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Thermodynamic perturbation theory for simple polar fluids. II†

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The study of polar fluids begun in a previous paper is continued. Calculations for the Stockmayer potential are extended to include the term of order μ^6, where μ is the dipole moment. The effects of higher-order terms are then approximated by means of a simple Padé extrapolation procedure, and the liquid–gas coexistence curve is located in this approximation. An orientation-independent but temperature-dependent potential that is thermodynamically equivalent to an arbitrary orientation-dependent potential is introduced and used to assess the lowest-order thermodynamic effects that result from the presence of quadrupole and octupole terms in the pair-potential. Several values of quadrupole and octupole moments representative of a dipolar molecule (HCl) as well as linear molecules (N_2, O_2 and CO_2, for which $\mu=0$) are considered.

1. INTRODUCTION

This paper is a sequel to an earlier publication [1] on the thermodynamics of polar fluids. We refer to that paper for the necessary background and notational details, but recall parts of the theory which are relevant to our discussion here. The perturbation theory that is used in our numerical work [2–4] assumes that the orientational part of the pair-potential $v(\mathbf{x}_i, \mathbf{x}_j)$ for two molecules can be treated as a perturbation of a spherically symmetric potential $v_0(r)$ which characterizes the reference system

$$v(\mathbf{x}_i, \mathbf{x}_j)=v_0(r)+\sum_k \lambda_k w(\mathbf{x}_i, \mathbf{x}_j)\,; \quad \lambda_k \geqslant 0. \tag{1.0}$$

Here we shall consider $v(\mathbf{x}_i, \mathbf{x}_j)$ such that the directional effects, which are represented in the perturbing potentials $\lambda_k w(\mathbf{x}_i, \mathbf{x}_j)$, are assumed to be due to

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interactions among point-dipoles, point-quadrupoles and point-octupoles situated at the centres of these molecules. Other orientational effects associated, for example, with the shapes of the molecular cores are (for the present) ignored [5, 6].

	Lennard–Jones parameters		Electric moments		Reduced electric moments†	
	ϵ/k	σ	$\mu \times 10^{18}$ (e.s.u. cm)	$\Theta \times 10^{26}$ (e.s.u. cm^2)	μ^*	Θ^*
CO_2	190	4·0	0	−4·3	0	0·83
O_2	118	3·46	0	−0·39	0	0·137
N_2	95·1	3·71	0	−1·52	0	0·501
HCl	218	3·51	1·03	3·8	0·903	0·949

† See (1·2) for definitions. The Lennard–Jones parameters for CO_2 (viscosity data) and N_2 (second virial-coefficient data) are from table 4.9 in ref. [26]. The corresponding parameters for O_2 (second virial-coefficient data) and HCl (viscosity data) are from ref. [27], tables 3.6-1 and 8.6-1, respectively. (The HCl parameters actually refer to an approximate Stockmayer potential.) The dipole moment of HCl is from ref. [27] while all of the quadrupole moments are from ref. [28]. We note that the reduced moments $\mu^* = (\mu^2/\epsilon\sigma^3)^{1/2}$ and $\Theta^* = (\Theta^2/\epsilon\sigma^5)^{1/2}$ are very sensitive to small changes in the potential energy, but in this paper we have used the above values simply as a guide to determine representative reduced-moment values that are of physical interest.

Table 1. Potential energy parameters for ‘ polar ’ molecules.

The strengths of the perturbations which are measured by the parameters $\{\lambda_k\}$ are related to the dipole moment μ, the quadrupole moment Θ and the octupole moment Φ. Higher moments are not explicitly considered in this study. In table 1 we summarize the moments of a few real molecules (CO_2, O_2, N_2 and HCl) that we have used as a guide in choosing representative sets of reduced moments in our numerical computations. Our model particles, like the real molecules we have listed, are assumed to have axial symmetry, which simplifies the application of the theory. Additional simplifications occur in the treatment of the perturbation $\mu^2 v^D$ due to point dipoles when the reference potential $v_0(r)$ is identified with the Lennard–Jones potential, $v^{LJ}(r)$. If the higher electric moments are ignored, the total potential $v^{LJ} + \mu^2 v^D$ is just the Stockmayer potential [7] v^S

$$v^S = v^{LJ}(r) + \mu^2 v^D(\mathbf{x}_1, \mathbf{x}_2), \tag{1.1}$$

where $v^{LJ}(r)$ is given in (2.2) and $v^D(\mathbf{x}_1, \mathbf{x}_2)$ was defined in our previous paper [1] as $(-2\cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2))/r^3$, where the angles θ_1, θ_2, $\phi_1 - \phi_2$ are those necessary to describe the mutual orientations of two dipoles. The Lennard–Jones parameters ϵ and σ which we use for our representative molecules are reproduced in table 1 with the reduced electric moments defined by

$$\mu^* = \left(\frac{\mu^2}{\epsilon\sigma^3}\right)^{1/2}, \quad \Theta^* = \left(\frac{\Theta^2}{\epsilon\sigma^5}\right)^{1/2} \quad \text{and} \quad \Phi^* = \left(\frac{\Phi^2}{\epsilon\sigma^7}\right)^{1/2}. \tag{1.2}$$

Our computations for the Stockmayer potential are mainly for $\mu^* = 1{\cdot}0$ which is close to tabulated values of the reduced dipole moment of HCl (0·903), ammonia (1·183), sulphur dioxide (0·916) and methyl chloride (1·0). We also discuss the contributions of the higher moments to the free energy for the molecular parameters of table 1.

When the reference potential is spherically symmetrical, the expansion of the free energy per particle f is given by [1]

$$f=f_0+\mu^4 f_2^{\mu}+\mu^2\Theta^2 f_{1,1}^{\mu\Theta}+\Theta^4 f_2^{\Theta}+\mu^2\Phi^2 f_{1,1}^{\mu\Phi}+\dots \tag{1.3}$$

to $0(\mu^i\Theta^j\Phi^k)$, where $i+j+k=4$. Here f_0 is the free energy of the reference system, and for molecules which possess axial symmetry

$$f_2^{\mu}=-\frac{\beta\rho}{6}\int g^0(r)r^{-6}\,d\mathbf{r}, \tag{1.4}$$

$$f_{1,1}^{\mu\Theta}=-\frac{\beta\rho}{2}\int g^0(r)r^{-8}\,d\mathbf{r}, \tag{1.5}$$

$$f_2^{\Theta}=-\frac{7\beta\rho}{10}\int g^0(r)r^{-10}\,d\mathbf{r}. \tag{1.6}$$

and

$$f_{1,1}^{\mu,\Phi}=-\frac{4\beta\rho}{3}\int g^0(r)r^{-10}\,d\mathbf{r}, \tag{1.7}$$

where $g^0(r)$ is the two-particle correlation function for the reference system, $\beta=1/kT$ and ρ is the number density. The sum of the first two terms of (1.3) is the free energy of the Stockmayer potential to $O(\mu^4)$ if $v_0(r)=v^{LJ}(r)$ and $g_0(r)=g^{LJ}(r)$. The term which must be added to (1.3) to determine the effects of dipole–dipole interactions to order μ^6 is

$$\mu^6 f_3^{\mu}=\frac{\mu^6\beta^2\rho^2}{6(4\pi)^3}\int g_{123}^{(0)}(r_{12},r_{13},r_{23})v^{DD}(\mathbf{x}_1,\mathbf{x}_2)v^{DD}(\mathbf{x}_1,\mathbf{x}_3)v^{DD}(\mathbf{x}_2,\mathbf{x}_3)\times d\mathbf{r}_2\,d\mathbf{r}_3\,d\omega_1\,d\omega_2\,d\omega_3, \tag{1.8}$$

where $g_{123}^{(0)}$ is the three-particle distribution function of the reference fluid. After the angular integrations in (1.8) are carried out, it turns out that

$$\mu^6 f_3^{\mu}=\frac{\mu^6\beta^2\rho^2}{6}\int g_{123}^{(0)}(r_{12},r_{13},r_{23})u(r_{12},r_{13},r_{23})\,d\mathbf{r}_2\,d\mathbf{r}_3, \tag{1.9}$$

where $u(r_{12},r_{13},r_{23})$ is of the form of the Axilrod–Teller–Muto three-body potential [8]:

$$u(r_{12},r_{13},r_{23})=\tfrac{1}{9}\left[\frac{1+3\cos\alpha_1\cos\alpha_2\cos\alpha_3}{(r_{12}r_{13}r_{23})^3}\right]. \tag{1.10}$$

Here α_1, α_2 and α_3 are the angles of the triangle formed by the particles located at $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$. The free energy of the Stockmayer potential to $O(\mu^6)$ is accordingly

$$f^{S(6)}=f^{LJ}+\mu^4 f_2^{\mu}+\mu^6 f_3^{\mu}+0(\mu^8), \tag{1.11}$$

in which the two-particle and three-particle correlation functions for Lennard-Jones systems are used in the definitions of f_2^{μ} and f_3^{μ}.

With the exception of the explicit form of the term of $O(\mu^6)$ almost all of the theory outlined above for polar fluids had already been described in the early 1950's by Cook and Rowlinson [2], Zwanzig [4] and Pople [3]. Nevertheless, it is only recently that the equilibrium properties of molecules with spherically symmetric potentials [9–15] have been available in a form sufficiently convenient and accurate to permit assessment of even the leading terms in (1.3).

