Perturbation theory for the free energy of hard quadrupolar diatomics

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The perturbation theory for the free energy of hard spheres with an embedded quadrupole is extended to molecules with a nonspherical core. Our system consists of quadrupolar hard homonuclear diatomics. The free energy is calculated to order Q^6 in the quadrupole strength. Several expressions for hard diatomics are examined to obtain the free energy of the unperturbed system. The term of order Q^2 is calculated using recent Monte Carlo results for the reference system and it is found that it gives an important contribution to the total free energy. The Padé approximant (PA) formed for the quadrupolar hard spheres with the terms of order Q^4 and Q^6 is evaluated with an effective diameter calculated analytically using the isothermal compressibility of the hard diatomics. It is concluded that it is necessary to take into account the nonsphericity of the molecules in the calculation of the free energy in order to obtain reliable results for real systems.

I. INTRODUCTION

In recent years much effort has been devoted to the study of the effects nonspherical intermolecular interactions have on the thermodynamic properties of molecular fluids.[1-3] In order to have a realistic description, the effects of anisotropic electrostatic forces as well as those due to core nonsphericity must be taken into account, which presents difficulties that do not arise in the theories of simple spherical fluids. In the case of nonsphericity resulting from multipolar interactions there exist several successful theories which predict thermodynamic quantities with great accuracy[4-6] as shown by comparison with Monte Carlo (MC) results.[7] This is the case for polar and quadrupolar molecules which have spherical reference potentials (hard spheres[4-6] or Lennard-Jones particles[4,8,9]). Point polarizability has also been included[9] and it appears that its contribution to the Helmholtz free energy is significant although only dipole-induced dipole terms have as yet been taken into account[6,9]

The successful theories for these fluids noted above have been based on the use of a Padé approximant (PA) technique.[4,5] The PA is formed by terms of order λ^2 and λ^3 in the free energy expansion, where λ is the strength parameter for any combination of two multipoles. As Larsen, Rasaiah, and Stell have discussed,[6] all terms of order λ are zero when a spherical reference system is used. This is not true when a nonspherical reference potential is considered, and these terms can contribute substantially to the free energy.[5,10]

In dealing with the short-range anisotropic forces which arise from repulsive core interactions, several alternative approaches have been used.[11,12] Here we shall employ a so-called atom–atom potential[13]; in our case, fused hard spheres forming a homonuclear diatomic molecule with an embedded point quadrupole. The molecular pair potential is represented by the sum of the central potentials between interaction sites within the molecule, i.e.,

$$u(r,\Omega)=\sum_{ij}u(r_{ij}/\sigma_{ij}) , \tag{1.1}$$

where $u(r_{ij}/\sigma_{ij})$ represents the central potential, r is the distance between the centers of the molecule, and Ω is the solid angle. When σ_{ij} is the same for all the atoms, the molecule is homonuclear. There are computer simulations for this model[14,15] which have enabled us to obtain the pair correlation function in a quasiexact way, thus making it possible to use a nonspherical reference potential in the calculation of thermodynamic functions and angular correlation parameters which appear in the expression for several physical quantities (e.g., dielectric constant and Rayleigh factor).[16]

The formalisms currently used to treat systems of anisotropic molecules are extensions of those developed for simple liquids. An example is Chandler's integral equation for the reference interaction site model (RISM),[17] which can be considered an extension of the Percus Yevick (PY)[18] equation devised to deal with hard nonspherical molecules. While not as accurate as the PY equation for hard spheres it gives results for atom-atom distribution functions which agree well with the MC simulations[19] (although its thermodynamic predictions, while not yet subject to exhaustive tests, appear much less promising[18,20]). Several perturbation schemes have been suggested to relate the short-range anisotropy to a spherical core potential with the anisotropy taken into account in various ways as a perturbation to a spherical reference system.[20,21] Some workers[22] have employed the blip method[23] to relate the properties of the distribution function of the spherical fluid

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to those of linear molecules. This method becomes less accurate as the nonsphericity of the molecules increases and it involves a large amount of computation. It appears unlikely that one can obtain accurate thermodynamic quantities (not to mention correlation functions) for hard-core particles that are markedly nonspherical using a perturbation theory with a spherical reference potential as the basis of the computation.

Since the reference interaction site model (RISM) and the associated RISM approximation for that model[17] offers a successful and extremely useful treatment of the structure of molecular fluids, it is natural to consider a thermodynamic perturbation theory that uses the hard fused-sphere polyatomic fluid of the RISM as a reference system. That is our purpose here. Perhaps the most straightforward way of doing this that promises to yield high accuracy would be to expand in powers of λ and form a Padé approximant that has the desired saturation properties at large λ. The terms beyond the linear term in λ, which have been set down in detail by Sandler,[10] appear prohibitively difficult to compute however. For this reason Rasaiah, Larsen, and Stell (RLS)[5] have suggested the alternative strategy of computing the sum of the reference term and linear term in λ as accurately as possible and appending to it a Padé approximant of the sum of higher order terms, which is computed through the use of an effective spherically symmetry reference potential. In our case here that will be a hard-sphere potential with an effective diameter.

