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Upper bounds on free energies in terms of hard-sphere results

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The Gibbs–Bogoliubov inequality is used to develop a first-order perturbation theory that provides an upper bound on the free energy. Charged systems as well as a system of Lennard-Jones particles are discussed, and detailed numerical estimates of the bounds are presented.

1. INTRODUCTION

We consider here the use of a simple inequality to obtain upper bounds on the Helmholtz free energy per unit volume F of a classical statistical mechanical system in terms of the free energy and pair distribution function (radial distribution function) $g(\mathbf{r})$ of a suitable reference system at the same temperature T and density ρ. These bounds are also equal to the sum of the zeroth and first-order terms of a perturbation expansion in a strength parameter λ for the system under consideration; the unperturbed system in the perturbation theory is the reference system used in obtaining the bounds.

For a system with a Lennard-Jones (L-J) pair potential we choose a system with a hard-sphere potential as our reference system and give detailed numerical estimates of our bound, which proves to be of sufficient accuracy to provide a reasonable approximation for the free energy over a wide range of densities and temperatures.

We also discuss the bound for a system of charged particles. For this case the choice of the uncharged system as the reference system yields a bound on βF that is exact through first order in $\beta = 1/kT$ and second order in e, the electronic charge. In the case of a symmetric system of charged spheres it reduces to the statement that $F \leqslant F^{\mathrm{HS}}$, where F^{HS} is the free energy of a system of uncharged spheres at the same ρ and T. These simple upper bounds complement nicely the lower bound on F that immediately follows from Onsager's [1] well-known lower bound on the energy per particle for this model, which is $-e^2/a$ where a is the hard-sphere diameter.

The properties of a hard-sphere system are available in tabulations and expressions that are of a relatively simple form and that for many purposes can be considered exact. In particular, there are the results of Monte-Carlo and molecular-dynamical studies, as well as the Padé approximants from density expansions. In addition there are the somewhat less accurate but extremely convenient Percus–Yevick (PY) values for F and $g(\mathbf{r})$.

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In general analogous results for L-J and ionic systems lack both the accuracy and simplicity found in the hard-sphere case. However, over certain restricted ranges of density and temperature, such systems can profitably serve as reference systems for still more complicated systems. For an example we give here some numerical estimates of an upper bound on the excess free energy per unit volume F^{ex} for the model of hard spheres interacting via a square-well plus coulombic potential. The bound is in terms of the properties of charged hard spheres (the primitive model). The equilibrium properties of the latter are available from the hypernetted chain (HNC) equation which has been shown to be accurate for the range of ρ and $e^2\beta/a$ that corresponds to aqueous solutions of 1–1 electrolytes at 25°c at concentrations up to 1·0 M [2]. We compare the upper bound with an accurate estimate of the exact result for the charged hard-sphere plus square-well model that has been obtained directly from the solution of the HNC equation for this model.

For charged hard spheres, the first-order theory (in $e^2\beta/a$) of Stell and Lebowitz [3] is found to yield an upper bound on F. In the L-J case however, the theory of Barker and Henderson [4] (BH) has a term of first order (in λ, a strength parameter defined below) that cannot be guaranteed to give an upper bound on F, because of the way the repulsive core of the L-J potential is handled. It is possible that the price we pay for a first-order theory in λ that yields a rigorous bound is some loss of numerical accuracy for certain ranges of ρ and T compared to first-order BH results. We are unable to verify this by a direct thoroughgoing comparison with BH however because in giving the results of their approximate second-order theory BH have not generally separated the second-order contributions in an explicit way. Kozak and Rice [5] have already considered a general procedure for replacing the L-J potential by the sum of a hard-sphere core plus L-J tail. They use a variational scheme for choosing a sphere diameter a which is different from ours and which can in principle be applied to any approximation, F^{approx}, that is expressible in terms of a hard-sphere core and L-J tail. When it happens that F^{approx} is greater than the Lennard-Jones F for some a at a given ρ and β, their scheme picks out the a that minimizes $|F-F^{\text{approx}}|$; a drawback to their scheme is that it picks an a associated with a local maximum (not minimum) of $|F-F^{\text{approx}}|$ if it so happens that $F^{\text{approx}}<F$ over a range of a, Our scheme coincides with theirs when (and only when) F^{approx} is chosen to be the sum of zeroth and first-order terms in λ. Thus our result shows that through first order in λ, their scheme will in fact minimize $|F-F^{\text{approx}}|$.

