi)^{1/2}$ and $T'=T/(1+2\chi)^2$. Making use of the definition of the excess free energy, ΔF:

$$\frac{\Delta F(\rho,T)}{NkT}\equiv\frac{F(\rho,T)}{NkT}-\ln\rho+1, \tag{3.7}$$

we see that (3.6) may be written in the simpler form

$$\frac{\Delta F^{\mathrm{ES}}(\rho,T)}{NkT}=\frac{\Delta F^{\mathrm{LJ}}(\rho',T')}{NkT'}. \tag{3.8}$$

For small χ, (3.6) reduces to an equation given by Rowlinson [7, 11]

$$\frac{F^{\mathrm{ES}}(\rho,T)}{NkT}=(1+4\chi)\cdot\frac{F^{\mathrm{LJ}}(\rho',T')}{NkT}+\chi \tag{3.9}$$

with $\rho'=\rho/(1+\chi)$ and $T'=T(1-4\chi)$. Equation (3.8) also yields on expanding $\Delta F^{\mathrm{LJ}}(\rho',T')/NkT'$ in a Taylor series in powers of $(\rho'-\rho)$ and $(T'-T)$ about its value at $\rho'=\rho$ and $T'=T$, the result [12]

$$\beta f^{\mathrm{ES}}=\beta f^{\mathrm{LJ}}+\chi\left[4\beta u^{\mathrm{LJ}}-\frac{\beta p^{\mathrm{LJ}}}{\rho}+1\right]+\mathrm{O}(\chi^2), \tag{3.10}$$

where $\beta f=F/NkT$ and u^{LJ} and p^{LJ} are the excess internal energy per particle and pressure of the Lennard–Jones system at a density ρ and temperature T. The first two terms of (3.10) also give the excess free energy of the Stockmayer system through order μ^4 exactly, a result which was derived by Zwanzig [3] from the observation that the integral $\int g^{\mathrm{LJ}}(r)r^{-6}d\mathbf{r}$ can be exactly expressed in terms of the thermodynamics of the Lennard–Jones system. To so express the integral, we note that from the development of the last section (with $v_0=v^{\mathrm{LJ}}$ and $w=v^{\mathrm{ED}}$)

$$\beta f^{\mathrm{ES}}-\beta f^{\mathrm{LJ}}=\frac{-\beta^2\rho\mu^4}{6}\int g^{\mathrm{LJ}}(r)r^{-6}\,d\mathbf{r}+\mathrm{O}(\chi^2). \tag{3.11 a}$$

Comparing (3.10) and (3.11 *a*) we have

$$\frac{-\beta^2\rho\mu^4}{6}\int g^{\mathrm{LJ}}(r)r^{-6}\,d\mathbf{r}=\chi\left[4\beta u^{\mathrm{LJ}}-\frac{\beta p^{\mathrm{LJ}}}{\rho}+1\right]. \tag{3.11 b}$$

In computing f^{ES} from (3.8), (3.9), or (3.10) one does not need g^{LJ}, which would be required in using (3.11 *a*). However, the avoidance of g^{LJ} afforded by (3.8)–(3.10) rests upon the occurrence of the r^6 that appears in (2.11) and (3.3) and hence is restricted to the quite special case of the Stockmayer potential.

To compute the compressibility factor $p^{\mathrm{ES}}/kT\rho$ for $v^{\mathrm{ES}}(r)$ one has the relation

$$\frac{p^{\mathrm{ES}}(\rho,T)}{kT\rho}=\frac{p^{\mathrm{LJ}}(\rho',T')}{kT'\rho'}. \tag{3.12}$$

If one instead differentiates (3.10) in order to find p^{S} to order μ^4, one needs $(\partial p^{\mathrm{LJ}}/\partial\rho)_T$ and $(\partial u^{\mathrm{LJ}}/\partial\rho)_T$[or $(\partial p^{\mathrm{LJ}}/\partial T)_\rho$ since $\rho^2(\partial u/\partial\rho)_T=p-T(\partial p/\partial T)_\rho$].