In this paper we present the calculation of the free energy for the model of a homonuclear fused-sphere diatomic molecule with an embedded point quadrupole. Our approximation for the free energy per particle excess to the ideal gas result $\beta\Delta f = \beta\Delta F/N$, is given by

$$\beta\Delta f = \beta\Delta f_0 + \beta\Delta f_1 Q^2 + \beta\Delta f^P \, , \qquad (1.2)$$

where β is $1/kT$, $\beta\Delta f_0$ and $\beta\Delta f_1$ are the terms of order Q^0 and Q^2, respectively, and $\beta\Delta f^P$ is the PA:

$$\beta\Delta f^P = \beta\Delta f_2 Q^4 [1 - \beta(\Delta f_{2,2} + \Delta f_3)Q^6/\beta\Delta f_2 Q^4]^{-1} \qquad (1.3)$$

with $\beta\Delta f_2$ and $(\beta\Delta f_{2,2} + \beta\Delta f_3)$ the terms of order Q^4 and Q^6, respectively, and Q the quadrupole moment. This is the expression suggested by RLS[5] for this model, but those workers had no reliable means of evaluating the right-hand side of Eq. (1.2), and could only give estimates of the terms there, based on previous estimates made by Sandler for $\beta\Delta f_0$ and $\beta\Delta f_1 Q^2$. In this paper we consider the terms of Eq. (1.2) in quantitative detail.

For the term of order zero in the free energy we use the new equation of state given for hard diatomics by Nezbeda.[24] The term of order λ which appears with the nonspherical reference system is evaluated explicitly by means of the recent MC results for the correlation function of hard homonuclear diatomics.[14] For the PA, the expressions given by RLS are employed with an effective diameter obtained by using the isothermal compressibility of the hard diatomics. An analytical expression for the effective diameter is obtained when the equivalent hard sphere system is treated by the PY theory. We limit our study of the free energy to densities $\rho^* = \rho\sigma^3$ not higher than 0.6, where σ is the diameter of an atom and ρ is the number density. This is due to the fact that the MC simulations are given only for this range of densities. In Sec. II we establish the formulas for the different terms in the expansion and discuss the approximation involved. We obtain also an expression for the effective diameter and comment on the alternatives in the use of this formula. In Sec. III we present the numerical results and compare them with those obtained in other theories. In Sec. IV we discuss briefly our results and possible extensions to include other interactions.

If one uses the best available polar moments and polarizabilities for molecular fluids to fix the strength of the first few multipole terms at large molecular separation r_{12} but neglects all higher terms as we do here, one might expect the resulting pair potential to be a poor representation of the actual potential at small r_{12} (i.e., close to the hard-core region) where a multipolar expansion is at its worst. To explore this question we intend to extend our computations to perturbing terms of multipole symmetry tempered at small r_{12} with parameterized damping functions. Varying the parameters will enable us to assess the relative sensitivity of the thermodynamic results upon the small-r contributions of the multipole terms and also quite possibly to approach certain real potentials more closely through the use of appropriately chosen parameter values. Until such a study is made, it is probably premature for us to try to directly associate the results of our model computations with those for any real molecule. On the other hand, it seems likely that a simple extension of the model studied here (with a quadrupole term appropriately tempered for small r if necessary, an added dispersion term, and a judiciously chosen effective Q) will prove useful in the study of simple diatomics such as N_2.

II. PERTURBATION THEORY FOR THE HELMHOLTZ FREE ENERGY OF HARD HOMONUCLEAR DIATOMICS

We consider a system formed by hard homonuclear diatomics (HHD) with an embedded point quadrupole. The molecule i is characterized by a position vector $\bar{r}$, and orientation vector $\Omega_i \equiv (\theta_i, \phi_i)$, where θ_i is the polar angle an ϕ is the azimuthal coordinate. Each atom of diameter σ in molecule i interacts with other atom in molecule j with a potential

$$u(r_{ab}) = \begin{Bmatrix} \infty \\ 0 \end{Bmatrix} \quad \begin{matrix} r_{ab} < \sigma \\ r_{ab} > \sigma \, , \end{matrix} \qquad (2.1)$$

where r_{ab} is the atom-atom distance. The quadrupolar interaction is given by

$$u^{QQ}(r, \Omega) = \frac{3Q^2}{4r^5} \{1 - 5(\cos^2\theta_1 + \cos^2\theta_2) - 15\cos^2\theta_1\cos^2\theta_2 + 2[\sin\theta_1\sin\theta_2\cos(\phi_1 - \phi_2) - 4\cos\theta_1\cos\theta_2]^2\} \, , \qquad (2.2)$$

where r is the distance between molecular centers. The distance between the centers of the atoms in a molecule is $L^* = L/\sigma$. As mentioned in Sec. I, Sandler has expanded the free energy in powers of Q^2 and obtained the expression

$$\beta\Delta f=\beta\Delta f_0+\beta\Delta f_1Q^2+\beta\Delta f_2Q^4+\beta(\Delta f_{2,2}+\Delta f_3)Q^6\ , \qquad (2.3)$$