In the treatment of Barker and Henderson, the definition of an effective hard-sphere diameter is such that for any β the hard-sphere reference expression will yield divergent results for ρ above a particular 'close-packing' ρ_{M}. In our approach, no such difficulty can arise, because of the nature of the density dependence of our effective hard-sphere diameter. This makes it possible for us to contemplate using our first-order theory to describe the entire solid phase as well as the solid–fluid transition. (BH combine their perturbation theory with a free-volume theory in order to treat the solid–fluid transition [4 (*b*)].) However, we have not attempted in this article to give numerical results for the ρ and β characteristics of the solid phase.

2. ANALYTIC EXPRESSIONS

Let the pair potential $v(\mathbf{r})$ of a one-species system whose potential energy consists of a sum of identical pair terms be written as $v(\mathbf{r})=v^0(\mathbf{r})+\lambda w(\mathbf{r})$, and let a superscript zero refer to quantities associated with the system in which $v(\mathbf{r})=v^0(\mathbf{r})$. Then our starting point can be written as the Gibbs–Bogoliubov inequality [6] on F, the Helmholtz free energy per unit volume:

$$F \leqslant F^0 + \tfrac{1}{2}\lambda\rho^2 \int g^0(\mathbf{r})w(\mathbf{r})\, d\mathbf{r}. \tag{2.1}$$

As one of us has pointed out elsewhere [7], if $v^0=v^{\mathrm{HS}}$, where $v^{\mathrm{HS}}=\infty$ for $r\leqslant a$ and 0 otherwise, with $r=|\mathbf{r}|$, and if $v^{\mathrm{LJ}}=4\epsilon[(\sigma/r)^{12}-(\sigma/r)^6]$ then (2.1) still holds despite the singular nature of $w(\mathbf{r})$ for $r<a$. One way of seeing this is to introduce $\lambda v^{>}=v^{\mathrm{LJ}}$ for $r>a$ and note that F for the potential $v^{\mathrm{HS}}+\lambda v^{>}$ is clearly less for any given β and ρ than F for v^{LJ}. If (2.1) is then applied to the case of the potential $v^{\mathrm{HS}}+\lambda v^{>}$ with $w=v^{>}$, the final result in obvious notation is:

$$F^{\mathrm{LJ}} \leqslant F^{\mathrm{HS}} + \tfrac{1}{2}\lambda\rho^2 \int g^{\mathrm{HS}} v^{>}\, d\mathbf{r}. \tag{2.2}$$

Inequality (2.2) holds for any a, so that we can choose a to minimize the right-hand side of (2.2) if a minimum proves to exist. We consider this choice numerically in §3.

In the ionic case it is necessary to think of a several-component system, in which the pair potential between two particles of species i and j with charge number z_i and z_j respectively is given by:

$$v_{ij} = v_{ij}^0 + z_i z_j (e^2/Dr), \tag{2.3}$$

where D is the dielectric constant of the solvent medium. It is conventional to work with the excess free energy per unit volume, F^{ex} rather than F. It is also convenient to begin with a fictitious damped potential:

$$v_{ij} = v_{ij}^0 + z_i z_j e^2[\exp(-\alpha r)/Dr], \quad \alpha \geqslant 0. \tag{2.4}$$