We have exploited some of this new information in an earlier publication [1] where we calculated the free energy of the Stockmayer system to $O(\mu^4)$ for $\mu^* = 1{\cdot}0$ at $T^* = 0{\cdot}75$, $1{\cdot}15$, $1{\cdot}35$ and $2{\cdot}74$. We now go beyond those calculations to include the effect of $\mu^6 f_3^{\mu}$, which proves to be of major significance at $\mu^* = 1{\cdot}0$. The $\mu^4 f_2^{\mu}$ and $\mu^6 f_3^{\mu}$ terms are negative and positive respectively with $\mu^4|f_2^{\mu}| > \mu^6|f_3^{\mu}|$ for $\mu^* \leqslant 1{\cdot}0$ at all T^* and ρ^* that we have studied. These observations suggest the following simple [1, 0] Padé approximation for the free energy of a Stockmayer system

$$\beta f^{\mathrm{S}} = \beta f^{\mathrm{LJ}} + \beta \mu^4 f_2^{\mu} \left(\frac{1}{1 + \left| \dfrac{\mu^6 f_3^{\mu}}{\mu^4 f_2^{\mu}} \right|} \right), \tag{1.12}$$

which is used to calculate the coexistence curve for a Stockmayer system in § 2, where other details of our computation for this potential are also available.

In our first paper [1] we also found it convenient to use thermodynamic perturbation theory within the context of an effective orientation-independent but temperature-dependent potential that is thermodynamically equivalent to a dipolar pair-potential through order μ^4. We generalize this notion here by introducing an orientation-independent but temperature-dependent potential Ψ_N that is exactly thermodynamically equivalent to a sum of orientation-dependent pair terms. It includes n-body terms for all $n \geqslant 3$ as well as pair terms; we assess quantitatively the two-body dipole–dipole term through order μ^8 and show that the μ^8 contribution is negligible compared with its μ^4 contribution for $\mu^* = 1{\cdot}0$.

In § 3 we go on to assess the effects of higher multipole interactions on the free energy by using the effective potential concept. In doing so, we retain only the lowest multipole-moment contributions in the expansion of the effective potential, which yields

$$v^{\mathrm{E}}(r) = v^{\mathrm{LJ}}(r) + v^{\mathrm{ED}}(r) + v^{\mathrm{EDQ}}(r) + v^{\mathrm{EQQ}}(r) + v^{\mathrm{EDO}}(r), \tag{1.13}$$

where

$$v^{\mathrm{ED}}(r) = -\frac{\mu^4}{3kT} r^{-6}, \tag{1.14}$$

$$v^{\mathrm{EDQ}}(r) = -\frac{\mu^2 \Theta^2}{kT} r^{-8}, \tag{1.15}$$

$$v^{\mathrm{EQQ}}(r) = -\frac{7\Theta^4}{5kT} r^{-10}, \tag{1.16}$$

$$v^{\mathrm{EDO}}(r) = -\frac{4\mu^2 \phi^2}{3kT} r^{-10}. \tag{1.17}$$

The dipole–quadrupole, quadrupole–quadrupole, and dipole–octupole contributions of $v^{\mathrm{E}}(r)$ are computed by using one of the thermodynamic perturbation theories (tpt) that has been developed for spherically symmetric potentials [16]. It is found that the effects of the higher multipole moments are large for moments typical of a real dipolar molecule such as HCl—large enough so that the simple lowest-order theory in those moments given by (1.13) is probably inadequate to describe not only the dipole–dipole effects, but also the effects of the higher poles. On the other hand, when our potentials are assigned value of the multipole moments characteristic of molecules like N_2 and O_2, which possess no permanent dipole moment, the contributions to the free energy from the quadrupole moments are small enough for a treatment based upon (1.13) to be fairly reliable.

In the Appendix some simple analytic approximations for the integrals that occur in our perturbation-theoretic work here are tabulated. Their usefulness, especially in thermodynamic perturbation theory, goes beyond the specific examples considered in this study.

2. THERMODYNAMICS OF THE STOCKMAYER POTENTIAL

2.1. *Recapitulation of results through $O(\mu^4)$*

The free energy of the Stockmayer system to $O(\mu^4)$ was discussed in our earlier paper [1]; it is given by

$$\beta f^{S(4)} + \beta f^{LJ} + \chi\left[4\beta u^{LJ} - \frac{\beta P^{LJ}}{\rho} + 1\right], \tag{2.1}$$

where $\chi = \mu^{*4}/24T^*$ and $T^* = kT/\epsilon$. For the Lennard–Jones potential

$$v^{LJ}(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{2.2}$$

the energy per particle u^{LJ} reads

$$\beta u^{LJ} = \tfrac{1}{2}\beta\rho \int v^{LJ}(r) g^{LJ}(r)\, d\mathbf{r} \tag{2.3}$$

$$= 2[I_{12}{}^{LJ} - I_6{}^{LJ}], \tag{2.4}$$

where

$$I_{12}{}^{LJ}(\rho^*, T^*) = \rho^*\beta^* \int r^{*-12} g^{LJ}(r^*, T^*)\, d\mathbf{r}^* \tag{2.5}$$

and

$$I_6{}^{LJ}(\rho^*, T^*) = \rho^*\beta^* \int r^{*-6} g^{LJ}(r^*, T^*)\, d\mathbf{r}^*, \tag{2.6}$$

in which we have used the reduced variables $\beta^* = 1/T^*$, $\rho^* = \rho\sigma^3$, and $r^* = r/\sigma$ ($I_6{}^{LJ}/6$ is the $\beta^* J$ of [1], mistabulated there as $-\beta^* J$ and missing an asterisk in (4.2)). The excess compressibility ΔZ^{LJ} from the virial equation

$$\Delta Z^{LJ} \equiv \frac{\beta P^{LJ}}{\rho} - 1 = -\tfrac{1}{6}\beta\rho \int r \frac{dv^{LJ}}{dr}\, g^{LJ}(r)\, d\mathbf{r} \tag{2.7}$$

can be written as

$$\Delta Z^{LJ} = 4[2I_{12}{}^{LJ} - I_6{}^{LJ}]. \tag{2.8}$$

From equations (2.4) and (2.8) we have

$$-I_{12}{}^{LJ} = \left[\frac{\beta u^{LJ}}{2} - \frac{\Delta Z^{LJ}}{4}\right], \tag{2.9}$$

$$-I_6{}^{LJ} = \left[\beta u^{LJ} - \frac{\Delta Z^{LJ}}{4}\right]. \tag{2.10}$$

This enables us to express the integrals $I_{12}{}^{LJ}$ and $I_6{}^{LJ}$ in terms of the thermodynamic properties of Lennard–Jones systems, avoiding the need to know the radial distribution function $g^{LJ}(r)$. It also enables us to write the free energies in (1.4) in the form

$$\beta\mu^4 f_2'' \equiv -4\chi I_6^{LJ} = \chi[4\beta\mu^{LJ} - \Delta Z^{LJ}]. \tag{2.11}$$

Equation (2.11) is equivalent to (2.1). The best estimates of the complete thermodynamics of a Lennard–Jones fluid are the essentially exact Monte-Carlo and molecular-dynamics results. We use the exact machine calculations (tabulated by Verlet and Weis [14] from various sources [13, 15]) to compute the integrals $I_{12}^{LJ}(\rho^*, T^*)$ and $I_6^{LJ}(\rho^*, T^*)$ at $T^* = 0{\cdot}75$, 1·15, 1·35 and 2·74. These are given in table 2.

At the temperatures for which the exact thermodynamic properties of the Lennard–Jones fluid are inaccessible, the Weeks *et al.* [17] (WCA) perturbation theory [in the form described by Verlet and Weis [14] (VW)] can be used to

T^*	0·75	1·15	1·35	2·74
ρ^*		$I_6^{LJ}(\rho^*, T^*)$		
0·1	1·34	0·65	0·51	0·22
0·2	2·21	1·19	0·99	0·44
0·3	2·98	1·73	1·38	0·69
0·4	3·73	2·21	1·86	0·92
0·5	4·30	2·73	2·32	—
0·55	—	—	2·59	1·34
0·6	5·05	3·37	—	—
0·65	—	3·70	—	—
0·70	6·08	—	3·51	1·83
0·80	7·32	—	4·25	2·21
0·84	7·90	—	—	—
0·90	—	—	5·09	2·65
0·95	—	—	5·56	—
1·00	—	—	—	3·12
1·08	—	—	—	3·53
		$I_{12}^{LJ}(\rho^*, T^*)$		
0·1	0·58	0·28	0·22	0·11
0·2	0·95	0·51	0·44	0·22
0·3	1·27	0·76	0·61	0·36
0·4	1·59	0·97	0·84	0·48
0·55	—	—	1·22	0·73
0·6	2·14	1·57	—	—
0·65	—	1·76	—	—
0·70	2·70	—	1·78	1·12
0·80	3·47	—	—	—
0·84	3·87	—	—	—
0·85	—	2·93	—	—
0·90	—	—	2·99	1·84
0·92	—	3·52	—	—
0·95	—	—	3·45	—
1·00	—	—	—	2·36
1·08	—	—	—	2·84

Table 2. The integrals $I_6^{LJ}(\rho^*, T^*)$ and $I_{12}^{LJ}(\rho^*, T^*)$ obtained through the use of equations (2.9) and (2.10) and the Monte-Carlo results (tabulated by Verlet and Weis) for μ^{LJ} and P^{LJ}.

calculate βf^{LJ}, βu^{LJ} and ΔZ^{LJ} in terms of the equilibrium properties of hard spheres. This method was used in some of our earlier calculations of the excess free energy of the Stockmayer potential to $O(\mu^4)$ represented there by $\beta\Delta f_{vw}{}^{S(1)}$, where the vw denotes the Verlet–Weis version of the WCA perturbation theory.