where Δf_2, $\Delta f_{2,2}$, and Δf_3 are intractably difficult to compute without further approximation, and where, even if computed exactly, Eq. (2.3) can only expected to yield as it stands accurate results for rather low Q. To cope with both these difficulties RLS suggested (i) the replacement of the true reference system by an effective hard-sphere reference system in the computation of Δf_2, $\Delta f_{2,2}$, and Δf_3, and (ii) the replacement of the Q^4 and Q^6 terms by the $\beta\Delta f^P$ of Eq. (1.3) using the Δf_2, $\Delta f_{2,2}$, and Δf_3 so computed, thus capturing the saturation effect which causes the free energy to behave more and more linearly in Q^2 as Q increases.

There are several alternative expressions which can be used for the free energy $\beta\Delta f_0$ of a homonuclear diatomic system. The scaled particle theory (SPT)[25] plays a central role in the calculation of the equation of state for nonspherical particles. Originally,[25] it was used to obtain the pressure of a hard-sphere system and later it was extended by Gibbons[26] to cover convex molecules of arbitrary shape. Boublik[27] has modified Gibbons equation by adding an extra term and obtains the formula

$$\beta P/\rho=[1+(\gamma-2)y+(1-\gamma-\gamma^2/3)y^2-(\gamma^2/3)y^3](1-y)^{-3}\ , \qquad (2.4)$$

where

$$y=\rho V$$

with V the molecular volume, and

$$\gamma=RS/V \qquad (2.5)$$

with R the mean radius and S the surface area of the molecule. The Boublik expression reduces to the Carnahan–Starling[28] equation when $\gamma=1$. Rigby[29] has suggested how to apply these formulas to nonconvex particles. Using the exact Isihara expression[30] for the second virial coefficient of hard dumbbells, one can fit γ from the equation

$$B_2=\tfrac{1}{4}(1+\gamma) \qquad (2.6)$$

and use its new value in the Boublik or Gibbons formulas. If we integrate Boublik's equation of state we get for the free energy

$$\beta\Delta f_0^B=\frac{(2\gamma+2)y+(\gamma^2/9-2\gamma-1)y^2}{2(1-\gamma/3)}-(1-\gamma^2/9)\ln(1-y)\ . \qquad (2.7)$$

Very recently, Nezbeda[24] has proposed an equation of state based on the RISM for HHD. This is given by

$$\beta P/\rho=\frac{1}{(1-y)}+\frac{ay}{(1-y)^2}+\frac{by^2}{(1-y)^3} \qquad (2.8)$$

with

$$a=\frac{(9+13.5L^*+6L^{*2}+0.5L^{*4})}{3(1+1.5L^*-0.5L^{*3})}\ ;$$

$$b=\frac{(3+4.5L^*+2L^{*2}-0.5L^{*4})^2}{3(1+1.5L^*-0.5L^{*3})^2}\ .$$

When compared with MC simulations[20] it shows very good agreement, especially in the range of reduced densities $\rho^*=0.2$ to 0.6 which we examine and exhibit in Table I. Integrating Eq. (2.8) we obtain for the free energy

$$\beta\Delta f_0^N=\frac{a}{(1-y)}+\frac{b(y-\frac{1}{2})}{(1-y)^2}+\ln\left(\frac{y}{1-y}\right)\ . \qquad (2.9)$$

TABLE I. Comparison of $(P/\rho kT)$ (Nezbeda) with MC results for hard homonuclear diatomics.[a]

$L^*=0.6$	y	$(P/\rho kT)_N$	$(P/\rho kT)_{MC}$
	0.1047	1.65	1.64
	0.2094	2.84	2.84
	0.3141	5.14	5.02
	0.4188	9.92	9.24

[a] Values taken from Table II in Ref. 24.

Alternative to these analytical formulas, use of "effective" hard-sphere diameters could be made employing the blip method along with the PY or CS equations of state. However, as discussed in Ref. 24, the Nezbeda equation appears to give good results and has the great advantage of its analyticity.

The term $\beta\Delta f_1Q^2$ which appears when a nonspherical reference system is used, is given by:

$$\beta\Delta f_1Q^2=\frac{\beta\rho^2}{2N}\int d1d2g_{\mathrm{HHD}}(1,2)u^{QQ}(1,2)\ . \qquad (2.10)$$

In the above expression, $g_{\mathrm{HHD}}(1,2)$ is the pair distribution function (pdf) of HHD and $di\equiv d\bar{r}\ d\Omega_i$.

A way to handle this integral is to make an expansion of the pdf in spherical harmonics.[10] Despite the poor convergence of this expansion and the attendant questions concerning whether a truncated series can reasonably represent the total function,[14] several quantities of interest can be unambiguously expressed as integrals over the coefficients of this expansion. If we know these coefficients, either from computer experiments or from some model, we are able to calculate thermodynamics functions, among them $\beta\Delta f_1Q^2$.