For v_{ij} given by (2.4) the analogue of (2.1) is:

$$F^{\mathrm{ex}} \leqslant F^{\mathrm{ex},0} + \tfrac{1}{2}(e^2/D) \sum_{i,j} z_i z_j \rho_i \rho_j \int g_{ij}^0 \exp(-\alpha r)/r\, d\mathbf{r}. \tag{2.5}$$

Each integral in (2.5) is finite only if $\alpha>0$, which is why we have started with (2.4) instead of (2.3). Assuming charge neutrality, so that

$$\sum_{i,j} z_i z_j \rho_i \rho_j = \Big(\sum_i z_i \rho_i\Big)^2 = 0,$$

(2.5) can be written in terms of $h_{ij}=g_{ij}-1$:

$$F^{\mathrm{ex}} \leqslant F^{\mathrm{ex},0} + \tfrac{1}{2}(e^2/D) \sum_{i,j} z_i z_j \rho_i \rho_j \int h_{ij}^0 \exp(-\alpha r)/r\, d\mathbf{r}. \tag{2.6}$$

We can now take the limit as $\alpha \to 0$. If one deals with v_{ij}^0 that have finite spatial moments of all order, the widely accepted assumption that all the spatial moments of h_{ij}^0 are also finite implies that (2.6) remains useful as $\alpha \to 0$ for such v_{ij}^0, yielding:

$$F^{\mathrm{ex}} \leqslant F^{\mathrm{ex},0} + \tfrac{1}{2}(e^2/D) \sum_{i,j} z_i z_j \rho_i \rho_j \int h_{ij}^0/r\, d\mathbf{r}. \tag{2.7}$$

The right-hand side of (2.7) is just the sum of the first two terms in the expansion of Stell and Lebowitz ([3], see their equation (2.9)). If v_{ij}^0 is the same for all ij pairs (symmetrical system) then the second term in (2.7) is identically zero and we have:

$$F^{\text{ex}} \leqslant F^{\text{ex},0} \quad \text{(symmetrical system).} \tag{2.8}$$

For arbitrary v_{ij} one can profitably introduce:

$$\begin{aligned} v_{ij}^{\text{HS}}(\mathbf{r}) &= \infty \quad \text{if} \quad r \leqslant a_{ij} \\ &= 0 \quad \text{otherwise} \end{aligned}$$

and

$$\begin{aligned} v_{ij}^{>}(\mathbf{r}) &= v_{ij} \quad \text{if} \quad r > a_{ij} \\ &= 0 \quad \text{otherwise.} \end{aligned} \tag{2.9}$$

One can show in analogy to (2.1) that

$$F^{\text{ex}} \leqslant F^{\text{ex, HS}} + \tfrac{1}{2}\lambda \sum_{i,j} \rho_i \rho_j \int g_{ij}^{\text{HS}} v_{ij}^{>} \, d\mathbf{r}. \tag{2.10}$$

One can then seek the choice of a_{ij} that will minimize the right-hand side of (2.10).

If v_{ij}^0 is already just v_{ij}^{HS} (primitive model of an ionic solution) then (2.7) already gives an upper bound for F^{ex} in terms of hard-sphere quantities. We note that the right-hand side of (2.7) is also a formally exact limiting law [3] for $\beta \to 0$ and fixed ρ_i. For any model with a hard core potential this differs from the Debye–Hückel expression, which becomes exact in the limit of fixed β as $\rho_i \to 0$. Also because (2.7) is a bound, unlike the Debye–Hückel limiting law, the limiting law as $\beta \to 0$ at fixed ρ_i must always be approached from lower values of F^{ex} and can never be crossed at any temperature. For the primitive model (2.7) provides an upper bound on F^{ex}, which compliments the lower bound on F^{ex} that follows from Onsager's lower bound on the energy per particle of a system of charged hard spheres. Onsager's bound is $-e^2/a$ for the simplest case $a_{ij} = a$, which yields immediately the bound $F^{\text{ex}} \geqslant F^{\text{ex},0} - e^2/a$ for that case. Our upper bound on F^{ex} is illustrated in figure 1. The Percus–Yevick (PY) equation for mixtures of hard-spheres was used to compute the zeroth- and first-order terms in (2.7) [8]. For the zeroth-order term, the PY compressibility equation was used:

$$\frac{F^{\text{ex, HS}}}{\rho k T} = -\ln(1-\xi_3) + \frac{18}{\pi\rho(1-\xi_3)^2}[\xi_1\xi_2(1-\xi_3) + \xi_2^3/2], \tag{2.11}$$

where

$$\left.\begin{aligned} \rho = \sum \rho_i, \qquad & \xi_1 = \frac{\pi}{6} \sum \rho_i a_i, \\ \xi_2 = \frac{\pi}{6} \sum \rho_i a_i^2, \quad & \xi_3 = \frac{\pi}{6} \sum \rho_i a_i^3 \end{aligned}\right\} \tag{2.12}$$

and a_i is the hard-sphere diameter of species i. To evaluate the term to $O(e^2/D)$, analytic expressions obtained by Friedman [9] for $\int h_{ij}^0/r \, dr$ in the PY theory for mixtures of hard spheres were used. The contributions of the term to $O(e^2/D)$ in (2.7) are also shown separately in figure 2.

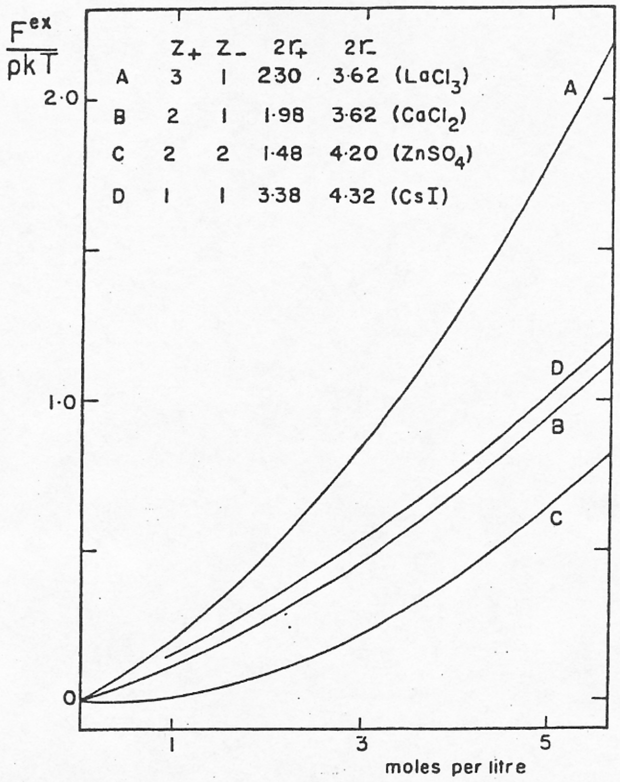

Figure 1. Upper bounds on $F^{ex}/\rho kT$ for systems of charged hard spheres. The charges, radii (Pauling) and other parameters ($D=78{\cdot}358$, $T=298{\cdot}16$) correspond to primitive model representations of aqueous solutions of $LaCl_3$, $CaCl_2$, $ZnSO_4$ and CsI at 25°c.

3. Numerical results

In this section we present numerical results for the upper bounds on the free energies of Lennard-Jones systems and the free energies of coulomb systems in terms of the properties of hard spheres. For the coulomb system the unperturbed system consists of charged hard spheres.

