Thermodynamic perturbation theory for potentials of multipolar symmetry. I

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(Received 24 February 1975)

Earlier work in simple polar fluids is extended to higher multipolar terms. Some general properties of multipolar expansions and of the three-body terms that appear in them are considered. Illustrative application is made to a system of quadrupolar spheres. A method of incorporating the effects of nonspherical molecular cores into our formalism is outlined, and some preliminary estimates are given for the relative size of such effects compared to that of the quadrupolar terms.

I. INTRODUCTION

This paper represents a continuation of earlier work[1,2] on simple polar fluids. In that work we developed a Padê technique to extrapolate our results beyond second order in the dipole moment; we also showed[1] that similar models with higher multipolar forces of appreciable strength would also have to be treated by such extrapolation techniques to obtain accurate results. Here we discuss certain general aspects of the multipolar expansion and the treatment of the three-body terms that appear in it. We go on to use these results in a Padê treatment of quadrupolar spheres as an illustrative example.

All of the above work is done in the context of reference-system distribution functions that are assumed to be functions of position but not orientation of the reference-system particles (where by reference system we mean the system in which the multipolar strength parameters are all set equal to zero). This assumption is strictly correct only for reference systems in which the interparticle potentials are orientation independent, but real molecules that interact anisotropically enough at large distances to have appreciable polar moments almost inevitably come with repulsive cores that also deviate appreciably from spherical symmetry. As a result, our work has so far been of limited direct applicability to real systems.

In the latter part of this paper we begin a study of the use of our results in treating models with nonspherical cores, and we continue the study in a companion paper.[3] But here it is perhaps worthwhile to elaborate on what we hope to accomplish—and believe we have accomplished—by studying the properties of the somewhat more restricted class of models with symmetric cores that we have been investigating in such detail.

Our prime motivation is a canonical one of the theoretician—to deal with the simplest possible models that will capture certain essential new features of the systems under study. For us the systems are polar fluids as well as several closely related systems to which we shall return later in this introduction, and the behavior we wish to understand is their thermodynamic behavior. We have begun with models designed to isolate the thermodynamic effects of the ideal polar terms with fixed polar moments so that we can clearly discern the new features that already arise from the presence of these terms before we attempt to further embellish our Hamiltonians with the complexity that characterizes real polar molecules and that will surely be necessary to bring our model computations into quantitative agreement with experimental results. Some key features of polar interactions that our work has either revealed or illuminated are the following.

(i) A characteristic "saturation" occurs in polar systems (including monopolar, i.e., charged systems) as the polar interaction strength λ increases, causing the free energy per particle to behave more and more linearly in λ as λ increases. The appropriate nondimensional λ for charges is $\beta e^2/R$, where $\beta = 1/kT$, e is charge, and R is particle diameter, while for dipoles it is $\beta\mu^2/R^3$ with μ the strength of the dipole moment, for quadrupoles it is $\beta\theta^2/R^5$, where θ is the quadrupole moment, etc. This saturation effect as a rigorous asymptotic result for $\lambda \to \infty$ was recognized by Onsager[4] long ago, but we find that it already makes itself felt in an important way in simple models as soon as λ is on the order of unity.[1,2,5,6]

(ii) The saturation effect for charges[5] and dipoles[1,2] can be captured with remarkable accuracy for all λ of interest by means of a simple Padê extrapolation technique.

(iii) The ideal dipole term is enough to induce a normal liquid–gas critical point in a dipolar model even without the further addition of any attractive dispersion forces.[2]

(iv) The critical behavior in the neighborhood of the liquid–gas critical point of polar liquids is unlikely to be qualitatively different from that of nonpolar liquids despite the great difference in the asymptotic symmetry of the pair potential; in particular we find[7] that the thermodynamic critical exponents are unlikely to differ from those of nonpolar fluids any more markedly than the exponents will differ from nonpolar fluid to fluid. Thus they may not differ at all. On the other hand certain key critical *constants* will be affected by the presence of permanent polar moments. The critical ratio $(\beta p/\rho)_c$, with p pressure and ρ number density, is one such constant that will depend on the relative strength of terms of order λ^n, $n>2$, in a dipolar fluid.[8] Similarly, partly because of the enhanced magnitude of the term in excess of the hard-core contribution to the free energy and partly because of the striking difference in temperature dependence of the polar contributions to this perturbing term compared to the dispersion contributions, one can anticipate characteristic global differences in the shape of the p-ρ-β surface—for example in the slope and relative linearity of the diameter of the coexistence curve[1,2]—between polar and nonpolar fluids.[9]

We return now to those systems other than polar fluids to which our work is relevant. First, it has an obvious application to polar solids, which has already begun to be explored.[10] Second, the simple dipolar models we have studied prove to be useful models of ferroelectric colloids[11] and of rotons.[12] Finally, we note that there is an immediate application of our techniques and results to the evaluation of the n-body contributions arising from induced forces of various sorts rather than from the presence of permanent multipolar moments. In particular our results carry over immediately into the assessment of 3-body dispersion forces[13] as well as to 3-body effects induced in mixtures.[14] We defer such application of our techniques and results to a future publication except to note that the techniques of the Appendix can be readily used to obtain the linear contributions to the nonadditive multipole–multipole–multipole contributions to virial coefficients. The results of Sec. III, for example, already include the quadrupole–quadrupole–quadrupole term for hard spheres.

We proceed next to a technical summary of our treatment, which explicitly includes contributions to the Helmholtz free energy f from the two-body interactions of $O(\lambda^3)$, where $\lambda^3=\lambda_a\lambda_b\lambda_c$, with λ_a the strength parameter related to the electric moments of the molecules. For instance, $\lambda_1\propto\mu^2$, $\lambda_2\propto\theta^2$, $\lambda_3\propto\Phi^2$, where μ, θ, and Φ are the dipole-moment, quadrupole-moment, and octupole-moment, respectively, of the molecules.

It is well known that the dipole and multipole contributions of $O(\lambda)$ to the free energy f are identically zero if the potential consists of a spherically symmetric reference term plus multipole terms, with no monopoles (i.e., charges) present. (We shall restrict our attention in Secs. I, II, and III to such potentials; in Sec. IV we take up briefly the important question of treating molecules with cores that are not spherically symmetric.) For uncharged particles with a pair potential that can be represented as a spherically symmetric term plus ideal multipole terms, the absence of the $O(\lambda)$ term comes about from the angular averaging of the various dipole and multipole terms to $O(\lambda)$ in f, so that the lowest order two-body term which survives is of $O(\lambda^2)$, where $\lambda^2=\lambda_a\lambda_b$. In considering the higher-order terms we shall prove a general theorem showing that any two-body term of $O(\lambda^{2n+1})$ in the free energy is zero if the interaction involves at least one dipole or an odd multipole (e.g., an octupole).[15] This result could also be seen from symmetry arguments. If we, for example, limit ourselves to electric moments no higher than the octupole moments, the only two-body term in the free energy to $O(\lambda^3)$ which does not vanish is the quadrupole–quadrupole interaction of $O(\theta^6)$. We have evaluated this here and find that like the three-body contribution of $O(\theta^6)$ it is opposite in sign to the term of $O(\theta^4)$, so that the partial cancellation of terms in the free energy expansion, which has been discussed earlier,[1] is enhanced for molecules with quadrupoles. The term of $O(\theta^6)$ must hence be included in any generalization of the Padé approximant for the free energy of polar fluids, which has been shown to be accurate for molecules with point dipoles.[1,2,6] In particular, for quadrupole particles, the free energy expansion (ignoring polarizability and assuming spherical symmetry of the particle cores) is

$$f=f^0+\theta^4 f_2+\theta^6(f^\theta_{2,2}+f^\theta_3)+\cdots\,, \qquad (1.1)$$

where f^0 is the free energy of the reference system and f^θ_2, $f^\theta_{2,2}$, and f^θ_3, for which detailed expressions are given below, are such that $f^\theta_2<0$ while $f^\theta_{2,2}$ and f^θ_3 are each >0. By analogy with the simple Padé approximant for dipoles, we may approximate the free energy of such quadrupole molecules by

$$f=f^0+\theta^4 f^\theta_2[1-\theta^6(f^\theta_{2,2}+f^\theta_3)/\theta^4 f^\theta_2]^{-1}\,. \qquad (1.2)$$

Section II contains the proof of the simple and almost transparent theorem concerning molecules with odd multiple moments. We then go on to derive, in the same section, the quadrupole–quadrupole term of $O(\theta^6)$ by a method that is readily extended to higher multipoles. (The next multipole of importance to the same order in λ at the level of two-body interactions is the hexadecapole moment.) In Sec. III numerical results are presented for quadrupole molecules with spherical cores and in Sec. IV we present a brief discussion of nonspherical quadrupolar molecules.