We note in passing that by applying the Gibbs–Bogolivbov inequality [8] to a system interacting according to (3.2), in which v^{LJ} is the reference-system potential and v^{ED} is the perturbation, we have the inequality

$$\beta f^{\mathrm{ES}} \leqslant \beta f^{\mathrm{LJ}} + \chi[4\beta u^{\mathrm{LJ}} - (\beta p^{\mathrm{LJ}}/\rho) + 1].$$

It does not follow that βf^{S} itself is bounded by the right-hand side of the above inequality, but since f^{S} and f^{ES} coincide through first order in χ, f^{S} can only exceed the right-hand side as a result of the effect of non-linear terms in χ.

Although neither (3.10) nor (3.8) can be used when $v_0 \neq v^{\mathrm{LJ}}$, or when dipole–quadrupole effects, quadrupole–quadrupole effects, etc., are included, the concept of an effective potential that depends only on r is of very general convenience since regardless of the exact form of v_0 it is still true that through order μ^4, v^{D} can be replaced by the v^{ED} of (3.3), while the dipole-quadrupole potential v^{DQ} can be replaced through order $\mu^2\Theta^2$ by

$$v^{\mathrm{EDQ}} = -\left(\frac{\mu^2\Theta^2}{kT}\right) r^{-8}. \tag{3.13}$$

The quadrupole–quadrupole v^{QQ} can be replaced through order Θ^4 by

$$v^{\mathrm{EQQ}} = -\left(\frac{7\Theta^4}{5kT}\right) r^{-10}, \tag{3.14}$$

and the dipole–octupole v^{DO} can be replaced through order $\mu^2\Phi^2$ by

$$v^{\mathrm{EDO}} = -\left(\frac{4\mu^2\Phi^2}{3kT}\right) r^{-10}. \tag{3.15}$$

As a result of the preceding observations, if one wishes to investigate the effect of the potential

$$v = v^{\mathrm{N}} + v^{\mathrm{D}} + v^{\mathrm{DQ}} + v^{\mathrm{QQ}} + v^{\mathrm{DO}} \tag{3.16}$$

through terms of order $\mu^i\Theta^j\Phi^k$, $i+j+k=4$, one can choose instead

$$v^{\mathrm{E}} = v^{\mathrm{N}} + v^{\mathrm{ED}} + v^{\mathrm{EDQ}} + v^{\mathrm{EQQ}} + v^{\mathrm{EDO}} \tag{3.17}$$

as the assumed potential and then apply any one of the various versions of tpt recently developed to treat v^{LJ}. For example, one has the Barker–Henderson approach, the Mansoori–Canfield, Rasaiah–Stell approach [14], and the Weeks–Chandler–Andersen approach [15] which has been reassessed and reformulated by Verlet and Weis [1], and which appears to be the most accurate of the current perturbative treatments when applied to a Lennard–Jones system. When applied to the potential v^{E} of (3.17), the reference potential would *not* be taken to be v^{N} in any one of these approaches. Instead in each one of them the properties of the full potential is related to those of a hard-sphere system. Of course, if the potential of (3.17) is taken as the starting point, none of these approaches can be expected *a priori* to yield accurate results beyond the order $\mu^i\Theta^j\Phi^k$, $i+j+k=4$. Furthermore, if v^{N} is chosen to be v^{LJ}, and Θ and Φ are zero so that $v^{\mathrm{E}} = v^{\mathrm{ES}}$, then none of these approaches can do better than the use of (3.8) with Monte-Carlo

LJ results, since this yields essentially exact information for the v^{ES} potential. An alternative use of tpt in treating the v given by (3.16) consists of taking v^{N} as the reference potential v_0 and $v-v^{N}$ as w, and treating the attendant problem of evaluating $\int g^{LJ}r^{-n}\,dr$ as a separate question. For the dipole case of $n=6$ the results of § 4 show that these two different approaches yield essentially the same approximation when $\mu^2/\epsilon\sigma^3 \leqslant 1$.

The concept of a central-force potential that is thermodynamically equivalent to v^{S} through order μ^4 was introduced by Cook and Rowlinson [7]. By using it in conjunction with conformality arguments of the sort discussed in this section, they were able to relate, through $O(\mu^4)$, the thermodynamic behaviour of Lennard–Jones and Stockmayer molecules, prior to the development of the expansion procedures of [2] and [3].