3.1. *Upper bounds for Lennard-Jones systems*

We choose for the reference and perturbing potentials the v^{HS} and $\lambda w(\mathbf{r})$ discussed immediately below equation (2.1) so that

$$\begin{aligned} \lambda w(r) &= v^{\mathrm{LJ}}(r)-v^{\mathrm{HS}}(r)=-\infty, \qquad r<c\sigma \\ &=4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12}-\left(\frac{\sigma}{r}\right)^{6}\right], \qquad r>c\sigma, \end{aligned} \tag{3.1}$$

where σ and ϵ are parameters in the Lennard-Jones potential and the hard-sphere diameter of the reference (unperturbed) system has been written as $c\sigma$. For any given ρ and T we obtain a least upper bound on the free energy by minimizing the right-hand side of the inequality with respect to c. We denote this optimum value of c by c_0, which in general is a function of temperature T and density ρ.

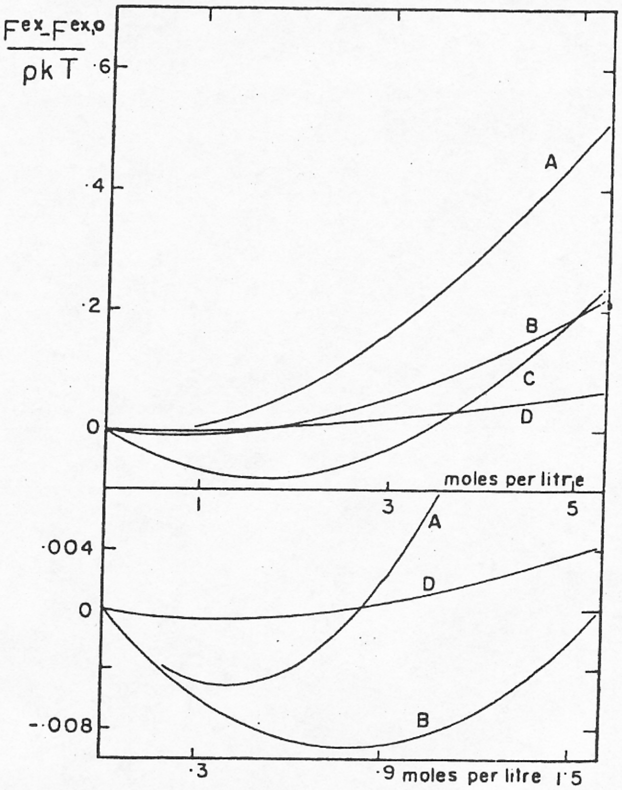

Figure 2. The contributions of the first-order term in (2·7) to the upper bound on $F^{ex}/\rho kT$ for the same systems illustrated in figure 1. The lower part of the figure is an expanded version of the upper part for three electrolytes at lower concentrations.

It is convenient to use the dimensionless variables $\rho^*=\rho\sigma^3$, $d^*=c^3\rho^*$, $T^*=kT/\epsilon$ and $y=r/c\sigma$. For the perturbation expressed by (3.1) we can write the inequality (2.2) in the form:

$$\frac{F}{\rho kT} \leqslant \psi(c, \rho^*, T^*), \tag{3.2}$$

where

$$\psi(c, \rho^*, T^*)=\frac{F^0}{\rho kT}(c^3\rho^*)+\frac{2\pi\rho^*}{c^3T^*}\left[I_{\rm A}(c^3\rho^*)+\left(\frac{1}{c^6}-1\right) I_{\rm B}(c^3\rho^*)\right] \tag{3.3}$$

and

$$I_{\rm A}(c^3\rho^*)=\int_0^\infty \left(\frac{4}{y^{12}}-\frac{4}{y^6}\right) g^0(y, c^3\rho^*)y^2\, dy, \tag{3.4}$$

$$I_{\rm B}(c^3\rho^*)=\int_0^\infty \frac{4}{y^{12}} g^0(y, c^3\rho^*)y^2\, dy. \tag{3.5}$$

The superscript zero refers to properties of the hard-sphere system.