II. A THEOREM FOR MOLECULES WITH ODD ELECTRIC MOMENTS, AND THE EVALUATION OF THE QUADRUPOLE-QUADRUPOLE TERM OF $O(\theta^6)$

In the perturbation theory of polar fluids the pair potential $v(\mathbf{x}_i,\mathbf{x}_j)$ is written as

$$v(\mathbf{x}_i,\mathbf{x}_j)=v_0(r)+\sum_k\lambda_k w(\mathbf{x}_i,\mathbf{x}_j),\quad \lambda_k>0 \qquad (2.1)$$

where $v_0(r)$ is potential energy of the reference system and $\lambda_k w(\mathbf{x}_i,\mathbf{x}_j)$ is one of the perturbing potentials, which for molecules with axial symmetry is given by

$$\sum_k\lambda_k w(\mathbf{x}_i,\mathbf{x}_j)=4\pi\sum_{l_i}\sum_{l_j}\sum_m X^{l_il_jm}(r)S_{l_im}(\theta_i^{ij},\Phi_i^{ij})S_{l_jm}(\theta_j^{ji},\Phi_j^{ji})\,. \qquad (2.2)$$

In (2.2) $X^{l_il_jm}$ is determined by the integers (l_i,l_j) which characterize the electric moments at the molecular centers at i and j and the integer m in the summation ranges over the values $-\min(l_i;l_j)$ to $+\min(l_i,l_j)$. If $l_i=1$ we have a dipole at i; $l_j=2$ denotes the presence of a quadrupole at j. An odd electric moment at the molecular center i corresponds to an odd value for the integer l_i. The orientations of the molecular axes at i and j are determined by the pairs of angles $(\theta_i^{ij}, \Phi_i^{ij})$ and $(\theta_j^{ji}, \Phi_j^{ji})$ defined with respect to the polar axis at i directed towards j and the polar axis at j directed towards i. The angular functions $S_{l_im}(\theta_i^{ij}, \Phi_i^{ij})$ are the surface harmonics defined below in (2.9), and the interaction coefficients $X^{l_il_jm}(r)$, which are determined by the electric moments at i and j, obey the symmetry relations

$$X^{l_il_jm}(r)=X^{l_il_j-m}(r)\ . \tag{2.3}$$

Now if we let

$$\lambda_k w_{l_1l_2}(\mathbf{x}_1,\mathbf{x}_2)$$

$$=4\pi\sum_m X^{l_1l_2m}(r)S_{l_1m}(\theta_1^{12}, \Phi_1^{12})S_{l_2m}(\theta_2^{21}, \Phi_2^{21})\ , \tag{2.4}$$

then $\lambda_k w_{l_1l_2}(\mathbf{x}_1,\mathbf{x}_2)$ represents the perturbation due to a given pair of electric moments centered at 1 and 2 which are defined by the integers l_1 and l_2. The angularly averaged two-body potential which contributes to the free energy is

$$\bar{u}_{l_1l_2}=-(1/\beta)\ln\langle\exp[-\beta\lambda_k w_{l_1l_2}(\mathbf{x}_1,\mathbf{x}_2)]\rangle_\omega\ , \tag{2.5}$$

where $\langle(\ \ )\rangle_\omega$ denotes $[1/(4\pi)^2]\int(\ \ )d\omega_1d\omega_2$. On expanding the exponential in (2.5) and interchanging the order of summation and integration we have

$$\langle\exp[-\beta\lambda_k w_{l_1l_2}(\mathbf{x}_1,\mathbf{x}_2)]\rangle_\omega=\sum_{n=0}^{\infty}-\frac{\beta^n}{n!}\langle[\lambda_k w_{l_1l_2}(\mathbf{x}_1,\mathbf{x}_2)]^n\rangle_\omega\ . \tag{2.6}$$

Substituting (2.6) in (2.5) and expanding the result in a power series in λ_k we get the coefficients $u_{l_1l_2}^{(n)}$ of λ_k^n in the series expansion

$$\bar{u}_{l_1l_2}=\sum_{n=1}^{\infty}u_{l_1l_2}^{(n)}\lambda_k^n\ , \tag{2.7}$$

which gives us the general two-body term of $O(\lambda_k^n)$ in the free energy. We observe that if, for a given (l_1, l_2), every term of $O(\lambda_k^{2n+1})$ in (2.6) is zero, then every term of $O(\lambda_k^{2n+1})$ in (2.7) is also zero. The question arises for what choice of (l_1, l_2) is this true, and the answer which is shown below is that it is so if either l_1 or l_2 is odd.

The general term of $O(\lambda_k^{2n+1})$ in (2.6) reads

$$\langle[\lambda_k w_{l_1l_2}(\mathbf{x}_1,\mathbf{x}_2)]^{2n+1}\rangle_\omega$$

$$=\frac{\lambda_k^{2n+1}}{(4\pi)^2}\int[w_{l_1l_2}(\mathbf{x}_2,\mathbf{x}_2)]^{2n+1}d\omega_1d\omega_2 \tag{2.8}$$

$$=(4\pi)^{2n-1}\lambda_k^{2n+1}\sum_{m_1}\sum_{m_2}\cdots\sum_{m_{2n+1}}\prod_{p=1}^{2n+1}X^{l_1l_2m_p}(r)$$

$$\times C_{m_1m_2\cdots m_{2n+1}}^{l_1}C_{m_1m_2\cdots m_{2n+1}}^{l_2}\ , \tag{2.9}$$

where

$$C_{m_1m_2\cdots m_{2n+1}}^{l_1}=\int\prod_{p=1}^{2n+1}S_{l_1m_p}(\theta_1^{12}, \Phi_1^{12})d\omega_1 \tag{2.10}$$

in which $d\omega_1=\sin\theta_1^{12}d\theta_1^{12}d\Phi_1^{12}$ and a similar expression holds for $C_{m_1m_2\cdots m_{2n+1}}^{l_2}$,

$$C_{m_1m_2\cdots m_{2n+1}}^{l_2}=\int\prod_{p=1}^{2n+1}S_{l_2m_p}(\theta_2^{21}, \Phi_2^{21})d\omega_2\ . \tag{2.11}$$

By using the definition of the spherical harmonics

$$S_{l,m}(\theta_1^{12}, \Phi_1^{12})=\left[\frac{2l+1}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}\right]^{1/2}P_l^{|m|}(\cos\theta)e^{im\Phi}\ , \tag{2.12}$$

integration over the angle Φ_1^{12} can be done independently of θ_1^{12}. Then since

$$\int_0^{2\pi}\exp\left\{i\sum_{p=1}^{2n+1}m_p\Phi_1^{12}\right\}d\Phi_1^{12}=2\pi\delta\left(\sum_{p=1}^{2n+1}m_p\right) \tag{2.13}$$

we have, after making the substitution $x=\cos\theta_1^{12}$,

$$C_{m_1m_2\cdots m_{2n+1}}^{l_1}=2\pi\delta\left(\sum_{p=1}^{2n+1}m_p\right)K\int_{-1}^{+1}\prod_{p=1}^{2n+1}P_{l_1}^{|m_p|}(x)dx, \tag{2.14}$$

where K is a normalization constant and $\delta(\sum m_p)$ the delta function. This means that $C_{m_1m_2\cdots m_{2n+1}}^{l_1}$ is zero unless

$$\sum_{p=1}^{2n+1}m_p=0\ . \tag{2.15}$$

The parity of the associated Legendre functions $P_{l_1}^{|m_p|}(x)$ is expressed by

$$P_{l_1}^{|m_p|}(-x)=(-1)^{l_1+|m_p|}P_{l_1}^{|m_p|}(x)\ , \tag{2.16}$$

from which it follows that

$$C_{m_1m_2\cdots m_{2n+1}}^{l_1}=\mathrm{const}[1+(-1)^{(2n+1)l_1+\Sigma|m_p|}]\int_0^1\prod_{p=1}^{2n+1}P_{l_1}^{|m_p|}(x)dx, \tag{2.17}$$

which is zero if

$$(2n+1)l_1+\sum_{p=1}^{2n+1}|m_p| \tag{2.18}$$

is odd. But the restriction (2.15) implies that

$$\sum_{p=1}^{2n+1}|m_p|$$

is even, and hence $C_{m_1m_2\cdots m_{2n+1}}^{l_1}$ is zero if l_1 is odd. Similarly, $C_{m_1m_2\cdots m_{2n+1}}^{l_2}$ is zero if l_2 is odd. This proves our theorem that $\bar{u}_{l_1l_2}^{(2n+1)}$ is zero if l_1 or l_2 is odd. Applying this result to two-body dipole (D), quadrupole (Q), octupole (O), and hexadecapole (H) interactions, we see that to $O(\lambda^3)$,

$$\bar{u}_{\mathrm{DD}}^{(3)}=\bar{u}_{\mathrm{DQ}}^{(3)}=\bar{u}_{\mathrm{DO}}^{(3)}=\bar{u}_{\mathrm{DH}}^{(3)}=\bar{u}_{\mathrm{QO}}^{(3)}=\bar{u}_{\mathrm{QH}}^{(3)}=\bar{u}_{\mathrm{OO}}^{(3)}=0\ , \tag{2.19}$$

while

$$\bar{u}_{\mathrm{QQ}}^{(3)}\neq0,\quad \bar{u}_{\mathrm{QH}}^{(3)}\neq0,\quad \bar{u}_{\mathrm{HH}}^{(3)}\neq0\ . \tag{2.20}$$

We can now obtain an expression for $\bar{u}_{\mathrm{QQ}}^{(3)}$ which in the notation introduced earlier is also $\bar{u}_{22}^{(3)}$ since $l_1=l_2=2$. Then from (2.7) and (2.5) we have

$$3!\,\beta^2\bar{u}_{\mathrm{QQ}}^{(3)}\equiv3!\,\beta^2\bar{u}_{22}^{(3)}=\frac{\lambda_2^3}{(4\pi)^2}\int W_{22}(\mathbf{x}_1,\mathbf{x}_2)^3d\omega_1d\omega_2 \tag{2.21}$$

$$=4\pi\theta^6\sum_{m_1=-2}^{+2}\sum_{m_2=-2}^{+2}\sum_{m_3=-2}^{+2}X^{22m_1}(r)$$

$$\times X^{22m_2}(r)X^{22m_3}(r)[C_{m_1m_2m_3}^2]^2\ , \tag{2.22}$$

where we have used (2.4) and $\lambda_2=\theta^2$ in going from (2.21) to (2.22). In (2.22)

TABLE I. Values of m_1, m_2, m_3, and $C^2_{m_1m_2m_3}$ for quadrupoles.