2.2. *The term of order μ^6*

Our evaluation of the three-body term of order μ^6 exploits an expression given by Barker *et al.* (BHS) [18] for the integral in (1.9) where the triplet correlation function $g_{123}{}^{(0)}$ refers to hard spheres. They used the superposition approximation for $g_{123}{}^{(0)}$, with the Percus–Yevick values of the pair correlation function $g_{12}{}^{(0)}$, and found that their results for the integral in (1.9) agreed well with a direct Monte-Carlo (MC) evaluation of the same integral. The superposition approximation method leads to numerical values for the integral that are reproduced to within 1 part in 10^5 by the following Padé approximant [18]

$$\beta\mu^6 f_3{}^{\mu} = \frac{\beta^{*3}\mu^{*6}\rho^{*2}}{9c^3}\left[\frac{2{\cdot}7097+1{\cdot}68918x-0{\cdot}31570x^2}{1-0{\cdot}59056x-0{\cdot}20059x^2}\right], \tag{2.13}$$

ρ^*	$\beta\Delta f^{LJ}$ (VW)	$\beta\mu^4 f_2{}^{\mu}$ (VW)	$\beta\mu^6 f_3{}^{\mu}$ (BHS)	$\beta\Delta f^{LJ}$ (VW)	$\beta\mu^4 f_2{}^{\mu}$ (VW)	$\beta\mu^6 f_3{}^{\mu}$ (BHS)
		$T^*=0{\cdot}75$			$T^*=1{\cdot}15$	
0·1	−0·552	−0·135	0·008	−0·293	−0·059	0·002
0·2	−1·153	−0·284	0·034	−0·605	−0·124	0·009
0·3	−1·787	−0·450	0·055	−0·923	−0·197	0·024
0·4	−2·434	−0·635	0·169	−1·232	−0·277	0·048
0·5	−3·067	−0·840	0·291	−1·510	−0·368	0·083
0·6	−3·649	−1·070	0·460	−1·731	−0·468	0·130
0·65	−3·906	−1·196	0·564	−1·809	−0·523	0·159
0·70	−4·131	−1·329	0·682	−1·859	−0·581	0·193
0·75	−4·313	−1·471	0·815	−1·874	−0·634	0·231
0·80	−4·442	−1·624	0·964	−1·846	−0·709	0·273
0·85	−4·505	−1·787	1·127	−1·767	−0·779	0·319
0·90	−4·486	−1·962	1·308	−1·628	−0·853	0·369
0·95	−4·367	−2·151	1·505	−1·418	−0·932	0·426
1·0	−4·128	−2·352	1·719	−1·125	−1·014	0·486
		$T^*=1{\cdot}35$			$T^*=2{\cdot}74$	
0·1	−0·222	−0·043	0·001	−0·020	−0·011	0·000
0·2	−0·455	−0·092	0·007	−0·031	−0·024	0·000
0·3	−0·688	−0·145	0·016	−0·027	−0·038	0·002
0·4	−0·906	−0·204	0·030	0·003	−0·054	0·004
0·5	−1·090	−0·271	0·052	0·069	−0·071	0·006
0·6	−1·218	−0·344	0·082	0·186	−0·091	0·010
0·65	−1·250	−0·384	0·099	0·269	−0·101	0·012
0·7	−1·256	−0·427	0·121	0·372	−0·113	0·015
0·75	−1·229	−0·472	0·143	0·497	−0·125	0·018
0·8	−1·164	−0·520	0·170	0·648	−0·137	0·021
0·85	−1·053	−0·571	0·199	0·828	−0·150	0·024
0·9	−0·888	−0·625	0·231	1·042	−0·155	0·029
1·0	−0·359	−0·741	0·303	1·585	−0·195	0·037

Table 3. Perturbation theory (Verlet–Weis [14]) and Padé approximant (Barker *et al.* [18]) estimates of $\beta\Delta f^{LJ}$, $\beta\mu^4 f_2{}^{\mu}$ and $\beta\mu^6 f_3{}^{\mu}$ for $\mu^*=1{\cdot}0$.

where $x = \rho^* c^3$ and $c = a/\sigma$; a being the hard-sphere diameter. In our use of (2.13), a represents the diameter of hard spheres that is appropriate to the Verlet–Weis perturbation scheme; very nearly the same results are obtained from other choices of the effective hard-sphere diameter [16]. Our results are summarized in table 3 which shows that the three-body interactions of order μ^6 are opposite in sign to the term of order μ^4. Their magnitude is not negligible, and we include them in computing the excess free energy of the Stockmayer potential to order μ^6 which is

$$\beta\Delta f^{S(6)} = \beta\Delta f^{S(4)} + \beta\mu^6 f_3{}^{\mu}, \tag{2.14}$$

where

$$\beta\Delta f^{S(4)} = \beta\Delta f^{LJ} + \chi[4\beta u^{LJ} - \Delta Z^{LJ}]. \tag{2.15}$$

The excess free energy per particle Δf is defined by

$$\beta\Delta f = \beta f - \ln \rho^* + 1. \tag{2.16}$$

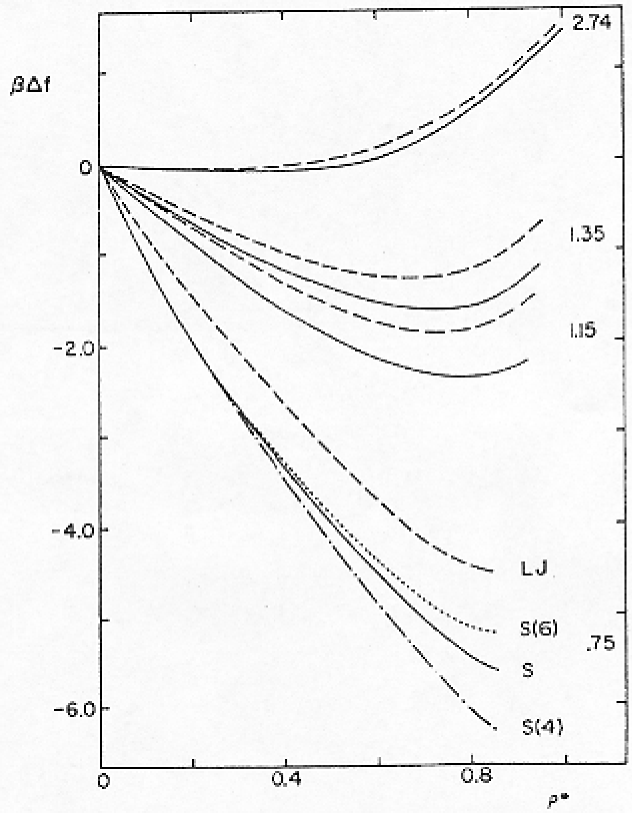

Figure 1. The reduced free energy per particle $\beta\Delta f^S$ for the Stockmayer system (for $\mu^* = 1{\cdot}0$), obtained from our [1, 0] Padé approximant, compared with the free energy of the corresponding Lennard–Jones system at four different temperatures $T^* = 0{\cdot}75$, $1{\cdot}15$, $1{\cdot}35$ and $2{\cdot}74$. At $T^* = 0{\cdot}75$, $\beta\Delta f^{S(4)}$ and $\beta\Delta f^{S(6)}$, the reduced free energies of the Stockmayer system to order μ^4 and μ^6, respectively, are also shown. All of the results, except for the term of order μ^6 (obtained from the Barker *et al.* [18] approximation) were derived from Monte Carlo results for the thermodynamics of Lennard–Jones molecules [13, 15].

Figure 1 depicts the contributions of the terms of order μ^4 and μ^6 to the excess free energy of the Stockmayer system at a reduced temperature $T^*=0{\cdot}75$. It also shows our best estimates of the excess free energy of the Stockmayer system $\beta\Delta f^S$ at four different temperatures $T^*=0{\cdot}75$, 1·15, 1·35 and 2·74. These were all obtained with the simple [1, 0] Padé approximant (equation (1.13)) discussed in the introduction; the details are provided in tables 4 and 5. Included in the

ρ^*	VW + BHS	MC + BHS	VW + BHS	MC + BHS
	$T^*=0{\cdot}75$		$T^*=1{\cdot}15$	
0·1	−0·68	−1·09	−0·35	−0·47
0·2	−1·41	−1·94	−0·72	−0·89
0·3	−2·17	−2·69	−1·10	−1·28
0·4	−2·94	−3·37	−1·47	−1·62
0·5	−3·69	−3·95	−1·81	−1·92
0·6	−4·40	−4·52	−2·10	−2·17
0·65	−4·72	—	−2·21	−2·25
0·70	−5·01	−5·06	−2·30	—
0·75	−5·26	—	−2·35	−2·37
0·80	−5·46	−5·49	−2·36	—
0·84	—	−5·62	—	—
0·85	−5·60	—	−2·32	−2·33
0·9	−5·66	—	−2·22	—
0·95	−5·63	—	−2·06	−2·18†
1·0	−5·49	—	−1·81	—

† $\rho^*=0{\cdot}92$

Table 4. The excess free energy of the Stockmayer system $\beta\Delta f^S$ for $\mu^*=1{\cdot}0$ obtained from the [1, 0] Padé approximant defined in (1.12). The term of $0(\mu^6)$ is calculated from the BHS expression (2.13), while the term of $0(\mu^4)$ (see (2.11)) is derived either from VW tpt or MC estimates of u^{LJ} and ΔZ^{LJ}. The two sets of [1, 0] Padé approximations to $\beta\Delta f^S$ are labelled VW + BHS and MC + BHS respectively.

ρ^*	VW + BHS	MC + BHS	VW + BHS	MC + BHS
	$T^*=1{\cdot}35$		$T^*=2{\cdot}74$	
0·1	−0·26	−0·35	−0·03	−0·04
0·2	−0·54	−0·68	−0·05	−0·08
0·3	−0·82	−0·96	−0·06	−0·09
0·4	−1·08	−1·20	−0·05	−0·06
0·5	−1·32	−1·40	0·00	—
0·55	—	−1·49	—	−0·04
0·60	−1·50	—	0·10	—
0·65	−1·56	—	0·18	—
0·70	−1·59	−1·63	0·27	0·27
0·75	−1·59	—	0·39	—
0·80	−1·56	−1·59	0·53	0·53
0·85	−1·48	—	0·70	—
0·90	−1·34	−1·37	0·90	0·90
0·95	−1·15	−1·17	1·14	—
1·0	−0·89	—	1·42	1·42

Table 5. The excess free energy of the Stockmayer system $\beta\Delta f^S$ obtained from the [1, 0] Padé approximant defined in (1.12) (see caption of table 4 for details).