The expansion of an arbitrary function $X(r_{12},\Omega_1,\Omega_2)$ of the configuration of linear molecules can be written as

$$X(r_{12},\Omega_1,\Omega_2)=4\pi\sum_{ll'm}X_{ll'm}(r)Y_{lm}(\theta_1,\varphi_1)Y_{l'-m}(\theta_2,\varphi_2)\ , \qquad (2.11)$$

where $Y_{lm}(\theta_i,\phi_i)$ are spherical harmonics and the coefficients in the expansion depend only on the distance between molecular centers. If we expand the pdf and take into account that for the quadrupole–quadrupole interactions the only coefficients which are not zero are $u_{220}(r)$, $u_{221}(r)$, and $u_{222}(r)$, Eq. (2.10) takes the form,

$$\beta\Delta f_1Q^2=\frac{4\pi}{5}\beta\rho^*\frac{Q^2}{\sigma^5}\int_0^\infty[3g_{220}^{\mathrm{HHD}}(r)-4g_{221}^{\mathrm{HHD}}(r)+g_{222}^{\mathrm{HHD}}(r)]\frac{dr^*}{r^{*3}}\ . \qquad (2.12)$$

Although there is no available approximation theory for the $g_{ll'm}(r)$, MC simulations[14] have been done recently for HHD. Their data are presented in terms of the

$g_{ll'm}(r)$ and therefore it is an easy task to make the numerical integration and obtain $\beta\Delta f_1 Q^2$. The blip technique has also been used for this problem[5,10] and we will show a comparison with it in the next section.

We can thus calculate the first-order term in a quasiexact way if we have very precise MC data as will be discussed in Sec. III. We turn next to the terms of order Q^4 and higher, using the formulation given by RLS[5] for quadrupolar hard spheres, but with an effective diameter calculated in our own way, as will be described below.

The $\beta\Delta f_2 Q^4$, $\beta\Delta f_{2,2} Q^6$ are given by integrals over the pair distribution function and the two body quadrupole–quadrupole term of $\mathcal{O}(Q^4)$ and $\mathcal{O}(Q^6)$, respectively, while $\beta\Delta f_3 Q^6$ involves an integration over the three particle correlation function and the three-body triple quadrupole potential. We refer to Refs. 5 and 6 for detailed analysis of these terms. They are functions of $x=\rho d^3$ and $t=kTd^5/Q^2$, where d is an effective hard-sphere diameter, which we determine according to our own prescription rather than follow RLS in the use of Sandler's[10] blip-function calculation. In order to facilitate controlled comparison with the RLS results, our method of calculating Δf_2, $\Delta f_{2,2}$, and Δf_3 is otherwise identical to theirs. Their expressions are[5]

$$\beta\Delta f_2 Q^4 t^2 = -8.7965\, I_{10}^{\mathrm{HS}}(x)$$

$$I_{10}^{\mathrm{HS}}(x) = \tfrac{1}{7} + \frac{0.1397x + 0.0308x^2}{1 - 0.37402x} \tag{2.13}$$

$$\beta\Delta f_{2,2} Q^6 t^3 = 1.8465\, I_{15}^{\mathrm{HS}}(x)$$

$$I_{15}^{\mathrm{HS}}(x) = \tfrac{1}{12} + \frac{0.0926x}{1 - 0.73710x + 0.14494x^2} \tag{2.14}$$

$$\beta\Delta f_3 Q^6 t^3 = 0.0833x^2 + 0.2011x^3 + 0.2262x^4 + 0.1603x^5 + 0.0872x^6 + 0.0039x^7 \,. \tag{2.15}$$

Reference 6 gives polynomial expressions for Δf_2 and $\Delta f_{2,2}$ that are negligibly different numerically but somewhat more conveniently manipulated, as well as a very slightly more accurate polynomial for Δf_3. We recommend the use of these improvements in future work but note that their use here makes no perceptible changes on the scale of our figures. These alternative expressions are[6]

$$I_{10}^{\mathrm{HS}} = \tfrac{1}{7} + 0.1397x + 0.0826x^2 + 0.0310x^3 + 0.0124x^4 - 0.0007x^5 \tag{2.16}$$

$$I_{15}^{\mathrm{HS}} = \tfrac{1}{12} + 0.0926x + 0.0681x^2 + 0.0359x^3 + 0.0152x^4 + 0.0117x^5 \tag{2.17}$$

$$\beta\Delta f_3 Q^6 t^3 = 0.0833x^2 + 0.2011x^3 + 0.2262x^4 + 0.1604x^5 + 0.0951x^6 - 0.0032x^7 \,. \tag{2.18}$$