m_1	m_2	m_3	Permutations	$C^2_{m_1m_2m_3}/2\pi$
0	0	0	1	$(5/4\pi)^{3/2}(\frac{4}{35})$
1	−1	0	6	$(5/4\pi)^{3/2}(\frac{2}{35})$
2	−1	−1	3	$(\frac{1}{6})^{1/2}(5/4\pi)^{3/2}(\frac{12}{35})$
−2	1	1	3	$(\frac{1}{6})^{1/2}(5/4\pi)^{3/2}(\frac{12}{35})$
2	−2	0	6	$-(5/4\pi)^{3/2}(\frac{4}{35})$

$$C^2_{m_1m_2m_3}=2\pi\delta(m_1+m_2+m_3)K\int_{-1}^{+1}P_2^{|m_1|}(x)P_2^{|m_2|}(x)P_2^{|m_3|}(x)dx \tag{2.23}$$

in which the constant K is expressed by

$$K=\left(\frac{5}{4\pi}\right)^{3/2}\left[\frac{(2-|m_1|)!\,(2-|m_2|)!\,(2-|m_3|)!}{(2+|m_1|)!\,(2+|m_2|)!\,(2+|m_3|)!}\right]^{1/2} . \tag{2.24}$$

The sets of integers which satisfy the requirement [see (2.23)]

$$m_1+m_2+m_3=0 \tag{2.25}$$

and the condition that $|m_i|<\min(l_1, l_2)=2$ are given in Table I. For these sets the direct evaluation of $C^2_{m_1m_2m_3}$ is easy once the associated Legendre functions $P_2^{|m_1|}(x)$, etc., are expressed explicitly as functions of x. Alternatively the integral of the product of three associated Legendre functions may also be expressed in terms of the Clebsch–Gordan coefficients or the Slater coefficients which are tabulated in Pauling and Wilson.[16] We have evaluated these integrals directly and checked them against Pauling and Wilson's tables. They are given in Table I. From these results and the appropriate interactions coefficients for quadrupoles defined by

$$\lambda_2\tfrac{1}{6}X^{220}(r)=\lambda_2\tfrac{1}{4}X^{221}(r)=\lambda_2X^{222}(r)=\theta^2/5r^5 , \tag{2.26}$$

we find that

$$\overline{u}^{(3)}_{QQ}=\tfrac{72}{245}\,(\theta^6/r^{15}) . \tag{2.27}$$

In contrast to this the three-body triple quadrupole term of $O(\theta^6)$ reads[17]

$$\overline{u}^{(3)}_{TQ}=\frac{\theta^6}{6400r_{12}^5r_{13}^5r_{23}^5}W_{TQ}(\alpha_1, \alpha_2, \alpha_3) , \tag{2.28}$$

where $(\alpha_1, \alpha_2, \alpha_3)$ are the internal angles of a triangle of sides r_{12}, r_{13}, r_{23} and the function $W_{TQ}(\alpha_1, \alpha_2, \alpha_3)$ is in Ref. 17. We also note that the two-body quadrupole–quadrupole term of $O(\theta^4)$ is[1]

$$\overline{u}^{(2)}_{QQ}=-\tfrac{7}{5}\,(\theta^4/r^{10}) . \tag{2.29}$$

Relations (2.27)–(2.29) are all we need to write down f^θ_2, $f^\theta_{2,2}$, and f^θ_3, in the free-energy expansion (1.1):

$$\theta^4f^\theta_2=\tfrac{1}{2}\beta\rho\int g^0_{12}(r)\overline{u}^{(2)}_{QQ}\,d\mathbf{r} , \tag{2.30}$$

$$\theta^6f^\theta_{2,2}=\tfrac{1}{2}\beta^2\rho\int g^0_{12}(r)\overline{u}^{(3)}_{QQ}\,d\mathbf{r} , \tag{2.31}$$

$$\theta^6f^\theta_3=\beta^2\rho^2\int g^0_{123}(r_{12}, r_{13}, r_{23})\overline{u}^{(3)}_{TQ}\,d\mathbf{r}_2\,d\mathbf{r}_3 , \tag{2.32}$$

where g^0_{12} and g^0_{123} are the two- and three-particle correlation functions, respectively, of the reference system and $\beta=1/kT$. Combining (2.30) and (2.31) and making use of results (2.27) and (2.29), we get

$$\theta^4f^\theta_2+\theta^6f^\theta_{2,2}=\frac{\rho}{2}\int g^0_{12}\left[-\frac{7}{5}\frac{\theta^4}{r^{10}}\beta+\frac{72\theta^6}{245r^{15}}\beta^2\right]d\mathbf{r} , \tag{2.33}$$

which implies that at the level of two-body forces, the quadrupole–quadrupole interactions to $O(\theta^6)$ are equivalent to an effective temperature-dependent potential $v^{EQQ}(r)$ given by

$$v^{EQQ}(r)=-\tfrac{7}{5}(\theta^4/r^{10})\beta+\tfrac{72}{245}\,(\theta^6/r^{15})\beta^2 , \tag{2.34}$$

in which a partial cancellation of terms is already present.

III. NUMERICAL RESULTS FOR QUADRUPOLAR MOLECULES WITH SPHERICAL CORES

We restrict ourselves here to a calculation of the change in free energy of hard spheres when quadrupole interactions are present. Our basic assumption is that this is given accurately by (1.2), which makes it necessary for us to evaluate only the two- and three-body contributions to $O(\theta^4)$ and $O(\theta^6)$. For the system of interest (nonpolarizable hard spheres with point-quadrupoles) there is a characteristic length which is the hard sphere diameter a and a characteristic energy which is θ^2/r^5. It is convenient now to use the reduced variables

$$x=\rho a^3, \quad y=r/a, \text{ and } t=kTa^5/\theta^2 , \tag{3.1}$$

which enables us to write (2.30) and (2.31) in the form

$$\beta\theta^4f^\theta_2=-\frac{14x\pi I^{HS}_{10}(x)}{5t^2}=-\frac{8.796459xI^{HS}_{10}(x)}{t^2} \tag{3.2}$$

and

$$\beta\theta^6f^\theta_{2,2}=\frac{144x\pi I^{HS}_{15}(x)}{245t^3}=\frac{1.846487xI^{HS}_{15}(x)}{t^3} , \tag{3.3}$$

where

$$I^{HS}_n(x)=\int_1^\infty g^{HS}(y, x)y^{2-n}dy \tag{3.4}$$

in which $g^{HS}(y, x)$ is the hard sphere radial distribution function. Accurate Padé approximants to this integral for several values of $n=6$ to $n=24$ (with the unfortunate exception of $n=15$) have been discussed in an earlier paper.[1] For $I^{HS}_{10}(x)$ we have already suggested the approximation

$$I^{HS}_{10}(x)=\frac{1}{7}+\frac{0.139665x+0.030805x^2}{1-0.374023x} \tag{3.5}$$

and for $I^{HS}_{15}(x)$ we obtain, by the method described in the Appendix of Ref. 1, the Padé approximant

$$I^{HS}_{15}(x)=\frac{1}{12}+\frac{0.0925527x}{1-0.737104x+0.1449389x^2} . \tag{3.6}$$

The calculation of the three-body integral in (2.32) is not quite so simple because of the presence of the three-particle correlation function $g^{(0)}_{123}=g^{HS}_{123}$ for hard spheres. Barker, Henderson, and Smith[18] have shown that the corresponding integral for the triple-dipole potential may be estimated accurately by using the superposition approximation for g^{HS}_{123} together with the Percus–Yevick

TABLE II. Various estimates of $I_{TQ}/6400$, all of which assume the superposition approximation.

	Eq. (A4)		Virial $O(x^3)$		Padé (2, 2)	Padé (1, 3)
x	Exact $g(r)$	PY$g(r)$[a]	Exact $g_n(r)$	PY$g_n(r)$	PY$g_n(r)$	PY$g_n(r)$
0.4	0.2162	0.2124	0.2131	0.2102	0.2143	0.2119
0.6	0.3376	0.3320	0.3277	0.3200	0.3456	0.3278
0.8	0.5100	0.5093	0.4864	0.4710	0.5784	0.4856
0.9	0.6153	0.6252	0.5850	0.5644	0.7699	0.5764
1.0	0.7280	0.7621	0.6977	0.6709	1.060	0.6687

[a] The "extended virial" (3.19) reproduces these results to within 0.3%.

radial distribution functions. We have done something similar for the triple-quadrupole integral in (2.32); the chief difference being that we have used the density expansion for the exact and Percus–Yevick radial distribution functions to obtain the corresponding density expansions for the triple-quadrupole integral to $O(\rho^3)$ from which Padé and other approximants were derived. The details of the method, which are given in the Appendix, are also useful in the evaluation of the three-body terms due to other combinations of dipoles and quadrupoles, a matter which we hope to take up in a forthcoming paper. For the pure quadrupole case, we can write (2.32) as

$$\beta\theta^6 f_3^\theta = \frac{\beta^3\rho^2\theta^6}{6400}\int g_{123}^{\mathrm{HS}}(r_{12}, r_{13}, r_{23}) W'_{\mathrm{TQ}}\, d\mathbf{r}_2\, d\mathbf{r}_3 \tag{3.7}$$

$$= (x^2/6400t^3) I_{\mathrm{TQ}}^{\mathrm{HS}}(x)\,, \tag{3.8}$$

where

$$I_{\mathrm{TQ}}^{\mathrm{HS}} = \int g_{123}^{\mathrm{HS}}(R, s, r) W'_{\mathrm{TQ}}(R, s, r)\, ds\, dr \tag{3.9}$$

in which

$$R = r_{12}/a\,, \quad s = r_{13}/a\,, \quad r = r_{23}/a\,, \tag{3.10}$$

and

$$\begin{aligned} W'_{\mathrm{TQ}} &= W_{\mathrm{TQ}} R^{-5} s^{-5} r^{-5} \\ &= \{-27 + 220\cos\alpha_1\cos\alpha_2\cos\alpha_3 + 490\cos 2\alpha_1\cos 2\alpha_2 \\ &\quad \times\cos 2\alpha_3 + 175[\cos 2(\alpha_1-\alpha_2) + \cos 2(\alpha_2-\alpha_3) \\ &\quad + \cos 2(\alpha_3-\alpha_1)]\} R^{-5} s^{-5} r^{-5}\,. \end{aligned} \tag{3.11}$$