4. SOME NUMERICAL RESULTS FOR THE STOCKMAYER POTENTIAL

It is convenient to express our results in terms of the dimensionless quantities $T^*=kT/\epsilon$ or $\beta^*=T^{*-1}$, $\rho^*=\rho\sigma^3$, $\mu^{*2}=\mu^2/\epsilon\sigma^3$ and $r^*=r/\sigma$. It is also convenient to consider the excess Helmholtz free energy per particle, $\Delta f=\Delta F/N$, given by

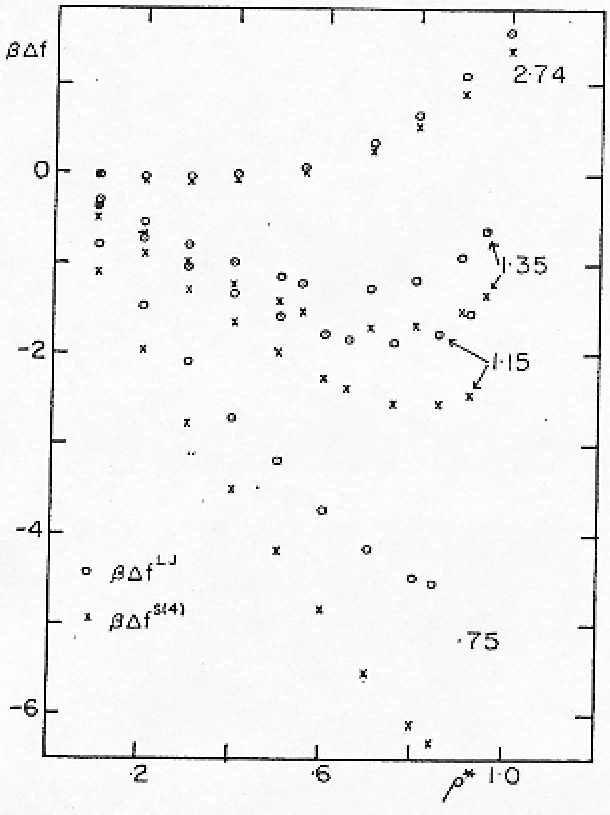

Figure 1. A comparison of the Monte-Carlo values of the Lennard–Jones free energy and the (approximate) Stockmayer free energy when $\mu^*=1$. The values, given for various $\rho\sigma^3=\rho^*$ at $kT/\epsilon=T^*$ equal to 0·75, 1·15, 1·35 and 2·74, are from Table 1.

(3.7), rather than f itself. The contribution to $\beta\Delta f^{\mathrm{S}}$ through order μ^{*4} can be written as

$$\beta\Delta f^{\mathrm{S}(4)}=\beta\Delta f^{\mathrm{LJ}}-\mu^{*4}\beta^{*2}J, \tag{4.1}$$

where

$$J=\rho^{*}\int g^{\mathrm{LJ}}(r^{*})r^{*-6}\,d\mathbf{r}/6. \tag{4.2}$$

All of our results are given here for $\mu^{*}=1$, which represents a value of μ that is typical of molecules with significant dipole moments. We consider the four reduced temperatures $T^{*}=0{\cdot}75$, $1{\cdot}15$, $1{\cdot}35$, and $2{\cdot}74$ in order to facilitate contact with existing Lennard–Jones results.

In table 1 we give the Monte-Carlo values of $\beta\Delta f^{\mathrm{LJ}}$, $\beta^{*2}J$, and $\beta\Delta f^{\mathrm{S}(4)}=\beta\Delta f^{\mathrm{LJ}}-\mu^{*4}\beta^{*2}J$. The latter equals $\beta\Delta f^{\mathrm{S}}$ through second order in