We obtain our values of an effective diameter by equating the isothermal compressibility K_T of the HHD and an effective hard-sphere fluid:

$$(\rho kTK_T)_{\mathrm{HHD}} = (\rho kTK_T)_{\mathrm{HS}} \,. \tag{2.19}$$

Note that this equation can be rewritten as

$$\int_0^d \{\exp[-\beta u_{\mathrm{HHD}}(1,2)]\, y_{\mathrm{HHD}}(1,2) - \exp[-\beta u_{\mathrm{HS}}(r)]\, y_{\mathrm{HS}}(r)\}\, d\mathbf{r}\, \frac{d\Omega}{4\pi} = 0 \,, \tag{2.20}$$

where

$$y(1,2) = g(1,2)\exp[-\beta u(1,2)] \tag{2.21}$$

since

$$(\rho kTK_T)_{\mathrm{HHD}} = 1 + 4\pi\rho^* \int_0^\infty (g_{000}^{\mathrm{HHD}}(r) - 1)\, r^{*2}\, dr^* \tag{2.22a}$$

and

$$(\rho kTK_T)_{\mathrm{HS}} = 1 + 4\pi\rho^* \int_0^\infty (g^{\mathrm{HS}}(r) - 1) r^{*2}\, dr^* \,, \tag{2.22b}$$

where

$$g_{000}^{\mathrm{HHD}}(r) = \int g_{\mathrm{HHD}}(1,2)\, d\Omega/4\pi \,. \tag{2.23}$$

If

$$y_{\mathrm{HHD}}(1,2) \simeq y_{\mathrm{HS}}(r) \tag{2.24}$$

one then obtains the blip expression for the effective diameter

$$\int_0^d (\exp[-\beta u_{\mathrm{HHD}}(1,2)] - \exp[-\beta u_{\mathrm{HS}}(r)]) \times y_{\mathrm{HS}}(r)\, d\mathbf{r}\, \frac{d\Omega}{4\pi} = 0 \,. \tag{2.25}$$

Equations (2.19) and (2.25) give similar results when the density is small but at larger densities the predicted diameter will be quite different.

If we take the PY isothermal compressibility for hard spheres, Eq. (2.22b) is given by

$$(\rho kTK_T)_{\mathrm{HS}} = \frac{(1-\eta)^4}{(1+2\eta)^2} \,, \tag{2.26}$$

where $c=\pi/6\rho d^3$. This is a very good approximation, especially for the range of densities we are dealing with in this paper. Using Eqs. (2.26) and (2.19) we obtain the equation

$$\alpha^4 - 4\alpha^3 + (6-4c)\alpha^2 - 4(1+c)\alpha + (1-c) = 0 \,, \tag{2.27}$$

where $c=(\rho kTK_T)_{\mathrm{HHD}}$, $\alpha=\eta^*\nu$, $\eta^*=\pi/6\rho\sigma^3$, and $\nu=(d/\sigma)^3$. Solving this equation we have that ν is given by

$$\nu = \eta^{*-1}(1 + \sqrt{c} - \sqrt{c + 3\sqrt{c}}\,) \,. \tag{2.28}$$

Therefore an effective diameter can be calculated analytically if we know the isothermal compressibility for the nonspherical system. This in turn, can be derived from an analytical equation of state or from knowledge of $g_{000}^{\mathrm{HHD}}(r)$ from MC data. As we shall see, only the first alternative is quantitatively useful.

III. NUMERICAL RESULTS

We make the computations for two values of the parameters L^*, σ, and Q which correspond roughly to nitrogen and chlorine. These values are shown in Table II. This choice allows us to make a comparison with other results in the literature. We examine each term in the expansion and give its contribution to the total free energy.