In (3.11) α_1, α_2, and α_3 are the internal angles of a triangle of sides R, s, and r. In the Appendix we have shown that $I_{\mathrm{TQ}}^{\mathrm{HS}}(x)$ has a density expansion

$$I_{\mathrm{TQ}}^{\mathrm{HS}}(x) = J_0 + J_1 x + J_2 x^2 + J_3 x^3 + \cdots\,, \tag{3.12}$$

where

$$J_0 = 54\pi^2 = 532.959 \tag{3.13}$$

and the coefficients J_1, J_2, and J_3, when evaluated within the context of the superposition approximation, are given by

$$J_1 = \tfrac{4923}{16} - 384\ln 2 = 1287.35\,, \tag{3.14}$$

$$J_2 = \begin{matrix} 1534.00 & \text{(exact)} \\ 1447.97 & \text{(Percus–Yevick)}\,, \end{matrix} \tag{3.15}$$

$$J_3 = \begin{matrix} 1110.66 & \text{(exact)} \\ 1025.65 & \text{(Percus–Yevick)}\,, \end{matrix} \tag{3.16}$$

where the qualifications "exact" and "Percus–Yevick" refer to the use of the exact or Percus–Yevick radial distribution functions in the definition of $I_{\mathrm{TQ}}(x)$. This leads to the following density expansions for $I_{\mathrm{TQ}}(x)$.

$$I_{\mathrm{TQ}}^{\mathrm{exact,SA}}(x) = 532.959 + 1287.35x + 1534.00x^2 + 1110.66x^3 + \cdots\,, \tag{3.17}$$

$$I_{\mathrm{TQ}}^{\mathrm{PY,SA}}(x) = 532.959 + 1287.35x + 1447.97x^2 + 1025.65x^3 + \cdots\,, \tag{3.18}$$

where the superscript SA stands for the superposition approximation.

We have also attempted to extend these expansions to higher densities by forming (1, 3) and (2,2) Padé approximants to $(1/x)[I_{\mathrm{TQ}} - J_0]$; the numerical results are summarized in Table II and Fig. 1. None of these is very successful when judged by the correct results obtained directly from (3.9) and the superposition approximation using the exact or PY$g(r)$'s in place of their density expansions. To do this we again use (A4) given in the Appendix, evaluating the kernels which contain the distribution functions numerically and splitting the range of integration as shown there into two parts from $R = 1$ to 2 and from $R = 2$ to ∞. With such a variety of results it is difficult to choose between them without any additional criterion for elimination, but we have settled on the PY plus superposition approximation (as Barker *et al.* have done for triple dipoles) as an adequate representation of the correct I_{TQ} since the virial expansion is easily extended empirically to fit the numbers to within 0.3% up to $x = 1.0$. An expression which does this is

$$I_{\mathrm{TQ}}^{\mathrm{PY,SA}} \simeq 532.959 + 1287.35x + 1447.97x^2 + 1025.65x^3 + 558.39x^4 + 25.0x^5\,. \tag{3.19}$$

We will call this the "extended virial" equation; it makes our subsequent work, especially in Sec. IV, much simpler and, of course, it has the correct zero density limit. By using it in (3.8) we get

$$\beta\theta^6 f_3^\theta \simeq (x^2/t^3)(0.083275 + 0.201148x + 0.226245x^2 + 0.160258x^3 + 0.087248x^4 + 0.003906x^5)\,. \tag{3.20}$$

It is now possible to assess the importance of the various quadrupole contributions to the free energy of spherically symmetric molecules. For the sake of notational brevity it is useful to define

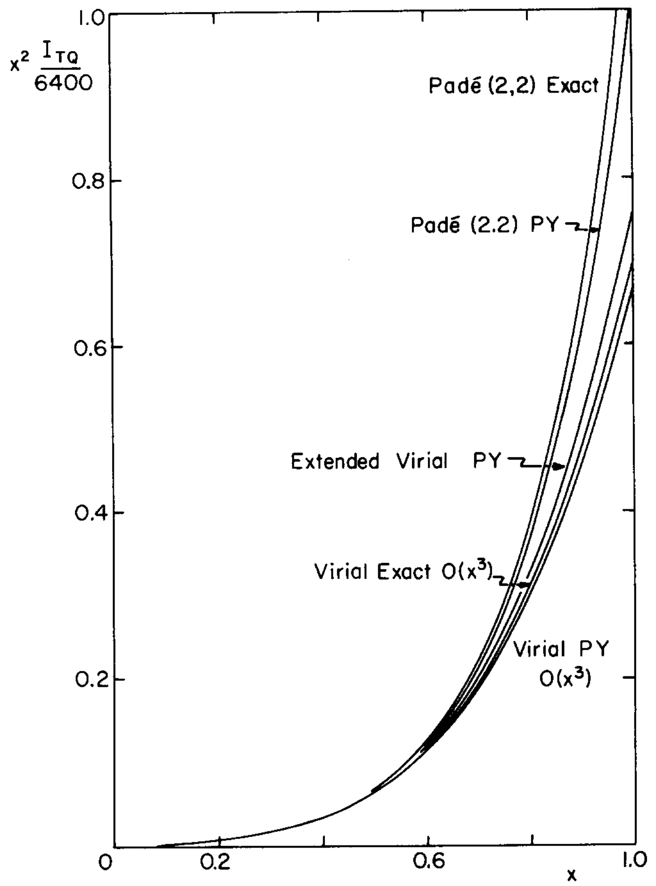

FIG. 1. Comparison of various estimates of the triple-quadruple term $x^2 I_{TQ}/6400$. The labels "exact" and "PY" refer to the use of the exact and Percus–Yevick distribution functions, respectively, in I_{TQ} when the superposition approximation is assumed.

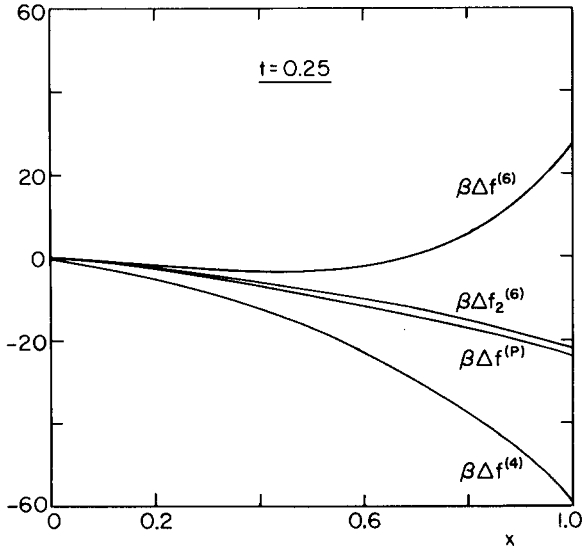

FIG. 2. The free energies of hard spheres plus point quadrupoles calculated to different levels of approximation at $t=0.25$. The label $\beta\Delta f^{(p)}$ refers to the Padé approximant given in (3.23), while $\beta\Delta f^{(4)}$ and $\beta\Delta f^{(6)}$ are the quadrupolar free energies to $O(\theta^4)$ and $O(\theta^6)$, respectively. The curve marked $\beta\Delta f_2^{(6)}$ represents the free energy to (θ^6) when only two-body interactions are counted while the three-body terms and those of higher order are ignored.

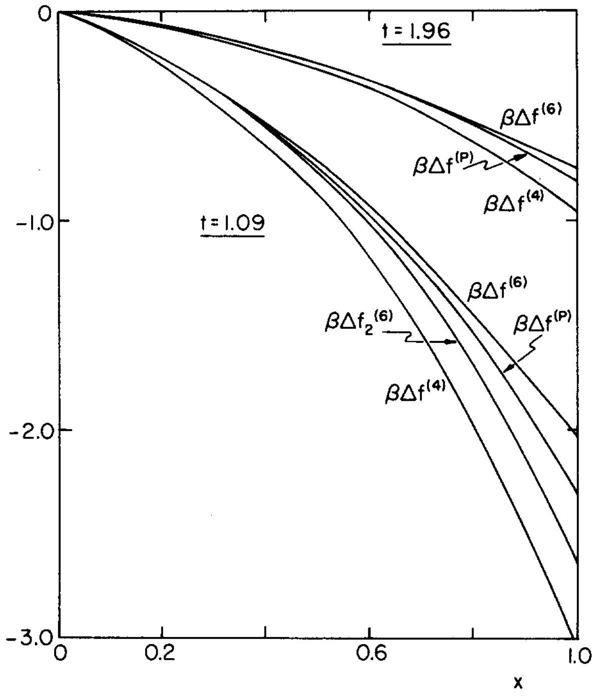

FIG. 3. The free energies of hard spheres, thus, point quadrupoles at $t=1.96$ and 1.09, respectively. See caption of Fig. 2 for details.

$$\Delta f^{(4)} = \theta^4 f_2^\theta \,, \tag{3.21}$$

$$\Delta f^{(6)} = \theta^4 f_2^\theta + \theta^6 f_{2,2}^\theta + \theta^6 f_3^\theta \,, \tag{3.22}$$

and

$$\Delta f^{(p)} = \theta^4 f_2^\theta [1 - \theta^6 (f_{2,2}^\theta + f_3^\theta)/\theta^4 f_2^\theta]^{-1} \,. \tag{3.23}$$

These free energies are plotted against the reduced density x in Figs. 2 and 3 for $t=0.25$, 1.09, and 1.96. At the two lowest temperatures $\Delta f_2^{(6)}$, which is the sum of the two-body quadrupole contributions to $O(\theta^6)$,

$$\Delta f_2^{(6)} = \theta^4 f_2^\theta + \theta^6 f_{2,2}^\theta \tag{3.24}$$

is also plotted.