ρ^{*}	$\beta\Delta f^{\mathrm{LJ}}$	$\beta^{*2}J$	$\beta\Delta f^{\mathrm{S}(4)}$	$\beta\Delta f^{\mathrm{LJ}}$	$\beta^{*2}J$	$\beta\Delta f^{\mathrm{S}(4)}$
		$T^{*}=0{\cdot}75$			$T^{*}=1{\cdot}15$	
0·1	−0·80	−0·30	−1·10	−0·38	−0·09	−0·47
0·2	−1·48	−0·49	−1·97	−0·73	−0·17	−0·90
0·3	−2·10	−0·67	−2·77	−1·05	−0·25	−1·30
0·4	−2·68	−0·83	−3·51	−1·34	−0·32	−1·66
0·5	−3·22	−0·96	−4·18	−1·59	−0·40	−1·99
0·6	−3·73	−1·12	−4·85	−1·78	−0·49	−2·27
0·65				−1·84	−0·54	−2·38
0·7	−4·17	−1·35	−5·52			
0·75				−1·89	−0·65	−2·54
0·8	−4·47	−1·63	−6·10			
0·84	−4·53	−1·76	−6·29			
0·85				−1·78	−0·78	−2·56
0·92				−1·56	−0·89	−2·45
		$T^{*}=1{\cdot}35$			$T^{*}=2{\cdot}74$	
0·1	−0·29	−0·06	−0·35	−0·03	−0·01	−0·04
0·2	−0·56	−0·12	−0·68	−0·05	−0·03	−0·08
0·3	−0·80	−0·17	−0·97	−0·05	−0·04	−0·09
0·4	−1·00	−0·23	−1·23	−0·01	−0·06	−0·07
0·5	−1·16	−0·29	−1·45			
0·55	−1·22	−0·32	−1·54	0·06	−0·08	−0·02
0·70	−1·29	−0·43	−1·72	0·37	−0·11	0·26
0·80	−1·19	−0·52	−1·71	0·65	−0·14	0·51
0·90	−0·91	−0·63	−1·54	1·04	−0·16	0·88
0·95	−0·67	−0·69	−1·36			
1·00				1·58	−0·19	1·39
1·08				2·16	−0·22	1·94

Table 1. Monte-Carlo values of $(kT)^{-1}$ times the Lennard–Jones excess Helmholtz free energy per particle, along with Monte-Carlo values of $\beta^{*2}J$ and $\beta\Delta f^{\mathrm{S}(4)}=\beta\Delta f^{\mathrm{LJ}}-\mu^{*4}\beta^{*2}J$ for $\mu^{*}=1$. These quantities are given by equations (4.1) and (4.2); $\Delta f^{\mathrm{S}(4)}$ is the excess free energy per particle for a Stockmayer system through fourth order in the dipole moment.

μ^{*2}, evaluated at $\mu^*=1$. These Monte-Carlo results, denoted by the subscript mc and taken from [1], are the best estimates available to us and are essentially exact. The right-hand side of (3.11 *b*) was used to evaluate $\beta^{*2}J$ in terms of the Monte-Carlo results for $u^{\rm LJ}$ and $p^{\rm LJ}$. In figure 1 we show the $\beta\Delta f^{\rm LJ}$ and $\beta\Delta f^{\rm S(4)}$ that are given in table 1.

In table 2 we compare $\beta\Delta f^{\rm ES}$ and $\beta\Delta f^{\rm S(4)}$, which represent two different approximations to $\beta\Delta f^{\rm S}$. Again we let $\mu^*=1$ and for reference, we also give $\beta\Delta f^{\rm LJ}$ (to which $\beta\Delta f^{\rm ES}$, $\beta\Delta f^{\rm LJ}-\mu^{*4}\beta^{*2}J$, and $\beta\Delta f^{\rm S}$ all reduce when $\mu^*=0$). For $\mu^*=1$ we have no simple and accurate means of using (3.8) to obtain $\beta\Delta f^{\rm ES}$ directly from the Lennard-Jones Monte-Carlo results at the four temperatures we have chosen to look at, so we have computed the right-hand side of (3.8)