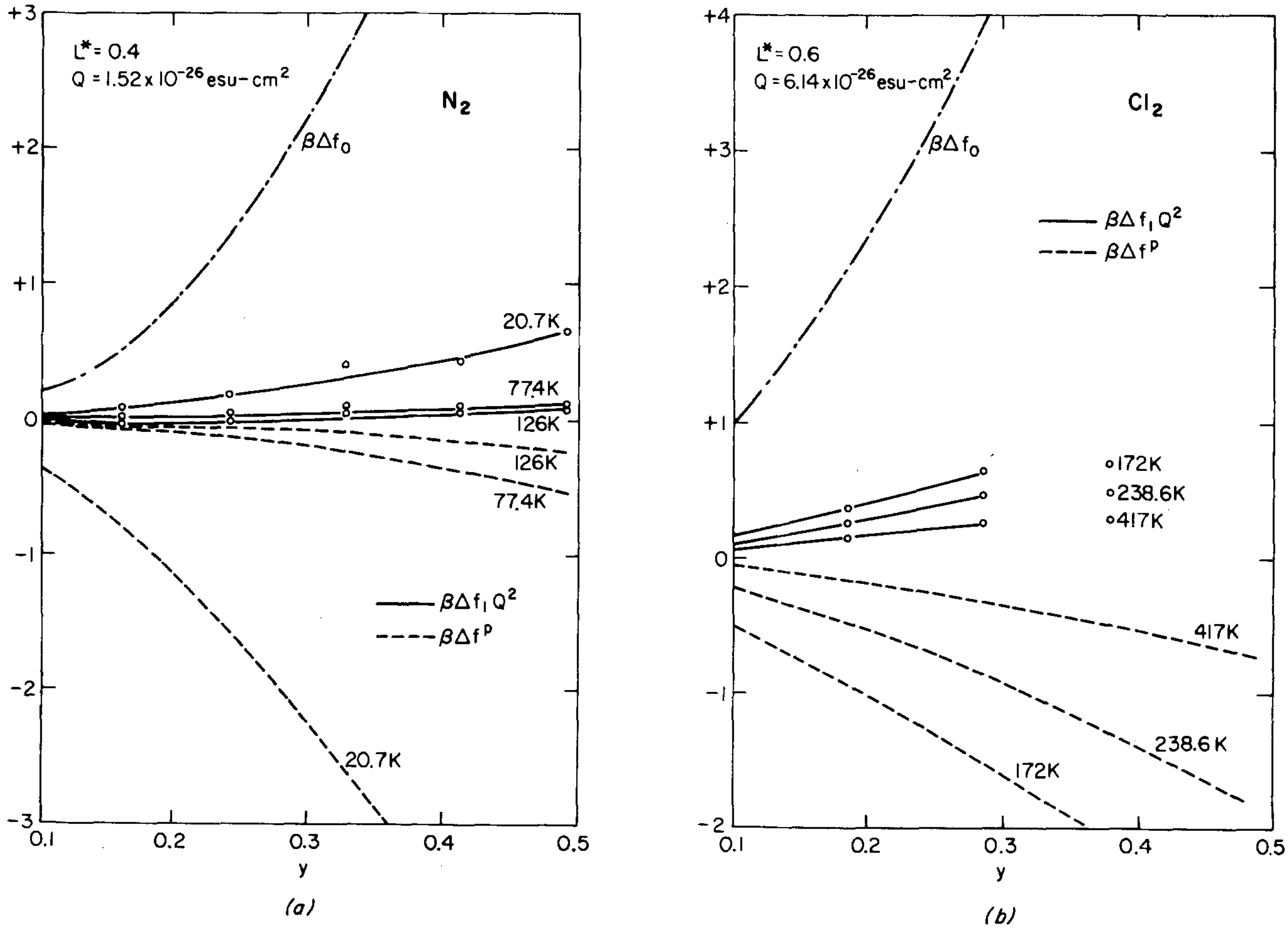
TABLE II. Parameters for the HHD model.

	L^*	σ(Å)	Q(esu cm^2)
N_2	0.4	3.0	-0.52×10^{-26}
Cl_2	0.6	3.6	6.14×10^{-26}

The results obtained for $\beta\Delta f_0$ using the Rigby–Boublik (RB) [Eq. (2.7)] and Nezbeda [Eq. (2.9)] formulas are shown in Table III. Also shown are the Sandler blip results.[10] It can be seen that Nezbeda equation predicts a larger free energy at higher densities than the other two expressions. At low density it gives a smaller value of $\beta\Delta f_0$. Nezbeda's equation for the pressure is in better agreement with computer simulations[31] and therefore it seems reasonable to use the $\beta\Delta f_0$ given by Eq. (2.9). In Fig. 1, $\beta\Delta f_0$ is plotted against y for each model and the above comments can be applied when we compare this curve with the one showed by RLS using an effective diameter with the CS equation. The contribution of $O(Q^2)$ was calculated using MC results[14] for the $g^{\text{HHD}}_{ll'm}(r)$ an integration Eq. (2.12) with Simpson's rule. The characteristics of the MC data are summarized in Table IV and the results for the free energy term $\beta\Delta f_1 Q^2$ are shown in Table V for temperatures corresponding to the critical point, boiling point, and melting point of each substance. One observes that for the model with $L^*=0.4$ at $\rho^*=0.6$ the two sets of MC data give free energy values which differ ~20%. As the contribution to the free energy by integrating $\beta\Delta f_1 Q^2$ in the interval $r^*=3$ to $r^*=4$ is very small, this discrepancy indicates that already at intermediate densities ($\rho^*\sim0.5$),

TABLE III. Comparison of the several expressions for the excess free energy $\beta\Delta f_0$ of hard diatomics.

ρ^*	$y=\rho V$	Rigby Eq. (2.7)[29]	Nezbeda Eq. (2.9)[24]	Blip[10]
		$L^*=0.4$ (N_2)		
0.2	0.164	0.813	0.511	0.7643
0.3	0.246	1.394	1.572	
0.4	0.328	2.139	2.749	3.0277
0.5	0.411	3.211	4.233	
0.6	0.493	4.727	6.305	5.2541
		$L^*=0.6$ (Cl_2)		
0.2	0.094	0.025	0.976	1.298
0.3	0.188	1.820	2.292	
0.4	0.282	2.950	3.905	
0.5	0.375	4.649	6.191	
0.6	0.469	6.738	9.862	6.956



(a) (b)

FIG. 1. Free energies of homonuclear hard diatomics with an embedded quadrupole according to Eq. (1.2). The parameters L^* and Q correspond to N_2 [Fig. (a)] and Cl_2 [Fig. (b)] and the temperatures are the experimental critical point, boiling point, and melting point for N_2 and Cl_2, respectively. See discussion in the text.