Some comments on these results, the details of which are available in Figs. 2 and 3 and Table III, are in order. First, it is obvious that the necessity to form the free energy Padé $\Delta f^{(p)}$ is greater the lower the temperature; this is in line with the observation made by Rushbrooke, Stell, and Høye[2] for dipoles. The three-body free energy term is relatively smaller for quadrupoles than for dipoles, but the total free energy contribution of $O(\theta^6)$ is greatly enhanced by the two-body term of the same order, which is comparable in magnitude, and often even greater, than the three-body term of $O(\theta^6)$. For dipoles, the corresponding two-body term, as discussed in Sec. II, is zero. The situation is so completely different here, that when the temperature is high, the free energy Padé is nearly equal to $\Delta f_2^{(6)}$, which ignores the three-body quadrupole term and the need for a free energy Padé altogether; this is probably a numerical accident, but it emphasizes indirectly the lessening importance of the three-body terms at high temperature, in sharp contrast to its behavior at low temperatures. Fi-

TABLE III. Perturbation-theory and Padé approximant estimates of the quadrupole contributions to the free energy of hard spheres with point quadrupoles.

x	$\beta\theta^4 f_2^\theta$	$\beta\theta^6 f_{2,2}^\theta$	$\beta\theta^6 f_3^\theta$	$\beta\Delta f^{(6)}$	$\beta\Delta f^{(p)}$
			$t=0.25$		
0.1	−2.219	1.103	0.0677	−1.048	−1.453
0.3	−8.156	4.197	0.9736	−2.985	−4.992
0.5	−16.76	9.02	4.256	−3.489	−9.356
0.7	−29.14	16.55	12.90	0.3173	−14.49
0.8	−37.20	21.79	20.81	5.398	−17.34
0.9	−46.86	28.37	32.35	13.86	−20.41
1.0	−58.43	36.66	48.77	27.00	−23.73
			$t=1.09$		
0.1	−0.1167	0.0133	0.0008	−0.1026	−0.1042
0.3	−0.4291	0.0506	0.0117	−0.3667	−0.3746
0.5	−0.8819	0.1088	0.0514	−0.7217	−0.7463
0.7	−1.533	0.1997	0.1557	−1.177	−1.244
0.8	−1.957	0.2629	0.2511	−1.443	−1.550
0.9	−2.465	0.3424	0.3903	−1.732	−1.900
1.0	−3.074	0.4424	0.5885	−2.043	−2.302
			$t=1.96$		
0.1	−0.0361	0.0023	0.0001	−0.0337	−0.0338
0.3	−0.1327	0.0087	0.0020	−0.1220	−0.1228
0.5	−0.2727	0.0187	0.0088	−0.2452	−0.2477
0.7	−0.4740	0.0343	0.0268	−0.4129	−0.4199
0.8	−0.6053	0.0452	0.0432	−0.5169	−0.5282
0.9	−0.7624	0.0589	0.0671	−0.6364	−0.6543
1.0	−0.9507	0.0761	0.1012	−0.7734	−0.8013

nally we would like to add that our results are not significantly affected by the use of (3.19) for I_{TQ}, the three-body term. If we had used either the virial series (3.18) or (3.17) instead of (3.19) or the (2,2) Padé approximant we would have, as Table IV indicates, essentially the same results, so that we think the three-body term has been treated with fidelity here.

One additional point of interest is that the quadrupolar free energies at our highest temperatures $t=1.09$ and 1.96 correspond essentially to what is present in a system of molecules interacting as Lennard-Jones particles with point-quadrupoles embedded in them such that $\theta^*=(\theta^2/\epsilon\sigma^5)^{1/2}=0.83$ and $T^*=kT/\epsilon=0.75$ and 1.35, respectively. Here ϵ and σ are the usual Lennard-Jones parameters and the connection between T^*, θ^*, and t is provided by (3.1) and

$$t=\left(\frac{kT}{\epsilon}\right)\left(\frac{\epsilon\sigma^5}{\theta^2}\right)\left(\frac{a}{\sigma}\right)^5=\frac{T^*}{\theta^{*2}}\left(\frac{a}{\sigma}\right)^5\simeq\frac{T^*}{\theta^{*2}}\,. \tag{3.25}$$

The magnitude of $\theta^*=0.83$ is the one appropriate for CO_2 (see Table I in Ref. 1) so that the difference between $\Delta f^{(4)}$ and $\Delta f^{(p)}$ at $t=1.09$ and 1.96 is essentially the error in the free energy of our model CO_2 at $T^*=0.75$ and 1.35, respectively, when the terms beyond those of $O(\theta^4)$ are neglected.

IV. A TREATMENT OF NONSPHERICAL MOLECULAR CORES

In the above discussion, it is assumed that the reference-system pair potential $v^0(1\ 2)$ is spherically symmetric, so that the reference-system pair distribution function $g^0(1\ 2)$ can be written as a function of $r=|\mathbf{r}_1-\mathbf{r}_2|$. Thus $g^0(1\ 2)=g_{12}^0(r)$. If $v^0(1\ 2)$ is not spherically symmetric there will be in the free energy per particle $F/N=f$ additional terms of the form

$$\lambda_i f_i=\frac{\rho^2}{2N}\int g^0(1\ 2)w_i(1\ 2)d(1)d(2)\,, \tag{4.1}$$

where $\lambda_1 w_1$ is the dipole–dipole interaction, $\lambda_2 w_2$ the quadrupole–quadrupole interaction, etc. Such terms of order μ^2, μ^6, etc., are surely present in the free energy of real polyatomic molecules, which do not have spherically symmetric cores.

One can imagine coping with this lack of spherical symmetry in several alternative ways. One of these, which has already been explored by Gubbins and his colleagues,[19] involves the introduction of the asymmetry in the form of anisotropic overlap terms. This method has been described elsewhere,[19] and we have nothing to add to its development in this paper.

A second possible method is based on the notion of a hypothetical system that is thermodynamical equivalent to the system of interest, with an orientation-independent but temperature-dependent potential energy[1,7] that includes n-body terms, $n\geqslant 3$. Using this method with a potential $v(1\ 2)=v^0(1\ 2)+\Sigma\lambda w_i(1\ 2)$ where $v^0(1\ 2)\neq v_{1\ 2}^0(r)$, one has an equivalent two-body potential $v_2^{\text{eq}}(r)$, an equivalent three-body potential $v_3^{\text{eq}}(r,R,s)$, etc. One can then choose $v_2^{\text{eq}}(r)$ as the reference potential associated with a new reference distribution $g_2^{\text{eq}}(r)$ and take $\sum_{n\geqslant 3}v_n^{\text{eq}}$ as the perturbing potential. In the free energy of this new reference system one *already* finds a term of order λ_i, and the main burden of this theory reduces to the (formidable) task of finding $v_2^{\text{eq}}(r)$, $g_2^{\text{eq}}(r)$, and the corresponding free energy accurately. The further contributions from the $\sum_{n\geqslant 3}v_n^{\text{eq}}$ cannot be expected to be small, but one can hope to handle them adequately using Padé techniques and a superposition approximation, just as one can handle the n-point terms for the Stockmayer potential and dipolar spheres. This method takes us somewhat afield of the first two sections of this paper and we shall not pursue it further here.

There is a third method that can profitably be used in conjunction with the development we have already given, however. It is based partly on the notion we have discussed in the previous paragraph and partly on the use of straightforward perturbation theory in the λ_i, which has already been discussed in this connection by Sand-

TABLE IV. Comparison of approximations for $\beta\theta^6 f_3^\theta$ and $\beta\Delta f^{(p)}$ evaluated using two different estimates of I_{TQ} which make use of PY$g(r)$ and the superposition approximation.

	$\beta\theta^6 f_3^\theta$		$\beta\Delta f^{(p)}$	
x	Padé (2,2)	Ext virial	Padé (2,2)	Ext virial
		$t=0.25$		
0.7	13.93	12.90	−14.24	−14.49
0.8	23.69	20.81	−16.74	−17.34
0.9	39.91	32.35	−19.07	−20.41
1.0	67.85	48.77	−20.95	−23.73
		$t=1.09$		
0.7	0.1680	0.1557	−1.236	−1.244
0.8	0.2858	0.2511	−1.529	−1.550
0.9	0.4815	0.3903	−1.847	−1.900
1.0	0.8187	0.5885	−2.180	−2.302

ler.[20] The use of this latter theory that we envision departs from that of Sandler in our handling of the higher-order terms; we propose adding to the term given in (4.1) a Padé approximant that employs the use of an "effective" spherically symmetric $v_2^0(r)^{\text{eff}}$, with its parameter adjusted to take account of the asymmetry of the actual $v^0(1\ 2)$. This method is a kind of hybrid, with the notion of an effective symmetric $v_2^0(r)^{\text{eff}}$ used to evaluate the higher-order λ_t terms, but not the term linear in λ_t. Its chief advantage over the full use of the effective-potential idea is simplicity; by explicitly subtracting out the term of order λ_t one can hope to do justice to the higher-order terms in λ_t by employing a relatively simple effective $v_2^0(r)^{\text{eff}}$ that is λ independent. For example, one might use a $v_2^0(r)^{\text{eff}}$ that is defined by the blip-function method[21] or the variational method[22] applied to $v^0(1\ 2)$. If one tried to use such a $v_2^0(r)^{\text{eff}}$ to evaluate the term of order λ_t, however, one would automatically get zero. The chief advantage of our proposed method over an attempt to do a straightforward evaluation of the higher-order terms in λ_t is again simplicity. By introducing the $v_2^0(r)^{\text{eff}}$ one can take over our earlier methods and results for a spherically symmetric reference potential.