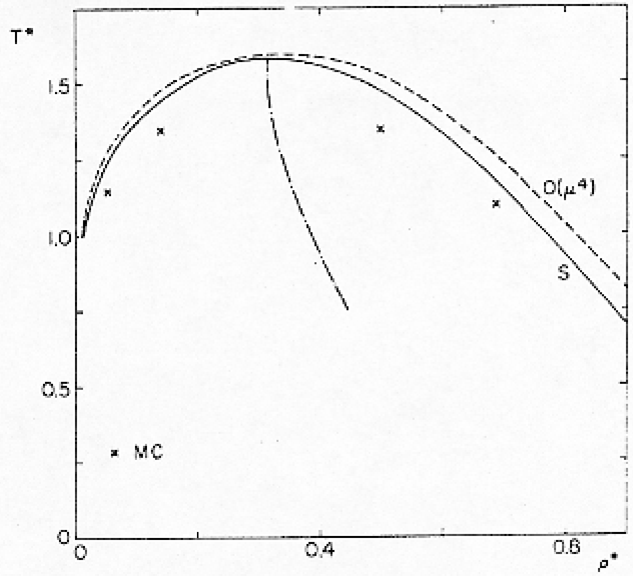

Figure 2. Liquid–vapour coexistence curve for the Stockmayer system calculated from $\beta f^{S(4)}$ and βf^S, using the Verlet–Weis tpt [14] for the thermodynamics of Lennard–Jones molecules. At $T^* = 1{\cdot}15$ and $T^* = 1{\cdot}35$, the densities of coexisting phases calculated from βf^S using Monte Carlo results for the thermodynamics of Lennard–Jones molecules are also shown, as is our best estimate of $(\rho_L^* + \rho_G^*)/2$. See comments in table 6.

	From $\beta f^{S(4)}$		From the [1, 0] Padé approximant for βf^S			
T^*	ρ_L^*	ρ_G^*	ρ_L^*	ρ_G^*	$\beta\mu$	$\beta P/\rho$
0·75	0·938	0·008	0·878	0·001	−6·79	0·0016
0·85	0·892	0·0084	0·835	0·004	−5·62	0·0033
0·95	0·838	0·012	0·793	0·008	−4·77	0·0067
1·05	0·790	0·013	0·745	0·017	−4·12	0·0167
1·15	0·740	0·025	0·700	0·025	−3·60	0·03
1·35	0·628	0·077	0·588	0·089	−2·89	0·0667
1·45	0·568	0·118	0·523	0·145	−2·63	0·093
1·55	0·473	0·208	0·407	0·225	−2·42	0·119
1·58	0·308	0·308	0·317	0·317	—	—

Table 6. Coexistence curve data in the Stockmayer system for $\mu^* = 1{\cdot}0$ from our [1, 0] Padé approximant for $\beta\Delta f^S$, and from $\beta\Delta f^{S(4)}$, using Verlet–Weis tpt for Lennard–Jones system†.

† The ρ_L^* and ρ_G^* values are sensitive to small uncertainties, and those given here are unlikely to be of high precision. They were determined to show at a glance the general extent of the coexistence region rather than to locate its boundary with great accuracy. The substantial differences between the tpt and Monte-Carlo phase-boundary location that appear in figure 2 indicate that efforts to obtain greater precision from our tpt results would be unwarranted, although we do hope to determine whether greater precision will alter the interesting curvature shown in our estimate of $(\rho_L^* + \rho_G^*)/2$.

same tables are more accurate estimates of $\beta\Delta f^{\mathrm{S}}$ derived from the same Padé approximation except that $\beta\Delta f^{\mathrm{LJ}}$ and $\beta\mu^4 f_2{}^{a}$ (or equivalently $\beta\Delta f^{\mathrm{S}(4)}$) are evaluated exactly from published MC computations of Δf^{LJ}, u^{LJ} and ΔZ^{LJ} (see equations (2.11) and (2.15)). That is to say, in forming the [1, 0] Padé approximant the term of order μ^4 is exact, whereas the term of order μ^6 is obtained from the BHS expression given in (2.13).

The discrepancies between the Monte Carlo and tpt estimates of $\beta\Delta f^{\mathrm{S}}$ are mainly within the two-phase region (see table 6), and since the latter estimates are more complete, we have used them to calculate the coexistence curve drawn in figure 2. The densities of the coexisting phases are available in table 6.

2.3. *The general concept of effective orientation-independent potentials ; quantitative evaluation of v^{ES2} through $O(\mu^8)$*

The configuration integral for N classical particles interacting via a sum of pair terms of the form expressed in (1.0) is

$$Q_N=\frac{1}{\Omega_N}\int d\mathbf{x}_1\, d\mathbf{x}_2 \ldots d\mathbf{x}_N \exp\left\{-\beta \sum_{1\le i<j\le N} v(\mathbf{x}_i, \mathbf{x}_j)\right\}, \tag{2.17}$$

where $\mathbf{x}_i=(\mathbf{r}_i, \boldsymbol{\omega}_i)$ is the vector describing both the location $\mathbf{r}_i$ of the centre of the ith particle and the orientation $\boldsymbol{\omega}_i$ of the particle, while $\Omega=\int d\boldsymbol{\omega}_i$. Defining $\Psi_N(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)$ by the equation

$$\exp\{-\beta\Psi_N(\mathbf{r}_1, \mathbf{r}_2, \ldots \mathbf{r}_N)\}=\frac{1}{\Omega_N}\int d\boldsymbol{\omega}_1 \ldots d\boldsymbol{\omega}_N \times \exp\left\{-\beta \sum_{i,j} v(\mathbf{x}_i, \mathbf{x}_j)\right\}, \tag{2.18}$$

(with the same limits on i and j) so that

$$Q_N=\int d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp\{-\beta\Psi_N(\mathbf{r}_1, \ldots \mathbf{r}_N)\}, \tag{2.19}$$

we see that a hypothetical system of N particles interacting with a $\boldsymbol{\omega}_i$-independent (but β-dependent) potential energy Ψ_N will have exactly the same free energy as our original system. However, Ψ_N will no longer be expressible as a sum of pair terms. In fact, we can uniquely decompose Ψ_N into a sum of two-body, three-body, . . ., n-body terms by letting

$$\Psi_N(\mathbf{r}_1, \ldots \mathbf{r}_N)=\sum_{1\le i<j\le N}\psi_2(\mathbf{r}_i, \mathbf{r}_j)+\sum_{1\le i<j<k\le N}\psi_3(\mathbf{r}_i, \mathbf{r}_j, \mathbf{r}_k)+\ldots, \tag{2.20}$$

where

$$\psi_2(\mathbf{r}_1, \mathbf{r}_2)=\Psi_2(\mathbf{r}_1, \mathbf{r}_2), \tag{2.21}$$

$$\psi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)=\Psi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)-\sum_{1\le i<j\le N}\Psi_2(\mathbf{r}_1, \mathbf{r}_2), \tag{2.22}$$

etc. When $v(\mathbf{x}_i, \mathbf{x}_j)$ in (2.17) is the Stockmayer potential, direct computation shows that

$$\psi_2(\mathbf{r}_1, \mathbf{r}_2)=v^{\mathrm{LJ}}(r)+v_1{}^{\mathrm{ED}}(r)+v_2{}^{\mathrm{ED}}(r)+O(\mu^{12}), \tag{2.23}$$

where v^{LJ} is the Lennard-Jones potential, $v_1{}^{\mathrm{ED}}$ is identically v^{ED} defined in (1.14), and

$$v_2{}^{\mathrm{ED}}=(7\beta^3\mu^8/450)r^{-12}, \tag{2.24}$$

while

$$\psi_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \mu^6\beta^2 u(r_{12}, r_{13}, r_{23}) + O(\mu^{10}), \tag{2.25}$$

where $u(r_{12}, r_{13}, r_{23})$ is given in (1.10). More generally (in more-or-less standard notation [19], with tr signifying trace):

$$-\beta\psi_n(\mathbf{r}_1, \dots \mathbf{r}_N) = \frac{(-1)^n(n-1)!}{2}\left(\frac{\beta\mu^2}{3}\right)^n \mathrm{tr}\ \mathbf{T}^n + O(\mu^{2n+4}). \tag{2.26}$$

The tensors $\mathbf{T}^n$ have been defined and discussed by Linder [19]. We see that through order μ^4, ψ_2 is just the 'effective Stockmayer potential' $v^{\mathrm{ES}} = v^{\mathrm{LJ}}(r) + v^{\mathrm{ED}}(r)$ of our previous paper [1]. As noted there v^{ES} is conformal with the Lennard–Jones potential v^{LJ}.

Denoting ψ_2 through order μ^8 as v^{ES2}, we see that v^{ES2} also is conformal with v^{LJ}, since from (2.2), (1.14) and (2.24),

$$v^{\mathrm{ES2}} = v^{\mathrm{LJ}}(r) + v_1{}^{\mathrm{ED}}(r) + v_2{}^{\mathrm{ED}}(r) \tag{2.27}$$

$$= 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}(1+2\gamma) - \left(\frac{\sigma}{r}\right)^{6}(1+2\chi)\right], \tag{2.28}$$

where $\chi = \mu^{*4}/24T^*$ and $\gamma = 28\chi^2/25T^* = 7\mu^{*8}/3600\,T^{*3}$.