ρ^*	$\beta\Delta f^{\rm ES}$	$\beta\Delta f^{\rm S(4)}$	$\beta\Delta f^{\rm LJ}$	$\beta\Delta f^{\rm ES}$	$\beta\Delta f^{\rm S(4)}$	$\beta\Delta f^{\rm LJ}$
	$T^*=0·75$			$T^*=1·15$		
0·1	−0·680	−0·687	−0·552	−0·351	−0·352	−0·293
0·2	−1·423	−1·437	−1·153	−0·726	−0·729	−0·605
0·3	−2·214	−2·237	−1·787	−1·116	−1·120	−0·923
0·4	−3·036	−3·069	−2·434	−1·504	−1·509	−1·232
0·5	−3·866	−3·907	−3·067	−1·871	−1·878	−1·510
0·6	−4·671	−4·719	−3·649	−2·193	−2·199	−1·731
0·65	−5·051	−5·102	−3·906	−2·326	−2·332	−1·809
0·70	−5·408	−5·460	−4·131	−2·435	−2·440	−1·859
0·75	−5·734	−5·784	−4·313	−2·514	−2·517	−1·874
0·8	−6·019	−6·066	−4·442	−2·554	−2·555	−1·846
0·85	−6·252	−6·292	−4·505	−2·550	−2·546	−1·767
0·9	−6·420	−6·449	−4·486	−2·490	−2·481	−1·628
0·95	−6·507	−6·518	−4·367	−2·366	−2·350	−1·418
1·0	−6·495	−6·480	−4·128	−2·165	−2·139	−1·125
	$T^*=1·35$			$T^*=2·74$		
0·1	−0·265	−0·265	−0·222	−0·031	−0·031	−0·020
0·2	−0·545	−0·547	−0·455	−0·056	−0·055	−0·031
0·3	−0·830	−0·833	−0·688	−0·065	−0·065	−0·027
0·4	−1·107	−1·110	−0·906	−0·051	−0·051	0·003
0·5	−1·357	−1·361	−1·090	−0·003	−0·002	0·069
0·6	−1·558	−1·562	−1·218	0·095	0·095	0·186
0·65	−1·632	−1·634	−1·250	0·167	0·168	0·269
0·7	−1·681	−1·683	−1·256	0·258	0·259	0·372
0·75	−1·701	−1·701	−1·229	0·371	0·372	0·497
0·8	−1·685	−1·684	−1·164	0·510	0·511	0·648
0·85	−1·628	−1·624	−1·053	0·676	0·678	0·828
0·9	−1·520	−1·513	−0·888	0·875	0·877	1·042
0·95	−1·354	−1·341	−0·660	1·110	1·113	1·293
1·0	−1·119	−1·100	−0·359	1·386	1·390	1·585

Table 2. Comparison of the ES and S(4) approximations to $\beta\Delta f$, where Δf is the excess free energy per particle. Values are given for the Stockmayer potential at $\mu^*=1$ along with the Lennard-Jones values, which both approximations yield when $\mu^*=0$. Here use has been made of the Verlet-Weis perturbation treatment in computing all quantities, as described in § 4.

according to the Verlet–Weis version of perturbation theory instead. (Alternatively the polynomials given by Levesque and Verlet [1] for $\beta\Delta f^{\mathrm{LJ}}$ could be used.) In order to minimize the effect of difference between the Monte-Carlo and Verlet–Weis values of f^{LJ} we compare $(\beta\Delta f^{\mathrm{ES}})_{\mathrm{vw}}$ with $(\beta\Delta f^{\mathrm{LJ}})_{\mathrm{vw}}-(\mu^{*4}\beta^{*2}J)_{\mathrm{vw}}$ rather than with $(\beta\Delta f^{\mathrm{LJ}})_{\mathrm{mc}}-(\mu^{*4}\beta^{*2}J)_{\mathrm{mc}}$. Here the subscripts vw and mc refer to the use of Verlet–Weis tpt values and Monte-Carlo values, respectively, in the evaluation of Lennard–Jones quantities. In figure 2 we show the $\beta\Delta f^{\mathrm{LJ}}$ and $\beta\Delta f^{\mathrm{ES}}$ of table 2. The $\beta\Delta f^{\mathrm{S(4)}}$ curves are not shown, since they are nearly indistinguishable from the $\beta\Delta f^{\mathrm{ES}}$ curves. Similarly, the $\beta p^{\mathrm{ES}}/\rho$ and $\beta p^{\mathrm{S(4)}}/\rho$ isotherms corresponding to these curves are also nearly indistinguishable from one another. In table 3 we give the values of $\beta p^{\mathrm{ES}}/\rho$, $\beta p^{\mathrm{S(4)}}/\rho$ and $\beta p^{\mathrm{LJ}}/\rho$ obtained by differentiating the free energies of table 2, and in figure 3 we draw the resulting $\beta p^{\mathrm{LJ}}/\rho$ and $\beta p^{\mathrm{ES}}/\rho$ curves, which correspond to the free-energy curves of figure 2. It is clear that the dipole contribution to the equation of state of the Stockmayer system is large for all but the highest of the four temperatures considered.