We have done just this for the two homonuclear diatomic models of chlorine and nitrogen discussed by Sandler.[20] He had derived an expression for the free energy $\beta\Delta f$ to $O(\theta^2)$,

$$\beta\Delta f = \beta(\Delta f_0)_d + \beta\Delta f_2\,, \tag{4.2}$$

where $\beta(\Delta f_0)_d$ is the reduced excess free energy of the reference system of rigid diatomic molecules which is also the free energy of a hypothetical hard sphere system of diameter d. We take this to be accurately expressed by the Carnahan and Starling equation of state

$$\beta(\Delta f_0)_d = \eta_d(4-3\eta_d)/(1-\eta_d)^2\,, \tag{4.3}$$

where $\eta_d = \frac{1}{6}\pi\rho d^3$. Sandler's term of $O(\theta^2)$ is given in our notation by

$$\beta(\Delta f_2)_d = \tfrac{3}{2}\pi(x/t)I(\hat\rho)\,. \tag{4.4}$$

Here x and t are defined in (3.1) but with the difference that a is now the diameter of one of the atoms in the homonuclear diatomic molecule. The function $I(\hat\rho)$ has been calculated by Sandler for several values of the reduced density $\hat\rho$ defined by

$$\hat\rho = \rho V_m = \tfrac{1}{6}\pi\rho a^3(1+\tfrac{3}{2}L^* - \tfrac{1}{2}L^{*3})\,, \tag{4.5}$$

where V_m is the volume of the diatomic molecule and $L^* = L/a$ is the reduced center to center distance which is approximately 0.6 for Cl_2 and 0.4 for N_2. The relationship between the atomic diameter a and the effective molecular diameter d as a function of density for a given L^* is known, so that all the information necessary to calculate the two terms is available. For the terms beyond $\beta\Delta f_2$, we use our free energy Padé $\Delta f^{(p)}$ of (3.20), with the effective diameter d employed in the calculation of Δf_0 as the appropriate hard-sphere diameter in the definitions of the reduced density and temperature x and t, respectively. Calling the free energy computed in this way $(\Delta f^{(p)})_d$, we have

$$\beta\Delta f \simeq \beta(\Delta f_0)_d + \beta\Delta f_2 + \beta(\Delta f^{(p)})_d\,. \tag{4.6}$$

The relative magnitudes of these terms for chlorine and nitrogen at the experimental critical point, boiling point, and melting point can be seen in Table V and Fig. 4. From our analysis of the higher-order terms it follows that they are opposite in sign to the term of $O(\theta^2)$, and the net effect of the term represented by $(\Delta f^{(p)})_d$ is comparable in magnitude to Sandler's Δf_2 at high ρ. The latter is negligible in the gas phase, but strongly influences the free energy of the liquid phase. We wish to emphasize that these computations are preliminary in nature and were undertaken simply to get an order-of-magnitude estimate of the effects of nonspherical cores relative to the effects of the ideal polar terms. One important aspect of real molecular interactions entirely left out of these results is the effect of the attractive dispersion term. (In Part II of this work[3] we shall continue the study of ways in which our results can be used in treating models that incorporate features lacking in our previous work.)

ACKNOWLEDGMENTS

We wish to acknowledge aid from the following sources. (a) J. C. R. and B. L. thank Dr. Carl Moser and Professor K. Singer for making it possible for them to attend the CECAM Workshop held at Orsay, France, in June 1974, where part of this work was done. (b) B. L. also thanks The Norwegian Research Council for Science and the Humanities and the A/S Norsk Varekrigsforsikrings Fond for financial assistance, and (c) G. S. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for partial support of the work reported here. We also wish to thank Professor Stanley Sandler and Professor David Chandler for helpful discussions of their work. Finally, we are very much indebted to Professor John Valleau and Dr. G. N. Patey for helpfully discussing an earlier draft of our

TABLE V. Comparison of the Padé free energy $\beta\Delta f^{(p)}$ with Sandler's calculation of $\beta\Delta f_2$ for chlorine and nitrogen at the critical point, boiling point, and melting point of each substance.

	Chlorine ($L^*=0.6$, $\theta=6.14\times10^{-26}$ esu cm^2)					
	$T=172$ °K		239 °K		417 °K	
$\hat\rho$	$\beta\Delta f_2$	$\beta\Delta f^{(p)}$	$\beta\Delta f_2$	$\beta\Delta f^{(p)}$	$\beta\Delta f_2$	$\beta\Delta f^{(p)}$
0.1	−0.01	−0.21	−0.01	−0.11	−0.01	−0.04
0.2	−0.02	−0.51	−0.02	−0.27	−0.01	−0.09
0.3	0.00	−0.95	0.00	−0.52	0.02	−0.18
0.4	0.13	−1.57	0.10	−0.86	0.06	−0.30
0.5	0.50	−2.41	0.36	−1.34	0.21	−0.48
0.6	1.46	−3.54	1.05	−2.00	0.60	−0.72
0.7	3.32	−5.02	2.40	−2.89	1.64	−1.07

	Nitrogen ($L^*=0.4$, $\theta=-1.52\times10^{-26}$ esu cm^2)					
	$T=21$ °K		77 °K		126 °K	
$\hat\rho$	$\beta\Delta f_2$	$\beta\Delta f^{(p)}$	$\beta\Delta f_2$	$\beta\Delta f^{(p)}$	$\beta\Delta f_2$	$\beta\Delta f^{(p)}$
0.1	−0.01	−0.53	−0.00	−0.04	−0.00	−0.02
0.2	−0.01	−1.29	−0.00	−0.11	−0.00	−0.04
0.3	0.02	−2.29	0.01	−0.20	0.00	−0.08
0.4	0.14	−3.61	0.04	−0.33	0.02	−0.13
0.5	0.49	−5.28	0.13	−0.51	0.08	−0.20
0.6	1.20	−7.43	0.32	−0.76	0.20	−0.30
0.7		−10.20		−1.10		−0.44

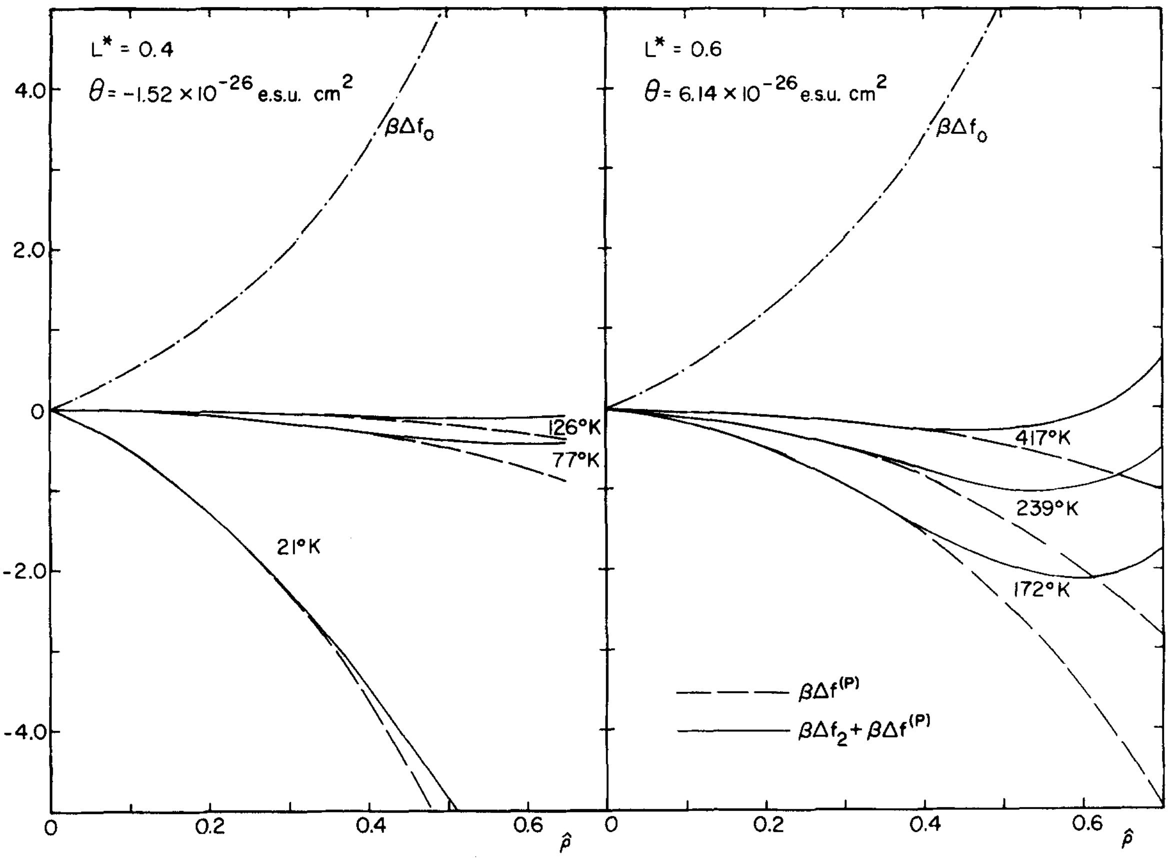

FIG. 4. The free energies of nonspherical hard-core plus point-quadrupole molecules according to Eq. (4.6). The molecular parameters L^* and θ in the figure to the left correspond to N_2, while the parameters in the figure to the right are for Cl_2. The three temperatures in the figures are the experimental critical point, boiling point, and melting point for N_2 and Cl_2, respectively.

manuscript with us, and in particular for uncovering an algebraic error therein.