Thus

$$v^{\mathrm{ES2}} = 4\epsilon''\left[\left(\frac{\sigma''}{r}\right)^{12} - \left(\frac{\sigma''}{r}\right)^{6}\right], \tag{2.29}$$

where $\epsilon'' = (1+2\chi)^2/(1+2\gamma)$ and $\sigma'' = (1+2\gamma)^{1/2}/(1+2\chi)^{1/2}$. By following the argument pertaining to v^{ES} outlined in our earlier paper [1], we have from the law of corresponding states a simple relation between the thermodynamics of the Lennard–Jones (LJ) and 'effective Stockmayer 2' (ES2) systems

$$\frac{\Delta f^{\mathrm{ES2}}(\rho, T)}{kT} = \frac{\Delta f^{\mathrm{LJ}}(\rho'', T'')}{kT''} \tag{2.30}$$

and

$$\frac{P^{\mathrm{ES2}}(\rho, T)}{\rho kT} = \frac{P^{\mathrm{LJ}}(\rho'', T''),}{\rho'' kT''} \tag{2.31}$$

where

$$T'' = \frac{(1+2\gamma)}{(1+2\chi)^2}\,T \quad \text{and} \quad \rho'' = \left(\frac{1+2\gamma}{1+2\chi}\right)^{1/2}\rho.$$

We already know from the Gibbs–Bogoliubov inequality applied to v^{ES} that [29]

$$\beta\Delta f^{\mathrm{ES}} \leqslant \beta\Delta f^{\mathrm{S(4)}}. \tag{2.32}$$

By applying the same inequality to v^{ES2}, we have

$$\beta\Delta f^{\mathrm{ES2}} \leqslant \beta\Delta f^{\mathrm{S(4)}} + \frac{7\mu^8\beta^3\rho^2}{900}\int g^0(r)r^{-12}\,d\mathbf{r}. \tag{2.33}$$

In table 7, $\beta\Delta f^{\mathrm{ES2}}$ and $\beta\Delta f^{\mathrm{ES}}$ are compared. The magnitude and sign of the difference are consistent with (2.33) and shows that the term of order μ^8 in v^{ES2} makes a negligibly small positive contribution to the free energy for $\mu^* = 1{\cdot}0$. The results reported in table 7 were obtained from (2.30) and the corresponding equation for v^{ES} by using the Verlet–Weis version of perturbation theory [14] to calculate Δf^{LJ} in terms of the properties of hard spheres.

ρ^*	$\beta\Delta f_{vw}^{ES2}$	$\beta\Delta f_{vw}^{ES}$	$\beta\Delta f_{vw}^{ES2}$	$\beta\Delta f_{vw}^{ES}$	$\beta\Delta f_{vw}^{ES2}$	$\beta\Delta f_{vw}^{ES}$	$\beta\Delta f_{vw}^{ES2}$	$\beta\Delta f_{vw}^{ES}$
	$T=^*0{\cdot}75$		$T^*=1{\cdot}15$		$T^*=1{\cdot}35$		$T^*=2{\cdot}74$	
0·1	−0·685	−0·689	−0·352	−0·353	−0·265	−0·266	−0·031	−0·031
0·3	−2·229	−2·245	−1·119	−1·122	−0·832	−0·834	−0·065	−0·065
0·5	−3·888	−3·918	−1·874	−1·880	−1·359	−1·362	−0·002	−0·002
0·7	−5·419	−5·470	−2·432	−2·443	−1·678	−1·684	0·260	0·260
0·85	−6·223	−6·299	−2·532	−2·548	−1·616	−1·624	0·680	0·679

Table 7. Comparison of the ES and ES2 approximations to $(kT)^{-1}$ times the excess free energy per particle of a Stockmayer system for $\mu^*=1{\cdot}0$. See also [29].

A direct evaluation of the free-energy contribution from the two-body term of order μ^8

$$\mu^8 f_{2,2}{}^{\mu} = \frac{7\mu^8\beta^3\rho^2}{900}\int g^0(r)r^{-12}\,d\mathbf{r} \tag{2·34}$$

is possible, because of (2.9), which leads to

$$\beta\mu^8 f_{2,2}{}^{\mu} \equiv 4\gamma I_{12}{}^{LJ} = -\gamma[2\beta u^{LJ} - \Delta Z^{LJ}], \tag{2.35}$$

where $\gamma = 7\mu^{*8}/3600T^{*3}$. Monte Carlo computations of u^{LJ} and ΔZ^{LJ} enable $\mu^8 f_{2,2}{}^{\mu}$ to be determined accurately. In table 8 we compare this with $\mu^4 f_2{}^{\mu}$ obtained from the analogous equation (2.11), and confirm our view that the effect of the two-body terms in μ beyond v^{ES} are negligible at $\mu^*=1$ over the entire range of temperatures and densities investigated here.

When the $v(\mathbf{x}_i, \mathbf{x}_j)$ in (2.17) is taken to be a v^{LJ} plus sum of ideal dipole–dipole, dipole–quadrupole, quadrupole–quadrupole, and dipole–octupole terms, then $\psi_2(\mathbf{r}_1, \mathbf{r}_2)$ is given by (1, 13) through order $\mu^i\Theta^j\Phi^k$, $i+j+k=4$.

ρ^*	$\beta\Delta f^{LJ}$	$\beta\mu^4 f_2{}^{\mu}$	$\beta\mu^8 f_{2,2}{}^{\mu}$	$\beta\Delta f^{LJ}$	$\beta\mu^4 f_2{}^{\mu}$	$\beta\mu^8 f_{2,2}{}^{\mu}$
		$T^*=0{\cdot}75$			$T^*=1{\cdot}15$	
0·1	−0·80	−0·30	0·01	−0·38	−0·09	0·00
0·3	−2·10	−0·67	0·02	−1·05	−0·25	0·00
0·5	−3·22	−0·96	0·03	−1·59	−0·40	0·01
0·70	−4·17	−1·35	0·05	—	—	—
0·80	−4·57	−1·63	0·06	—	—	—
0·85	−4·53†	−0·75†	0·07†	−1·78	−0·78	0·02
		$T^*=1{\cdot}35$			$T^*=2{\cdot}74$	
0·1	−0·29	−0·06	0·00	−0·03	−0·01	0·00
0·3	−0·80	−0·17	0·00	−0·05	−0·04	0·00
0·5	−1·16	−0·29	0·00	—	—	—
0·70	−1·29	−0·43	0·01	0·37	−0·11	0·00
0·80	−1·19	−0·52	0·01	0·65	−0·14	0·00
0·95	−0·67	−0·69	0·01	—	—	—

† $\rho^*=0{\cdot}84$.

Table 8. Monte Carlo estimates of $\beta\Delta f^{LJ}$, $\beta\mu^4 f_2{}^{\mu}$ and $\beta\mu^8 f_{2,2}{}^{\mu}$ for $\mu^*=1{\cdot}0$. (When $\mu^*=1{\cdot}0$, $\beta\mu^4 f_2{}^{\mu}$ is identically equal to $-\beta^{*2}J$ defined in our previous paper [1], where of more complete tabulation of Monte Carlo estimates of this term are available at $T^*=0{\cdot}75$, 1·15, 1·35 and 2·74). In table 1 of [1], $\beta^{*2}J$ should be $-\beta^{*2}J$.

3. Numerical estimates of quadrupole and octupole terms

We restrict ourselves here to an exploratory investigation of the effect of multipoles using a version of tpt that we have previously employed in obtaining bounds on the free-energy of Lennard–Jones fluids [16]. Recent advances in the use of tpt [17] will make it possible to improve the numerical accuracy of future computations if necessary ; here we limit ourselves to aspects of the problems that are relatively insensitive to the finer points of the computational technique used.

In order to discuss the significance of our numerical results it is of value to briefly review the details of the perturbation scheme that we have used in obtaining them. We shall start our discussion by considering the decomposition of $v^{\mathrm{LJ}}(r)$ into a hard-sphere part and a remainder $w(r)$

$$v^{\mathrm{LJ}}(r)=v^{\mathrm{HS}}(r)+w(r), \tag{3.1}$$

where

$$\begin{aligned} v^{\mathrm{HS}}(r)&=\infty, \quad r<c\sigma \\ &=0, \quad r>c\sigma \end{aligned} \tag{3.2}$$

and

$$\begin{aligned} w(r)&=-\infty+v^{\mathrm{LJ}}(r), \quad r<c\sigma \\ &=v^{\mathrm{LJ}}(r), \qquad r>c\sigma. \end{aligned} \tag{3.3}$$

Despite the highly singular nature of w for $r<c\sigma$

$$\int g^{\mathrm{HS}}(r, c\sigma)w(r)\, d\mathbf{r}=\int g^{\mathrm{HS}}(r, c\sigma)v^{\mathrm{LJ}}(r)\, d\mathbf{r} \tag{3.4}$$

exists and is well behaved because $g^{\mathrm{HS}}(r, c\sigma)=0$ for $r<c\sigma$. Then the Gibbs–Bogoliubov inequality guarantees that

$$\Delta f^{\mathrm{LJ}}(\rho^*, T^*)\leqslant \Delta f^{\mathrm{HS}}(\rho^* c^3)+\frac{\rho}{2}\int g^{\mathrm{HS}}(r, c\sigma)v^{\mathrm{LJ}}(r)\, d\mathbf{r}, \tag{3.5}$$

which means that the right-hand side of (3.5) is an upper bound. By choosing a c that minimizes the right-hand side of (3.5) we have chosen the best c because we will have minimized our upper bound. Through a similar decomposition of

$$v^{\mathrm{ES}}(r)=v^{\mathrm{LJ}}(r)+v^{\mathrm{ED}}(r), \tag{3.6}$$

where $v^{\mathrm{ED}}(r)$ is defined in (1.14), we have

$$\Delta f^{\mathrm{ES}}(\rho^*, \mu^*, T^*)\leqslant \Delta f^{\mathrm{HS}}(\rho^* c^3)+\frac{\rho}{2}\int g^{\mathrm{HS}}(r, c\sigma)v^{\mathrm{ES}}(r)\, d\mathbf{r}. \tag{3.7}$$