TABLE IV. Characteristics of the MC data for homonuclear diatomics used in the evaluation of $\beta\Delta f_1 Q^2$.

ρ^*	No. of particles	No. of configurations	Cutoff of $g_{ll'm}(r)$ in units of σ
		$L^* = 0.4$	
0.2	256	10^6	3
0.3	256	10^6	3
0.4	256	10^6	3
0.5	500	5×10^6	4
0.6	256	10^6	3
0.6	500	5×10^6	4
		$L^* = 0.6$	
0.2	256	10^6	3
0.3	256	10^6	3
0.4	256	10^6	3
0.5	256	10^6	2

the MC data must be obtained from simulations with a large number of particles and configurations. We expect this to be particularly important for the molecules that are most highly elongated (e.g., $L^* = 0.6$). At somewhat lower densities, ($\rho^* < 0.4$) the simulations with smaller samples should be reliable. However, even if we assume a decrease of 10% in the values shown in Table V, they are still larger than those obtained with the blip method,[5,10] at least for the densities studied in this paper. This shows how important is to use an accurate nonspherical pdf to obtain reliable results for the contribution of $\beta\Delta f_1 Q^2$ to the total free energy. As we mentioned before, we calculate the free energy only up to $\rho^* = 0.6$, because the lack of MC data for HHD at higher densities prevents us from making the evaluation of $\beta\Delta f_1 Q^2$ there. This term is most important at low temperatures where it is of the same order as the difference between $\beta\Delta f_0$ and $\beta\Delta f^P$.

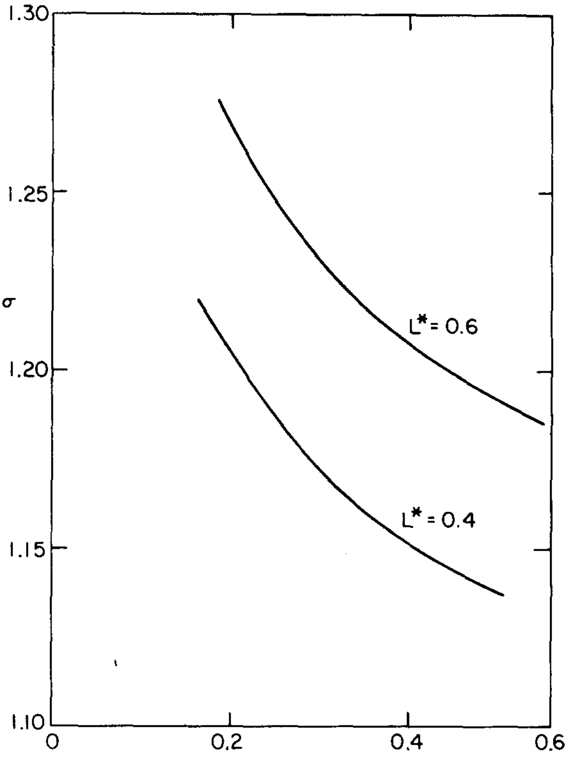


FIG. 2. Values for the effective rigid-sphere diameter d used to obtain $\beta\Delta f^P$ according to Eq. (3.1) as function of the reduced density $y = \rho V$.

To calculate the effective diameter for the Padé approximant we cannot use the MC $g_{000}^{\mathrm{HHD}}(r)$ to obtain the isothermal compressibility because we must have $g_{000}^{\mathrm{HHD}}(r)$ accurately calculated at distances much larger than 3σ or 4σ in order to avoid large uncertainties due to the factor $(g_{000}^{\mathrm{HHD}}(r) - 1)$ which appears in the integral of the compressibility. But reliable MC results are not available for $r > 4\sigma$. Therefore we make a self-consistent calculation using the equation of state given by Nezbeda. The diameter is shown in Fig. 2. When compared with the effective diameters predicted with the blip method, we notice that at low densities a larger ef-

TABLE V. Free energy for quadrupolar hard diatomics.

ρ^*	y	ρd^3	$\beta\Delta f_0^N$	$\beta\Delta f_1 Q^2$			$\beta\Delta f^P$		
					$L = 0.4$ (N_2)				
				$T = 20.7$	$T = 77.4$	$T = 126.1$	$T = 20.7$	$T = 77.4$	$T = 126$
0.2	0.1642	0.3662	0.5113	0.104	0.028	0.017	−0.8283	−0.0678	−0.0261
0.3	0.2463	0.5619	1.5717	0.210	0.056	0.035	−1.635	−0.1393	−0.0539
0.4	0.3284	0.6324	2.7486	0.433	0.116	0.071	−2.693	−0.2389	−0.0932
0.5[a]	0.4105	0.7590	4.2327	0.447	0.119	0.074	−3.987	−0.3692	−0.1451
0.6	0.4926	0.8850	6.3052	0.851	0.223	0.140	−5.506	−0.5328	−0.2112
0.6[a]	0.4926	0.8850	6.3052	0.676	0.181	0.111	−5.506	−0.5328	−0.2112
					$L = 0.6$ (Cl_2)				
				$T = 172$	$T = 238.6$	$T = 417$	$T = 172$	$T = 238.6$	$T = 417$
0.2	0.0938	0.4127	0.9760	0.158	0.114	0.065	−0.4274	−0.2300	−0.0784
0.3	0.1877	0.5665	2.2915	0.1385	0.277	0.159	−0.8836	−0.4811	−0.1663
0.4	0.2815	0.7111	3.9050	0.653	0.470	0.270	−1.508	−0.8313	−0.2917
0.5	0.3753	0.8254	6.1905	0.686	0.493	0.283	−2.302	−1.2855	−0.4585
0.6	0.4692	0.9447	9.8621	···	···	···	−3.273	−1.8511	−0.6717

[a] 500 particles.