APPENDIX. THE DENSITY EXPANSION OF THE TRIPLE-QUADRUPOLE INTEGRAL WITHIN THE CONTEXT OF THE SUPERPOSITION APPROXIMATION

Using the superposition approximation

$$g_{123}(R, s, r) = g(R)g(s)g(r) \tag{A1}$$

and bipolar coordinates in (3.9), we have

$$I_{TQ}(x) = 8\pi^2 \int_0^\infty g(R)R\,dR \int_0^\infty g(s)s\,ds \times \int_{|R-s|}^{R+s} g(r)r\,W'_{TQ}(R, s, r)\,dr\ , \tag{A2}$$

where the density (x) dependence of the integral arises from the corresponding density dependence of the radial distribution functions $g(R)$, $g(s)$, and $g(r)$. For hard spheres, we follow Sinanoğlu,[14] and write the integrals over s and r as the sum of two terms within the interval $1 \leq R \leq 2$, and as the sum of three terms (Fig. 5) in the range $2 \leq R < \infty$. These correspond to integration over the regions II′ and III in the lower figure and over the regions denoted by I, II, and III in the upper figure. To see this, define the indefinite integral

$$K(q; [g(r)]) \equiv \int^q g^{HS}(r) W'_{TQ}(R, s, r)\,r\,dr\ , \tag{A3}$$

where the functional dependence of the integral on the radial distribution function $g(r)$ is explicitly denoted by writing it in square brackets. The integral depends on

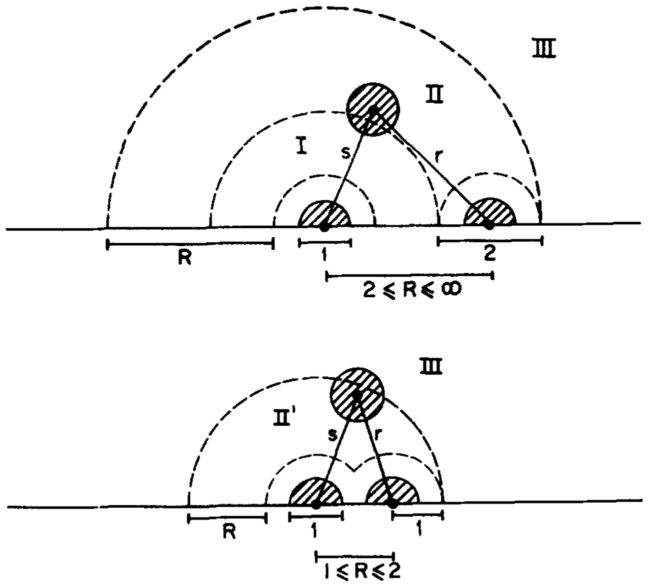

FIG. 5. Integration intervals used in the evaluation of the triple-quadrupole integral I_{TQ} for quadrupolar hard spheres assuming the superposition approximation.

the variables R, s, and q, where q is the upper limit of integration. Then (A2) can be written as

$$\begin{aligned} I^{\mathrm{HS}}_{\mathrm{TQ}}(x) = 8\pi^2 \int_1^2 &\{\mathrm{II}'(R;[g(s),g(r)]) \\ &+ \mathrm{III}(R;[g(s),g(r)])\} g^{\mathrm{HS}}(R) R\,dR \\ &+ 8\pi^2 \int_2^\infty \{\mathrm{I}(R;[g(s),g(r)]) + \mathrm{II}(R;[g(s),g(r)]) \\ &+ \mathrm{III}(R;[g(s),g(r)])\} g^{\mathrm{HS}}(R) R\,dR \ , \end{aligned} \tag{A4}$$

in which

$$\begin{aligned} \mathrm{I}(R;[g(s),g(r)]) = \int_1^{R-1} &\{K(R+s;[g(r)]) \\ &- K(R-s;[g(r)])\} g^{\mathrm{HS}}(s) s\,ds \ , \end{aligned} \tag{A5}$$

$$\begin{aligned} \mathrm{II}(R;[g(s),g(r)]) = \int_{R-1}^{R+1} &\{K(R+s;[g(r)]) \\ &- K(1;[g(r)])\} g^{\mathrm{HS}}(s) s\,ds \ , \end{aligned} \tag{A6}$$

$$\begin{aligned} \mathrm{II}'(R;[g(s),g(r)]) = \int_1^{R+1} &\{K(R+s;[g(r)]) \\ &- K(1;[g(r)])\} g^{\mathrm{HS}}(s) s\,ds \ , \end{aligned} \tag{A7}$$

$$\begin{aligned} \mathrm{III}(R;[g(s),g(r)]) = \int_{R+1}^{\infty} &\{K(R+s;[g(r)]) \\ &- K(s-R,[g(r)])\} g^{\mathrm{HS}}(s) s\,ds \ . \end{aligned} \tag{A8}$$

For the density expansion of the various distributions functions we have, for example,

$$\begin{aligned} g^{\mathrm{HS}}(R) &= 0 \ , & R &< 1 \\ &= 1 + \sum_{m=1}^{\infty} g_m(R) x^m \ , & R &> 1 \end{aligned} \tag{A9}$$

which leads us to the density expansion for the integral $I^{\mathrm{HS}}_{\mathrm{TQ}}(x)$,

$$I^{\mathrm{HS}}_{\mathrm{TQ}}(x) = J_0 + J_1 x + J_2 x^2 + J_3 x^3 + \cdots \ , \tag{A10}$$

where

$$\begin{aligned} J_0 = 8\pi^2 &\int_1^2 \{\mathrm{II}'(R;[1,1]) + \mathrm{III}(R;[1,1])\} R\,dR \\ &+ 8\pi^2 \int_2^\infty \{\mathrm{I}(R;[1,1]) + \mathrm{II}(R;[1,1]) + \mathrm{III}(R;[1,1])\} R\,dR \ , \end{aligned} \tag{A11}$$

with related expressions for the coefficients J_1, J_2, J_3, etc., which are discussed below.

Before proceeding further, it is useful to examine the kernels $K(q;[g(r)])$ more closely when $g(r) = 1$. By using the cosine theorem to express the various angles α_1, α_2, α_3 of W_{TQ} in terms of the sides of the triangle R, s, r, we have[17]

$$\begin{aligned} W'_{\mathrm{TQ}}(R,s,r) = (1/4R^9 s^9 r^9)[&245 r^{12} - 630 c r^{10} \\ &+ 45(6c^2 + d^2) r^8 + 20c(4c^2 + 3d^2) r^6 \\ &+ 9(8c^4 + 24c^2 d^2 + 3d^4) r^4 - 90 c d^2 (4c^2 \\ &+ 3d^2) r^2 + 35 d^4 (6c^2 + d^2)] \ , \end{aligned} \tag{A12}$$

where $c = R^2 + s^2$ and $d = R^2 - s^2$. On carrying out the integration in (A3),

$$\begin{aligned} K(q;[1]) = \tfrac{1}{4} R^{-9} s^{-9} [&49 q^5 - 210 c q^3 + 45(6c^2 + d^2) q \\ &- 20c(4c^2 + 3d^2) q^{-1} - 3(8c^4 + 24c^2 d^2 + 3d^4) q^{-3} \\ &+ 18 c d^2 (4c^2 + 3d^2) q^{-5} - 5d^4 (6c^2 + d^2) q^{-7}] + L, \end{aligned} \tag{A13}$$

where L is the integration constant. Now the crucial point, which leads to a considerable simplification in the following argument, is that one finds

$$K(R-s;[1]) = K(s-R;[1]) = K(R+s;[1]) = L \ , \tag{A14}$$

which leads immediately to

$$\mathrm{I}(R;[g(s),1]) = \mathrm{III}(R;[g(s),1]) = 0 \ . \tag{A15}$$

We find that expressions like (A14) and (A15) are true not only for the triple-quadrupole term, but for all the other combinations of dipoles and quadrupoles which can be placed at the corners of a triangle. The validity of (A14) for triple dipoles was first shown by Sinanoglu.[14] It is obvious from the argument which leads to (A15) that we may replace $g(s)$ in (A15) by any well behaved function, so that in particular

$$\mathrm{I}(R;[1,1]) = \mathrm{I}(R;[g_1(s),1]) = \mathrm{III}(R;[1,1]) = \mathrm{III}(R;[g_1(s),1]) = 0, \tag{A16}$$

where $g_1(s)$ is the coefficient of x in the density expansion of $g^{\mathrm{HS}}(s)$. [See (A9).] We then have, from (A11), that

$$J_0 = 8\pi^2 \int_1^2 \mathrm{II}'(R;[1,1]) R\,dR + 8\pi^2 \int_2^\infty \mathrm{II}(R;[1,1]) R\,dR \ , \tag{A17}$$

where

$$\mathrm{II}(R;[1,1]) = \int_{R-1}^{R+1} \{L - K(1;[1])\} s\,ds \tag{A18}$$

and

$$\mathrm{II}'(R;[1,1]) = \int_1^{R+1} \{L - K(1;[1])\} s\,ds \ . \tag{A19}$$

For the triple-quadrupole potential,

$$\begin{aligned} K(1;[1]) = \tfrac{1}{4} R^{-9} s^{-9} [&-35 s^{12} + 18(5R^2 + 7) s^{10} - 15(3R^4 + 6R^2 + 7) s^8 \\ &- 4(5R^6 + 9R^4 + 15R^2 + 35) s^6 - 9(5R^6 + 9R^4 + 15R^2 \\ &+ 35)(R^2 - 1) s^4 + 30(3R^4 + 6R^2 + 7)(R^2 - 1)^3 s^2 \\ &- 7(5R^2 + 7)(R^2 - 1)^5] + L \ , \end{aligned} \tag{A20}$$

which on substitution in (A18) and (A19) and integration leads to

$$\mathrm{II}(R;[1,1]) = 0 \tag{A21}$$

and

$$\mathrm{II}'(R;[1,1]) = \tfrac{1}{4}(5R^3 - 36R + 48R^{-1} + 64R^{-3}) \ . \tag{A22}$$

As required by the defining relations (A6) and (A7), $\mathrm{II}(R;[1,1])$ and $\mathrm{II}'(R;[1,1])$ are continuous at $R = 2$. Hence, we are finally able to reduce (A11) to

$$J_0 = 8\pi^2 \int_1^2 \mathrm{II}'(R;[1,1]) R\,dR \ , \tag{A23}$$

which with the help of (A22) leads to

$$J_0 = 54\pi^2 = 532.9586 \tag{A24}$$

(It seems pertinent to comment here that (A21) is true not only for triple quadrupoles but for all other combination of dipoles and quadrupoles, except for the triple-dipole term!)