The right-hand side is an upper bound on an expression that coincides through $O(\mu^4)$ with the excess free energy Δf^{S} of the Stockmayer potential. (It is not an upper bound on Δf^{S} itself, but when the difference between the two is negligible, we can replace the upper bound on Δf^{S} by the upper bound on Δf^{ES}.) For a given c the only difference between our upper bound for Δf^{ES} and Δf^{LJ} at a fixed T^* and ρ^* is the term

$$\begin{aligned} f^{\Delta \mathrm{D}}&=\frac{\rho}{2}\int g^{\mathrm{HS}}(r, c\sigma)v^{\mathrm{ED}}\, d\mathbf{r} \\ &=\frac{-\rho\mu^4}{6kT}\int g^{\mathrm{HS}}(r, c\sigma)r^{-6}\, d\mathbf{r} \end{aligned} \tag{3.8}$$

where $g^{\mathrm{HS}}(r, c\sigma)$ is the distribution function of hard spheres of diameter $c\sigma$. This is a function of two variables $y=r/c\sigma$ and $x=\rho^* c^3$, so that once

$$I_n^{\mathrm{HS}}(x)=\int_1^\infty g^{\mathrm{HS}}(y, x) y^{2-n}\, dy \tag{3.9}$$

is computed for $n=6$, the term

$$\beta f^{\Delta\mathrm{D}}=-\frac{\rho\mu^4 4\pi I_6^{\mathrm{HS}}(x)}{6(kT)^2(c\sigma)^3}=\frac{-2\cdot094395x\mu^{*4}I_6^{\mathrm{HS}}(x)}{c^6T^{*2}} \tag{3.10}$$

is known for given ρ^*, μ^* and T^* if c is known. Thus our upper bound to f^{ES} is $f^{\mathrm{HS}}+f^{\Delta\mathrm{LJ}}+f^{\Delta\mathrm{D}}$, where

$$\begin{aligned}\beta f^{\Delta\mathrm{LJ}} &=\frac{\rho}{2}\left(\frac{4\epsilon}{kT}\right)(c\sigma)^3 4\pi\left[\frac{I_{12}^{\mathrm{HS}}(x)}{c^{12}}-\frac{I_6^{\mathrm{HS}}(x)}{c^6}\right]\\ &=\frac{25\cdot132741x}{c^6T^*}\left[\frac{I_{12}^{\mathrm{HS}}(x)}{c^6}-I_6^{\mathrm{HS}}(x)\right].\end{aligned} \tag{3.11}$$

More generally, if v^{EDQ}, v^{EQ} and v^{EDO} are included in the potential, then our upper bound for f^{E}, the free energy that corresponds to $v^{\mathrm{E}}(r)$ in (1.13), is $f^{\mathrm{HS}}+f^{\Delta\mathrm{LJ}}+f^{\Delta\mathrm{D}}+f^{\Delta\mathrm{Q}}+f^{\Delta\mathrm{DQ}}+f^{\Delta\mathrm{DO}}$, where

$$\beta f^{\Delta\mathrm{DQ}}=-\frac{\rho\mu^2\Theta^2 4\pi I_8^{\mathrm{HJ}}(x)}{2(kT)^2(c\sigma)^5}=-\frac{6\cdot283185x\Theta^{*2}I_8^{\mathrm{HS}}(x)}{c^8T^{*2}}, \tag{3.12}$$

$$\beta f^{\Delta\mathrm{Q}}=-\frac{7\rho\mu^4 4\pi I_{10}^{\mathrm{HS}}(x)}{10(kT)^2(c\sigma)^7}=-\frac{8\cdot796459x\Theta^{*4}I_{10}^{\mathrm{HS}}(x)}{c^{10}T^{*2}}, \tag{3.13}$$

$$\beta f^{\Delta\mathrm{DO}}=-\frac{2\rho\mu^2\Phi^2 4\pi I_{10}^{\mathrm{HS}}(x)}{3(kT)^2(c\sigma)^7}=-\frac{8\cdot37758x\mu^{*2}\Phi^{*2}I_{10}^{\mathrm{HS}}(x)}{c^{10}T^{*2}}. \tag{3.14}$$

Thus one can obtain the best upper bound for f^{E} with the hard-sphere reference system by minimizing $f^{\mathrm{HS}}+f^{\Delta\mathrm{LJ}}+f^{\Delta\mathrm{D}}+f^{\Delta\mathrm{DQ}}+f^{\Delta\mathrm{Q}}+f^{\Delta\mathrm{DQ}}$ with respect to c.

Polynomial approximations to $I_n^{\mathrm{HS}}(x)$ for $n=6$ and $n=12$ have already been given by Kozak and Rice [20]. These were obtained using the Percus–Yevick $g^{\mathrm{HS}}(y, x)$. In the course of our work we have derived approximations for $I_n^{\mathrm{HS}}(x)$ with $n=6$, 8, 10, 12, 18 and 24 which are better than those obtainable from the Percus–Yevick theory. They appear to be in good agreement with the $I_n^{\mathrm{HS}}(x)$ calculated from the exact $g^{\mathrm{HS}}(y, x)$ for hard spheres which are available from the computer studies made by Schiff and Verlet [12]. Verlet and Weis [14] have also given analytic approximations to $I_6^{\mathrm{HS}}(x)$ and $I_{12}^{\mathrm{HS}}(x)$ somewhat similar to those discussed here. We consider the I_n^{HS} in detail in an Appendix. Since the functions are ubiquitous in the statistical mechanics of hard-sphere fluids, accurate and simple closed-form approximations to them enormously reduce the time involved in perturbation-theory calculations. This is particularly so far our own variational procedure [16] which requires the calculation of $I_n^{\mathrm{HS}}(x)$ (where $x=\rho^*c^3$) at several closely spaced values of c for each given ρ^* and T^*.

Using the new approximations for $I_n^{\mathrm{HS}}(x)$ and a Padé approximant for Δf^{HS} (Ree and Hoover [10]) we recomputed the upper bounds on the free energy of

The results for CO_2, N_2 and HCl are shown in figures 3–5 while those for O_2 are not displayed because of the negligible contribution to the free energy from the quadrupole moment of O_2. The reduced quadrupole moment Θ^* occurs as the fourth power in (3.13), and since $\Theta^* = 0{\cdot}137$ for O_2 the effect on the free energy is small in comparison to what it is for $N_2(\Theta^* = 0{\cdot}501)$ and $CO_2(\Theta^* = 0{\cdot}83)$. In the case of a molecule characterized by the reduced dipole moment of HCl, the results of § 2 already made clear that the contribution of the dipole–dipole

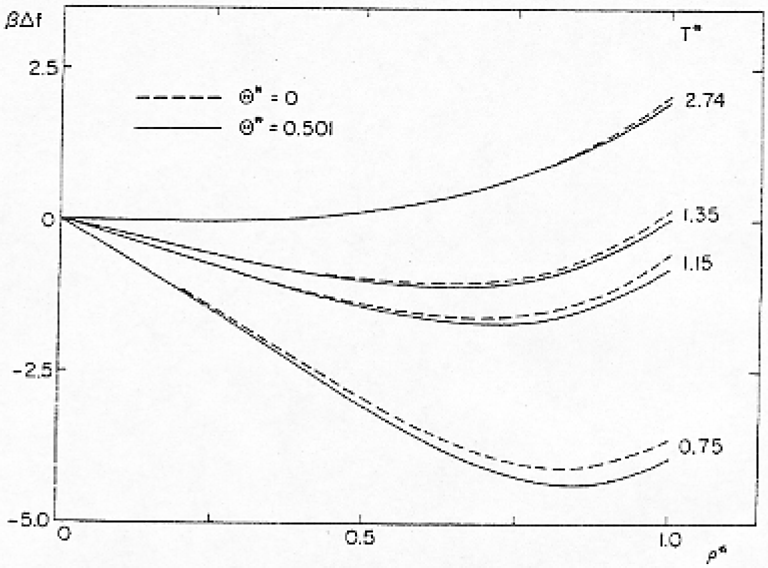

Figure 3. Approximation to $(kT)^{-1}$ times the free energy per particle of a system with potential energy parameters (ϵ, σ and Θ) that correspond to N_2 (see table 1). (The experimentally determined reduced critical temperature of N_2 is $T_c^* = kT_c/\epsilon = 1{\cdot}31$, where k is Boltzmann's constant.)

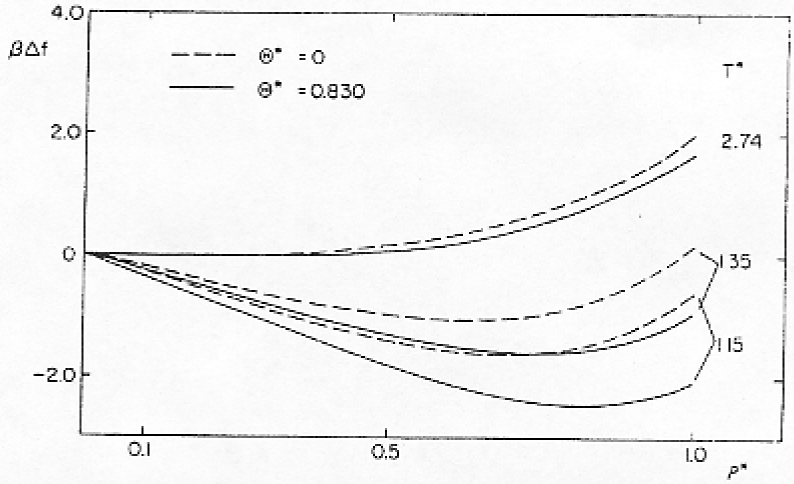

Figure 4. Approximation to $(kT)^{-1}$ times the free energy per particle of a system with potential energy parameters that correspond to CO_2 (see table 1). (For CO_2, $T_c^* \equiv kT_c/\epsilon = 1{\cdot}60$ if the experimental T_c is used.)