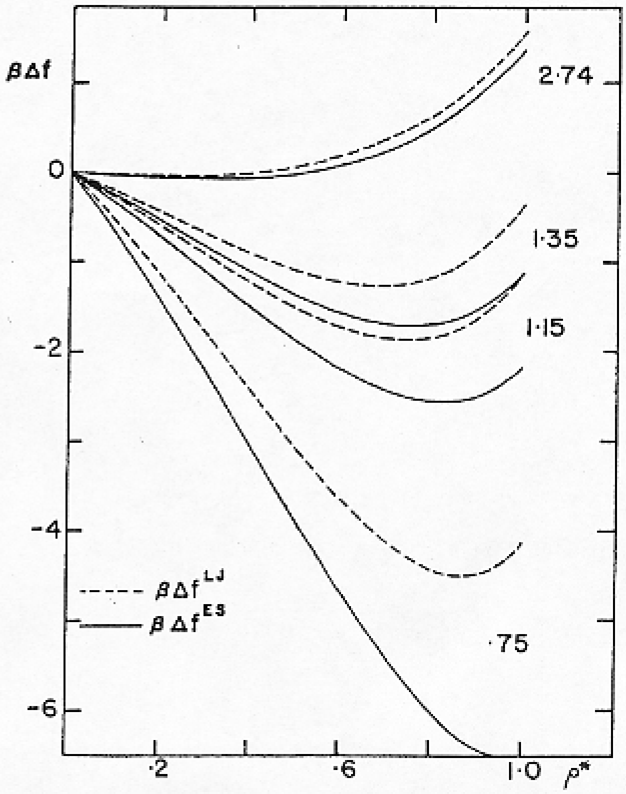

Figure 2. A comparison of Lennard–Jones and (approximate) Stockmayer free energies when $\mu^*=1$, computed by means of the Verlet–Weis perturbation method. The four pairs of curves (in ascending order) are for $kT/\epsilon=T^*$ equal to 0·75, 1·15, 1·35, and 2·74. The values are those of Table 2. The approximate Stockmayer curves shown are ES curves; the S(4) curves are virtually the same as these on the scale of this graph.

It should be noted that none of our results as they stand indicate the liquid-gas phase boundary. A double-tangent construction on βf or the equivalent Maxwell construction on βp must be made to locate the co-existence region, which will include segments of all but the $T^*=2{\cdot}74$ isotherm when $\mu^*=1$. We shall locate the phase boundaries in Part II of this work, but it is worth remarking here that discrepancies between the Monte-Carlo results of table 1 and the tpt results of table 2 are only substantial in a p^*-T^* domain that lies within the coexistence region. Outside of this region the differences are small, for $\mu^*=1$ as well as for $\mu^*=0$.

ρ^*	$\beta p^{\mathrm{ES}}/\rho$	$\beta p^{\mathrm{S(4)}}/\rho$	$\beta p^{\mathrm{LJ}}/\rho$	$\beta p^{\mathrm{ES}}/\rho$	$\beta p^{\mathrm{S(4)}}/\rho$	$\beta p^{\mathrm{LJ}}/\rho$
		$T^*=0{\cdot}75$			$T^*=1{\cdot}15$	
0·1	0·287	0·283	0·421	0·635	0·635	0·696
0·2	−0·539	−0·559	−0·241	0·231	0·226	0·366
0·3	−1·430	−1·460	−0·933	−0·174	−0·179	0·051
0·4	−2·321	−2·355	−1·580	−0·525	−0·527	−0·188
0·5	−3·114	−3·156	−2·070	−0·744	−0·746	−0·270
0·6	−3·671	−3·716	−2·239	−0·721	−0·730	−0·076
0·65	−3·798	−3·842	−2·131	−0·573	−0·585	0·174
0·7	−3·782	−3·812	−1·843	−0·302	−0·314	0·562
0·75	−3·579	−3·580	−1·325	0·123	0·116	1·118
0·8	−3·139	−3·091	−0·519	0·735	0·741	1·879
0·85	−2·401	−2·279	0·645	1·576	1·603	2·889
0·9	−1·293	−1·068	2·244	2·690	2·746	4·186
0·95	0·274	0·640	4·368	4·123	4·222	5·823
1·0	2·389	2·989	7·092	5·931	6·102	7·832
		$T^*=1{\cdot}35$			$T^*=2{\cdot}74$	
0·1	0·726	0·724	0·771	0·971	0·970	0·983
0·2	0·430	0·428	0·530	0·963	0·964	0·990
0·3	0·150	0·148	0·316	1·001	1·004	1·046
0·4	−0·066	−0·067	0·182	1·118	1·119	1·184
0·5	−0·147	−0·150	0·202	1·356	1·352	1·449
0·6	0·005	−0·004	0·480	1·773	1·760	1·899
0·65	0·210	0·198	0·759	2·072	2·054	2·217
0·7	0·528	0·514	1·161	2·447	2·424	2·613
0·75	0·985	0·971	1·713	2·909	2·882	3·099
0·8	1·612	1·601	2·447	3·474	3·440	3·689
0·85	2·442	2·438	3·394	4·156	4·111	4·400
0·9	3·510	3·520	4·590	4·972	4·908	5·246
0·95	4·856	4·890	6·075	5·938	5·849	6·243
1·0	6·520	6·603	7·876	7·065	6·960	7·403