The extension of these arguments to calculate J_1, J_2, J_3, etc., is tedious but straightforward, if we make full use of (A15), (A16), (A21), and (A22). One easily sees that

$$J_1 = 24\pi^2 \int_1^2 \Pi'(R;[1,1])g_1(R)RdR \;, \tag{A25}$$

where the factor 3 in $24\pi^2$ comes from the three ways in which a g_1 bond can be drawn parallel to the sides of a triangle. Since it is known that

$$\begin{aligned} g_1(R) &= \tfrac{4}{3}\pi(1 - \tfrac{3}{4}R + \tfrac{1}{16}R^3) \;, && R \le 2 \\ &= 0 \;, && R \ge 2 \end{aligned} \tag{A26}$$

we find that

$$J_1 = (\tfrac{4923}{16} - 384 \ln 2)\pi^3 = 1287.349 \;. \tag{A27}$$

In extending the above argument to J_2 and J_3, we also make use of the fact that $g_2(R) = 0$ for $R > 3$. The results for ***triple quadrupoles*** are

$$\frac{J_2}{24\pi^2} = \int_1^2 \Pi'(R;[1,1])g_2(R)RdR + \int_1^2 \Pi'(R;[g_1(s),1])g_1(R)RdR \tag{A28}$$

and

$$\begin{aligned} \frac{J_3}{24\pi^2} = {} & 2\int_1^2 \Pi'(R;[g_1(s),1])g_2(R)RdR \\ & + 2\int_2^3 \Pi(R;[g_1(s),1])g_2(R)RdR \\ & + \int_1^2 \Pi'(R;[1,1])g_3(R)RdR \\ & + \frac{1}{3}\int_1^2 \Pi'(R;[g_1(s),g_1(r)])g_1(R)RdR \;. \end{aligned} \tag{A29}$$

TABLE VI. Summary of integrals which contribute to J_2 and J_3 using the exact and Percus–Yevick $g_2(R)$ and $g_3(R)$ coefficients in the density expansion of the pair correlation function $g(R)$.

J_2	
$24\pi^2\int_1^2 \Pi'(R;[1,1])g_2(R)RdR$	$24\pi^2\int_1^2 \Pi'(R;[g_1(s),1])g_1(R)RdR$
415.308 (exact) 329.324 (PY)	1118.688 (exact and PY)
J_3	
$48\pi^2\int_1^2 \Pi'(R;[g_1(s),1])g_2(R)RdR$	$48\pi^2\int_2^3 \Pi(R;[g_1(s),1])g_2(R)RdR$
879.371 (exact) 724.662 (PY)	6.3863 (exact and PY)[a]
$24\pi^2\int_1^2 \Pi'(R;[1,1])g_3(R)Rdr$	$8\pi^2\int_1^2 \Pi'(R;[g_1(s),g_1(r)])g_1(R)RdR$
−120.023 (exact) −50.326 (PY)	344.932 (exact and PY)

[a] Numerical tabulations[23] of the exact and PY $g_2(R)$ *between* $R = 2$ and 3 are identical.

The calculation of the kernels $\Pi'(R;[g_1(s),1])$, etc., in (A29) for a hard-sphere system requires a great deal of tedious algebra, but is otherwise not very difficult. From (A7) we have

$$\Pi'(R;[g_1(s),1]) = \int_1^{R+1} \{K(R+s;[1]) - K(1,[1])\}g_1^{\mathrm{HS}}(s)sds \quad (1 \le R \le 2) \;, \tag{A30}$$

in which the upper limit of integration can be replaced by 2 since $g_1^{\mathrm{HS}}(s) = 0$ for $s \ge 2$. Making use of (A14), (A20), and (A26) we find

$$\begin{aligned} \Pi'(R;[g_1(s),1]) = \pi\{ & \tfrac{1195}{3072}R^3 - \tfrac{1353}{512}R + (\tfrac{2627}{1024} + \tfrac{15}{16}\ln 2)R^{-1} \\ & + (\tfrac{4967}{768} - \tfrac{17}{4}\ln 2)R^{-3} + (\tfrac{8127}{1024} - \tfrac{63}{8}\ln 2)R^{-5} \\ & + (\tfrac{3375}{512} - \tfrac{45}{4}\ln 2)R^{-7} + (\tfrac{29757}{1024} - \tfrac{665}{16}\ln 2)R^{-9}\} \;. \end{aligned} \tag{A31}$$

Similarly from (A6) we have

$$\Pi(R;[g_1(s),1]) = \int_{R-1}^{R+1} \{K(R+s;[1]) - K(1;[1])\}g_1(s)sds \;, \tag{A32}$$

where again the upper limit of integration can be replaced by 2 for a hard-sphere system. On carrying out this integration we obtain

$$\begin{aligned} \Pi(R;[g_1(s),1]) = \pi\Bigg\{ & \frac{-5}{3072}R^3 + \frac{39}{512}R - \left[\frac{277}{1024} - \frac{15}{16}\ln\left(\frac{2}{R-1}\right)\right]R^{-1} \\ & - \frac{15}{16}R^{-2} - \left[\frac{1937}{768} + \frac{17}{4}\ln\left(\frac{2}{R-1}\right)\right]R^{-3} + \frac{63}{16}R^{-4} \\ & + \left[\frac{8143}{1024} - \frac{63}{8}\ln\left(\frac{2}{R-1}\right)\right]R^{-5} + \frac{437}{48}R^{-6} \\ & + \left[\frac{5823}{512} - \frac{45}{4}\ln\left(\frac{2}{R-1}\right)\right]R^{-7} + \frac{409}{16}R^{-8} \\ & + \left[\frac{13373}{1024} - \frac{665}{16}\ln\left(\frac{2}{R-1}\right)\right]R^{-9} \\ & - 16(R-1)^{-1}R^{-9}\Bigg\} \;. \end{aligned} \tag{A33}$$

A check on these expressions is provided by the requirement that $\Pi'(R;[g_1(s),1])$ and $\Pi(R;[g_1(s),1])$ are exactly equal at $R = 2$. For the last kernel

$$\Pi'(R;[g_1(s),g_1(r)]) = \int_1^{R+1} sg_1(s)ds \int_1^{R+s} rW'_{\mathrm{TQ}}(R,S,r)g_1(r)dr \;, \tag{A34}$$

each upper limit of integration can be replaced by 2 for a hard-sphere system. Then by going through the same routine algebra as before, we have

$$\begin{aligned} \Pi'(R;[g_1(s),g_1(r)]) = \pi^2\{ & \tfrac{285605}{2359296}R^3 - \tfrac{12667}{16384}R + (\tfrac{10817}{24576} + \tfrac{1195}{2048}\ln 2)R^{-1} \\ & + (\tfrac{23341}{9216} - \tfrac{259}{96}\ln 2)R^{-3} + (\tfrac{40653}{8192} - \tfrac{39}{8}\ln 2 + \tfrac{9}{32}(\ln 2)^2)R^{-5} \\ & + (\tfrac{-1035}{2048} + \tfrac{75}{16}\ln 2 - \tfrac{15}{2}(\ln 2)^2)R^{-7} + (\tfrac{335083}{16384} - \tfrac{20545}{384}\ln 2 \\ & + 35(\ln 2)^2)R^{-9}\} \;. \end{aligned} \tag{A35}$$

We now have all the information necessary to calculate the one-dimensional integrals in (A28) and (A29). For $g_2(R)$ and $g_3(R)$ we use the tabulations of Ree, Keeler, and McCarthy[23] and obtain the results given in Table VI by numerical integration. A few of the PY results involving $g_2(R)$ were confirmed analytically. Our final results for J_2 and J_3 are

$$J_2 = \begin{matrix} 1534.0 & \text{(exact)} \\ 1447.97 & \text{(Percus–Yevick)} \end{matrix} \tag{A36}$$

and

$$J_3 = \begin{matrix} 1110.66 & \text{(exact)} \\ 1025.65 & \text{(Percus–Yevick)} \end{matrix}, \tag{A37}$$

where the analytic result for J_2(PY) is

$$J_2(\mathrm{PY}) = \pi^4\left[\tfrac{50669883667}{88309760} - \tfrac{1552087}{1792}\ln 2 + \tfrac{345}{4}(\ln 2)^2\right] . \tag{A38}$$

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