		$\beta\Delta f^{\mathrm{LJ}}$			$\beta\mu^4 f_2^{\mu}$	
ρ^*	VW	Var	MC	VW	Var	MC
$T^*=0{\cdot}75$						
0·1	−0·55	−0·56	−0·80	−0·14	−0·14	−0·30
0·2	−1·15	−1·15	−1·48	−0·28	−0·29	−0·49
0·4	−2·43	−2·37	−2·68	−0·64	−0·65	−0·83
0·6	−3·65	−3·47	−3·73	−1·07	−1·09	−1·12
0·8	−4·44	−4·07	−4·47	−1·62	−1·65	−1·63
$T^*=1{\cdot}15$						
0·1	−0·29	−0·29	−0·38	−0·06	−0·06	−0·09
0·2	−0·60	−0·59	−0·73	−0·12	−0·13	−0·17
0·4	−1·23	−1·17	−1·34	−0·28	−0·29	−0·32
0·6	−1·73	−1·57	−1·78	−0·47	−0·48	−0·49
0·85	−1·76	−1·38	−1·78	−0·78	−0·80	−0·78
$T^*=1{\cdot}35$						
0·1	−0·22	−0·23	−0·29	−0·04	−0·05	−0·06
0·2	−0·45	−0·44	−0·56	−0·09	−0·09	−0·12
0·4	−0·90	−0·84	−1·00	−0·20	−0·21	−0·23
0·7	−1·26	−1·03	−1·29	−0·43	−0·44	−0·43
0·9	−0·89	−0·47	−0·91	−0·63	−0·64	−0·63
$T^*=2{\cdot}74$						
0·1	−0·02	−0·01	−0·03	−0·01	−0·01	−0·01
0·2	−0·03	−0·01	−0·05	−0·02	−0·03	−0·03
0·4	0·00	0·07	−0·01	−0·05	−0·06	−0·06
0·7	0·37	0·57	0·37	−0·11	−0·11	−0·11
0·9	1·04	1·38	1·04	−0·16	−0·17	−0·16

Table 10. Comparisons of $\beta\Delta f^{\mathrm{LJ}}$ and $\beta\mu^4 f_2^{\mu}$ (for $\mu^*=1{\cdot}0$) obtained from the Verlet–Weis tpt [14] and the variational method [16] respectively with Monte Carlo results.

interactions to $0(\mu^4)$ in the Stockmayer potential i.e. the term $\beta\mu^4 f_2^{\mu}$ in the free energy defined in (2.11). Since we have already evaluated this term by two different methods (using MC and VW tpt for u^{LJ} and ΔZ^{LJ} respectively) we are able to compare in table 10 our earlier calculations of $\beta\mu^4 f_2^{\mu}$ with our present estimates derived from the bounds (3.15) and (3.16). We conclude that although our upper bounds on the free energy of a Lennard–Jones system are not as accurate as the free energies obtained from VW tpt, the strength of the dipole–dipole interactions can be assessed to $O(\mu^4)$ as accurately as in the VW tpt.

We now turn to an investigation of our model polar fluid with finite μ^* and Θ^*. Although the model is a gross over-simplification of real polar fluids, it is adequate for the purpose of estimating the strengths of the various dipole and multipole interactions and their effect on the free energy. Accordingly, we have chosen values of μ and Θ tabulated [28] for O_2, N_2, CO_2 and HCl for study; the appropriate Lennard–Jones parameters and multipole moments are in table 1. Higher moments, the effects of polarizability and the non-spherical shapes of the molecular cores are neglected. The upper bounds on the free energies of these systems have been computed with the best c's that correspond to the effective potential defined in (1.13), i.e. the free energy bounds are the best upper bounds derived from the inequality

$$\Delta f^{\mathrm{E}} \leqslant \Delta f^{\mathrm{HS}} + f^{\Delta\mathrm{LJ}} + f^{\Delta\mathrm{D}} + f^{\Delta\mathrm{DQ}} + f^{\Delta\mathrm{Q}}. \tag{3.17}$$

ρ^*	c^{LJ}	$\beta\Delta f^{\mathrm{LJ}}$	$\beta\Delta f^{\mathrm{LJ}}$(MC)	c^{LJ}	$\beta\Delta f^{\mathrm{LJ}}$	$\beta\Delta f^{\mathrm{LJ}}$(MC)
	$T^*=0{\cdot}75$			$T^*=1{\cdot}15$		
0·1	0·982	−0·561	−0·80	0·971	−0·294	−0·38
0·2	0·989	−1·152	−1·48	0·976	−0·594	−0·73
0·3	0·995	−1·762	−2·10	0·981	−0·890	−1·05
0·4	1·001	−2·373	−2·68	0·984	−1·167	−1·34
0·5	1·005	−2·959	−3·22	0·986	−1·403	−1·59
0·6	1·006	−3·476	−3·73	0·987	−1·568	−1·78
0·65	—	—	—	0·987	−1·612	−1·84
0·70	1·007	−3·871	−4·17	0·986	−1·622	—
0·75	—	—	—	0·985	−1·593	−1·89
0·80	1·004	−4·070	−4·47	0·983	−1·517	—
0·84	1·003	−4·075	−4·53	—	—	—
0·85	—	—	—	0·981	−1·386	−1·78
0·90	1·000	−3·982	—	0·978	−1·192	—
0·92				0·977	−1·095	−1·56
1·00	0·993	−3·500	—	0·972	−0·576	—
	$T^*=1{\cdot}35$			$T^*=2{\cdot}74$		
0·1	0·966	−0·220	−0·29	0·941	−0·011	−0·03
0·2	0·971	−0·441	−0·56	0·943	−0·008	−0·05
0·3	0·975	−0·652	−0·80	0·943	0·018	−0·05
0·4	0·977	−0·839	−1·00	0·945	0·074	−0·01
0·5	0·979	−0·983	−1·16	0·944	0·175	—
0·55	0·979	−1·03	−1·22	0·944	0·247	0·06
0·6	—	—	—	0·943	0·336	—
0·7	0·978	−1·025	−1·29	0·941	0·574	0·37
0·8	0·975	−0·847	−1·19	0·938	0·914	0·65
0·9	0·970	−0·469	−0·91	0·933	1·382	1·04
0·95	0·967	−0·187	−0·67	—	—	—
1·00	0·964	0·168	—	0·928	2·007	1·58

Table 9. Upper bounds for the excess free energy of Lennard-Jones systems compared with Monte Carlo results.

LJ systems at $T^*=0{\cdot}75$, $1{\cdot}15$, $1{\cdot}35$ and $2{\cdot}74$ from (3.5) which can be written in the form

$$\beta\Delta f^{\mathrm{LJ}}(\rho^*, T^*) \leqslant \beta\Delta f^{\mathrm{HS}}(x) + \frac{8\pi x}{T^* c^6}\left[\frac{I_{12}{}^{\mathrm{HS}}(x)}{c^6} - I_6{}^{\mathrm{HS}}(x)\right]. \tag{3.15}$$

The minimum value with respect to c gives the best upper bound. They are given in table 9 with the corresponding values of $c \equiv c^{\mathrm{LJ}}$. The bounds are slightly worse at higher densities than those reported earlier [16] which were calculated using approximations for $I_{12}{}^{\mathrm{HS}}(x)$ and $I_6{}^{\mathrm{HS}}(x)$ obtained by Kozak and Rice [21] using the PY $g^{\mathrm{HS}}(r, c\sigma)$. We next obtained our best upper bound on the free energy of the Stockmayer potential to $O(\mu^4)$ by minimizing (3.7) with respect to c. This may be written in the form

$$\beta\Delta f^{\mathrm{GS}}(\rho^*, T^*) \leqslant \beta\Delta f^{\mathrm{HS}}(x) + \frac{8\pi x}{T^* c^6}\left[\frac{I_{12}{}^{\mathrm{HS}}(x)}{c^6} - (1+2\chi) I_6{}^{\mathrm{HS}}(x)\right], \tag{3.16}$$

where we recall that $\chi = \mu^{*4}/24T^*$. Our calculations are as usual for $\mu^*=1{\cdot}0$. The difference between these two bounds is a measure of the dipole-dipole

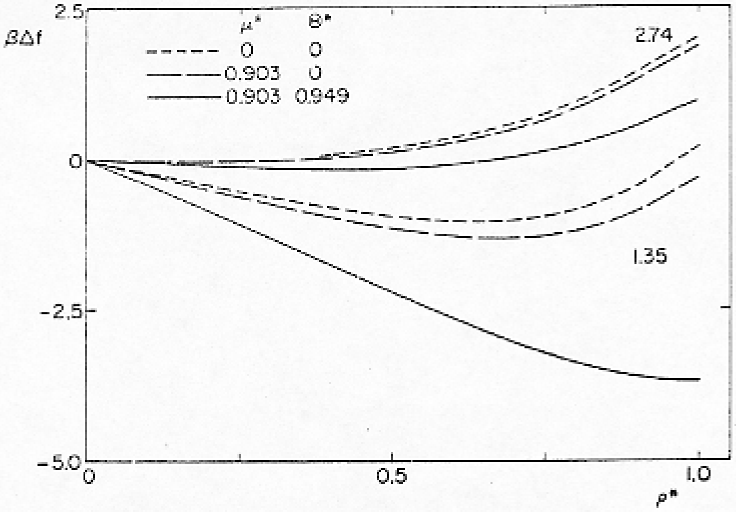

Figure 5. Approximation to $(kT)^{-1}$ times the free energy per particle of a system with potential energy parameters that correspond to HCl (see table 1). For HCl, $T_c^* = kT_c/\epsilon = 1{\cdot}49$.

potential to the free energy is inadequately described by an effective orientation-independent potential that includes only the pair term v^{ED} or v^{ED2} while neglecting the ψ_3 of equation (2.25). We see further from figure 5 that if a molecule also possesses reduced higher moments characteristic of HCl then the contribution from those moments will also be large when only the two-body terms given by equations (1.15)–(1.17) are included in the effective potential. The fact that these contributions do not turn out to be small perturbations suggests that any theory that neglects the ψ_n for $n \geqslant 3$ of equation (2.20) will prove unequal to the task of providing a quantitative explanation of the behaviour of molecules like HCl with relatively strong electric moments. For systems like O_2 and N_2 [30] (and for molecules with small dipole moments) such a theory seems promising. For systems with such relatively weak moments, the various contributions to the free energy can even be accurately assessed from equations (3.10), (3.12)–(3.14) using our approximations for I_n^{HS} with $c = c^{\mathrm{LJ}}$ (given in table 9) rather than the best c's that correspond to the effective potential in (1.13).