TABLE VI. Free energy contribution of order Q^4 and Q^6 from perturbation theory and the Padé approximant for two temperatures.

y	$\beta\Delta f_2 Q^4$	$\beta\Delta f^{(6)}$	$\beta\Delta f^P$
	$T=20.7$, $L=0.4$ (N_2)		
0.164	−1.0014	−0.7921	−0.8283
0.246	−2.0924	−1.507	−1.635
0.328	−3.6619	−2.345	−2.693
0.411	−5.7835	−3.177	−3.987
0.493	−8.5499	−3.824	−5.506
	$T=172$, $L=0.6$ (Cl_2)		
0.094	−0.4876	−0.4189	−0.4274
0.188	−1.056	−0.8499	−0.8836
0.282	−1.897	−1.408	−1.508
0.375	−3.062	−2.052	−2.302
0.469	−4.617	−2.721	−3.273

fective diameter is predicted, but it diminishes faster as the density is increased. At $\rho^* \simeq 0.6$, it is about 15% smaller than the blip diameter. That indicates the same trend shown in the free energy, i. e., the blip method does not describe in a satisfactory way the correlation of nonspherical molecules at these intermediate densities.

The effective diameter thus obtained was used to calculate $\beta\Delta f_2 Q^4$ [Eq. (2.13)], $\beta\Delta f_{2,2} Q^6$ [Eq. (2.14)], and $\beta\Delta f_3 Q^6$ [Eq. (2.17)] and the PA

$$\beta\Delta f^P = \beta\Delta f_2 Q^6 \left[1 - \frac{\beta(\Delta f_{2,2} Q^4 + \Delta f_3 Q^6)}{\beta\Delta f_2 Q^4}\right]^{-1} . \tag{3.1}$$

The PA free energy is shown in Table VI and $\beta\Delta f^P$ is plotted in Fig. 1. The PA value is about 10% more negative than indicated by the cruder estimate of RLS.

It is clear that the PA must be used at lower temperatures and higher densities. This is seen from Table VI where already at $\rho^* = 0.6$ there is a large discrepancy between the PA and $\beta\Delta f^{(6)}$, where

$$\beta\Delta f^{(6)} = \beta\Delta f_2 Q^4 + \beta\Delta f_{2,2} Q^6 + \beta\Delta f_3 Q^6 . \tag{3.2}$$

At higher densities $\beta\Delta f^{(6)}$ differs noticeably from $\beta\Delta f^P$ and therefore is not able to yield satisfactory results for the total free energy if used in place of $\beta\Delta f^P$ in Eq. (1.2). On the other hand, use of only the $\beta\Delta f_2 Q^4$ term in place of $\beta\Delta f^P$ appears to yield results that are much in error, even at lower densities.

IV. CONCLUSIONS

The results obtained in the preceding sections have made clear that to have a reasonable theory for the free energy of nonspherical multipolar molecules, the Q^2 contribution must be calculated using an accurate distribution function for the reference system. Also important is a correct account of the free energy of hard diatomics. Although the Nezbeda equation gives good results for the function up to the densities we have examined in this paper, the highest of which approaches typical liquid densities, it becomes increasingly unreliable at higher densities. Thus it is probably acceptable—but just barely—as a representation of reference-system thermodynamics in the liquid state, and an expression of increased accuracy would be welcome.

Due to the complexities of the computation for higher order terms, the PA was calculated using an effective diameter. With the analytic expression used here (equating isothermal compressibilities of the HHD and the effective HS systems) our results are about 5% (higher densities) to 10% (lower densities) larger in absolute value than the preliminary free energy contribution of the PA given by RLS. There is no MC simulation for the full quadrupolar system and therefore we cannot asses in a definitive way the exactness of our results. Also, simulations for the $g_{ll'm}^{\mathrm{HHD}}(r)$ of the reference system are lacking for densities higher than $\rho^* = 0.6$. Both simulations must be made if the results appearing in this paper are to be assessed in a definitive way.

An extension of this method to other systems can be easily made if only permanent multipolar forces are considered. In particular, particles with heteronuclear hard cores can be treated with little modifications using the techniques of Ref. 6 and the dipole contribution to the free energy can be examined. The effects of polarizability can also be included using the results of Ref. 6. This will be the subject of a future study, along with the effects of moderating the multipole terms with appropriate switching functions as $r \to 0$.

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