Table 3. Comparison of the ES and S(4) approximate compressibility factors for the Stockmayer potential at $\mu^*=1$, along with the Lennard–Jones factor to which they reduce when $\mu^*=0$. Here use has been made of the Verlet–Weis perturbation treatment in computing all quantities, as described in § 4. (The required differentiation of $\beta f^{\mathrm{S(4)}}$ was done by differentiating polynomials in ρ fitted for each temperature; care was taken to minimize fitting errors but they probably contribute as much to the small differences between the $(\beta p/\rho)^{\mathrm{ES}}$ and $(\beta p/\rho)^{\mathrm{S(4)}}$ values shown as do the true differences.)

Our two main conclusions are the following: (i) for a potential in which $\mu^* \approx 1$, the thermodynamic contribution of the dipole interaction must be taken into consideration with care in any accurate theory of the liquid state of polar molecules, since the contribution will be a significant part of the effect of the interaction potential in the liquid region; and (ii) for $\mu^* \leqslant 1$, the S(4) and ES expressions that give approximations to the Stockmayer thermodynamics in terms of the Lennard–Jones thermodynamics yield nearly identical results. Thus the choice between them in any particular application involving this range of μ^* can be dictated largely by matters of convenience.

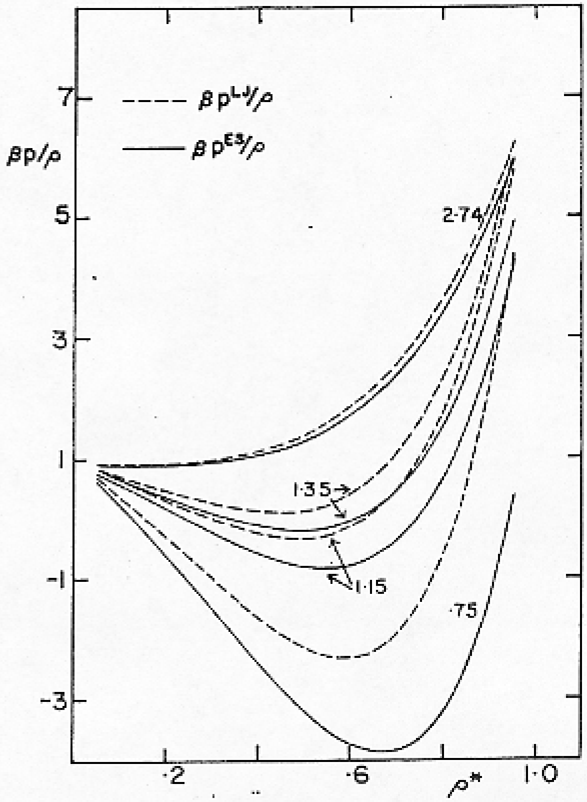

Figure 3. A comparison of the Lennard–Jones and approximate Stockmayer compressibility factors where $\mu^* = 1$, computed by means of the Verlet–Weis perturbation method. The four pairs of curves (in ascending order) are for $kT/\epsilon = T^*$ equal to 0·75, 1·15, 1·35 and 2·74. The values are those of Table 3. The approximate Stockmayer curves are ES curves; the S(4) curves are virtually the same (except for $T^* = 0{\cdot}75$ and high ρ^*).

In closing, we wish to call attention to the extreme sensitivity of the thermodynamic contribution of the dipole to the value of μ^*, owing to the fourth power of μ^* that appears in the lowest-order dipole term. If one considers $\mu^* = \frac{1}{2}$ instead of $\mu^* = 1$, the thermodynamic contribution of the dipole interaction is almost negligible for all but the lowest of the temperatures we have considered here.

The research was supported in part by the National Science Foundation, Grants GP 21311 and GU-3850.

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