We wish to thank Loup Verlet and D. Schiff for sending us their unpublished machine computations of the radial distribution functions of hard spheres.

APPENDIX

Evaluation of the integrals $I_n^{\mathrm{HS}}(x)$ for $n = 6$, 8, 10, 12, 18, 24, we define

$$I_n(x) \equiv \int_1^\infty g^{\mathrm{HS}}(y, x) y^{2-n}\, dy, \tag{A 1}$$

where $y = r/a$, $x = \rho a^3$, a is the diameter of the hard spheres and ρ is the density of the system. From the density expansion of $g^{\mathrm{HS}}(y, x)$ we have

$$\begin{aligned} g^{\mathrm{HS}}(y, x) &= 0, \quad y \leqslant 1 \\ &= 1 + \sum_{m=1}^{\infty} g_m(y) x_m, \quad y > 1. \end{aligned} \tag{A 2}$$

For $n > 3$

$$I_n(x) = \frac{1}{n-3} + \sum_{m=1}^{\infty} x^m J_{mn}, \tag{A 3}$$

where

$$J_{mn} \equiv \int_1^{\infty} g_m(y) y^{2-n} \, dy. \tag{A 4}$$

We evaluated J_{1n} analytically from Kirkwood's [22] result for $g_1(y)$ and calculated J_{2n} and J_{3n} numerically using the tabulations of $g_2(y)$ and $g_3(y)$ give by Nijboer and VanHove [23] and by Ree *et al.* [24] respectively. This gave us the following polynomial approximations to $I_n(x)$ for $n = 6, 8, 10, 12, 18, 24$: (A 5)

$$I_6^{HS}(x) = \tfrac{1}{3} + 0{\cdot}225099x + 0{\cdot}066438x^2 + 0{\cdot}002679x^3, \tag{A 6}$$

$$I_8^{HS}(x) = \tfrac{1}{5} + 0{\cdot}173442x + 0{\cdot}083223x^2 + 0{\cdot}020761x^3, \tag{A 7}$$

$$I_{10}^{HS}(x) = \tfrac{1}{7} + 0{\cdot}139665x + 0{\cdot}083043x^2 + 0{\cdot}031060x^3, \tag{A 8}$$

$$I_{12}^{HS}(x) = \tfrac{1}{9} + 0{\cdot}116298x + 0{\cdot}078044x^2 + 0{\cdot}035537x^3, \tag{A 9}$$

$$I_{18}^{HS}(x) = \tfrac{1}{15} + 0{\cdot}076670x + 0{\cdot}061607x^2 + 0{\cdot}035581x^3, \tag{A 10}$$

$$I_{24}^{HS}(x) = \tfrac{1}{21} + 0{\cdot}056931x + 0{\cdot}050743x^2 + 0{\cdot}031477x^3. \tag{A 11}$$

We call these collectively the virial series approximations to $O(x^3)$ for $I_n(x)$.

x†	MC	Virial‡	Error	PY	Error	Padé (1, 3)§	Error	Padé (2, 2)§	Error
$I_6^{HS}(x)$									
0·6684	0·5158	0·5143	0·0015	0·5107	0·0051	0·5132	0·0026	0·5143	0·0015
0·7639	0·5461	0·5453	0·0018	0·5413	0·0048	0·5434	0·0027	0·5453	0·0018
0·8594	0·5791	0·5776	0·0015	0·5735	0·0056	0·5746	0·0045	0·5776	0·0015
0·8976	0·5934	0·5909	0·0025	0·5868	0·0066	0·5873	0·0061	0·5909	0·0025
0·9358	0·6046	0·6044	0·0002	0·6005	0·0041	0·6001	0·0045	0·6044	0·0002
$I_{12}^{HS}(x)$									
0·6684	0·2382	0·2343	0·0039	0·2319	0·0062	0·2372	0·0010	0·2390	0·0008
0·7639	0·2669	0·2613	0·0056	0·2598	0·0071	0·2665	0·0004	0·2698	0·0029
0·8594	0·3015	0·2912	0·0103	0·2918	0·0103	0·2996	0·0019	0·3058	0·0043
0·8976	0·3174	0·3041	0·0133	0·3033	0·0133	0·3141	0·0033	0·3218	0·0044
0·9358	0·3311	0·3174	0·0137	0·3182	0·0129	0·3293	0·0018	0·3390	0·0079

† These values of x correspond to $\eta = 0{\cdot}35$, $0{\cdot}40$, $0{\cdot}45$, $0{\cdot}47$ and $0{\cdot}49$ respectively, where $\eta = \pi\rho a^3/6 = \pi x/6$.

‡ Contribution of $1 + xg_1(y) + x^2g_2(y) + x^3g_3(y)$ to $I_n(x)$, where $x = \rho a^3$ in which ρ is the density and a the hard-sphere diameter.

§ Padé (1, 3) $I_6^{HS}(x) \equiv \frac{1}{3} + [0{\cdot}22509x/(1 - 0{\cdot}295150x + 0{\cdot}075212x^2)]$. Padé (2, 2) $I_6^{HS}(x)$ is given in (A 12). Padé (1, 3) $I_{12}^{HS}(x)$ is given in (A 15). Padé (2, 2):

$$I_{12}^{HS}(x) \equiv \tfrac{1}{9} + [(0{\cdot}1162984x + 0{\cdot}0250880x^2)/(1 - 0{\cdot}455346x)].$$

Our best Padé approximants of $I_6^{HS}(x)$ and $I_{12}^{HS}(x)$ are the expressions given in (A 12) and (A 15) respectively.

Table A 1. Comparison of several approximations to $I_n^{HS}(x)$ for $n = 6$ and 12, with Monte Carlo estimates.

In an attempt to extend these results to larger values of x we formed the (1, 3) and (2, 2) Padé approximants to $(1/x)[I_n{}^{\mathrm{HS}}(x)-(1/n-3)]]$ and compared them with calculations of $I_n{}^{\mathrm{HS}}(x)$ using Monte Carlo (MC) and Percus–Yevick (PY) values respectively for the radial distribution functions of hard spheres. The MC $I_n{}^{\mathrm{HS}}(x)$ were obtained using Schiff and Verlet's [12] MC computations for $g^{\mathrm{HS}}(y, x)$ at $x=0{\cdot}6685$, $0{\cdot}7639$, $0{\cdot}8594$, $0{\cdot}8976$ and $0{\cdot}9358$. Their tabulations of $g^{\mathrm{HS}}(y, x)$ extend up to $y=5$, beyond which we assumed a value of unity for $g^{\mathrm{HS}}(y, x)$. The Percus–Yevick $I_n{}^{\mathrm{HS}}(x)$ were obtained by the method first introduced by Frisch *et al.* [25]. We compare our virial series approximation and our Padé approximants with the MC and PY values in table A 1 for $n=6$ and $n=12$. Our Padé approximants are superior to the results obtained from the PY approximation. The astonishing accuracy of the virial series approximation to $O(x^3)$ is also worth noting even though the radial distribution functions to this level of approximation are very different from the true values! Our best Padé approximations for $I_n{}^{\mathrm{HS}}(x)$ are

$$I_6{}^{\mathrm{HS}}(x)=\tfrac{1}{3}+\frac{0{\cdot}225099x+0{\cdot}0573613x^2}{1-0{\cdot}0403233x}, \tag{A 12}$$

$$I_8{}^{\mathrm{HS}}(x)=\tfrac{1}{5}+\frac{0{\cdot}173442x+0{\cdot}0399557x^2}{1-0{\cdot}249462x}, \tag{A 13}$$

$$I_{10}{}^{\mathrm{HS}}(x)=\tfrac{1}{7}+\frac{0{\cdot}139665x+0{\cdot}030805x^2}{1-0{\cdot}374023x}, \tag{A 14}$$

$$I_{12}{}^{\mathrm{HS}}(x)=\tfrac{1}{9}+\frac{0{\cdot}116298x}{1-0{\cdot}671067x+0{\cdot}144763x^2}, \tag{A 15}$$

$$I_{18}{}^{\mathrm{HS}}(x)=\tfrac{1}{15}+\frac{0{\cdot}076670x}{1-0{\cdot}803539x+0{\cdot}181588x^2}, \tag{A 16}$$

$$I_{24}{}^{\mathrm{HS}}(x)=\tfrac{1}{21}+\frac{0{\cdot}056931x}{1-0{\cdot}891307x+0{\cdot}241531x^2}, \tag{A17}$$

The first four of these were used in the computations of the dipole, quadrupole and octupole contributions to the free energy reported in the last section.

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[30] It is worth noting that *both* the two-body ϕ_2 and the three-body ϕ_3 will include a term of $O(\Theta^8)$ for molecules with non-zero quadrupole moment, in contrast to the corresponding $O(\mu^8)$ term for dipolar molecules, which comes entirely from ϕ_4. In the lowest-order theory in Θ considered here, one neglects both contributions of $O(\Theta^8)$.