For the radial distribution functions $g^0(y, c^3\rho^*)$ of hard spheres we use the results from the Percus–Yevick equation which have been tabulated by Throop and

Bearman [10]. More explicitly, we use the least-squares fit for I_A and I_B to a power series in d^* $(=c^3\rho^*)$ that Kozak and Rice [4] have obtained from these tables. Their equations for I_A and I_B are:

$$I_A(d^*) = -0{\cdot}9021 - 0{\cdot}3321d^* - 0{\cdot}2052d^{*2} + 0{\cdot}3558d^{*3}, \tag{3.6}$$

$$I_B(d^*) = 0{\cdot}4353 + 0{\cdot}5540d^* - 0{\cdot}0273d^{*2} + 0{\cdot}4187d^{*3}. \tag{3.7}$$

For the excess free energy of the hard spheres we have investigated three separate approximations.

(1) The Percus–Yevick compressibility equation [11, 12]:

$$\frac{F^{\mathrm{ex},0}}{\rho kT} = -\frac{3}{2} + \frac{3}{2(1-\pi d^*/6)^2} - \ln(1-\pi d^*/6). \tag{3.8}$$

(2) The Padé approximant of Hoover and Ree [13] which in our notation reads:

$$\frac{F^{\mathrm{ex},0}}{\rho kT} = 2{\cdot}094395d^* \frac{[1-0{\cdot}23195814d^* + 0{\cdot}02058281d^{*2}]}{[1-0{\cdot}88645657d^* + 0{\cdot}18120022d^{*2}]}. \tag{3.9}$$

(3) The expression for $F^{\mathrm{ex},0}$ which corresponds to a ρ expansion for $P/\rho kT$ obtained by Levesque and Verlet [14] from the first seven virial coefficients and the Monte-Carlo results at high density. In our notation their equation is equivalent to

$$\frac{F^{\mathrm{ex},0}}{\rho kT} = 2{\cdot}09439d^* + 1{\cdot}37078d^{*2} + 0{\cdot}878741d^{*3} + 0{\cdot}53058d^{*4} + 0{\cdot}31111d^{*5} + 0{\cdot}19412d^{*6} + 0{\cdot}20055d^{*8} + 0{\cdot}03550d^{*13}. \tag{3.10}$$

These approximations are compared in table 1 up to reduced densities of 1·2. At the highest densities (3.9) and (3.10) are of comparable accuracy while at reduced

d^*	$F^{\mathrm{ex},0}/\rho kT$		
	PY†	Approx. virial‡	Padé§
0·1	0·2241	0·2241	0·2241
0·2	0·4820	0·4817	0·4817
0·3	0·7820	0·7806	0·7806
0·4	1·135	1·131	1·131
0·5	1·556	1·546	1·546
0·6	2·066	2·045	2·045
0·7	2·694	2·653	2·654
0·8	3·485	3·408	3·408
0·9	4·502	4·366	4·364
1·0	5·851	5·616	5·604
1·1	7·777	7·306	7·263
1·2	1·035	0·9702	0·9576

† Percus–Yevick compressibility equation.
‡ Levesque and Verlet [14].
§ Hoover and Ree [13].

Table 1. Comparison of several approximate expressions for the excess free energy per unit volume.

densities below 0·2 all three equations are accurate to three significant figures. We use the Padé approximant in all our numerical computations except as noted below.

In the Barker and Henderson perturbation scheme the diameter of their hard-sphere reference potential is a function only of temperature. In our procedure, the diameter $c_0\sigma$ is a function of density and temperature except of course in the limit of zero density when c_0 is a function of temperature alone. Moreover, the Barker and Henderson perturbing potential is different from ours since their $\lambda w(\mathbf{r})$ is given by $v^{\mathrm{LJ}}(r)$ for $r > \sigma$ and is 0 otherwise. Despite these fundamental differences in the two schemes, the diameters of the effective hard-sphere cores behave quite similarly at small ρ^*. To see this we first obtain the functional dependence of c_0 on T^* as $\rho^* \to 0$ and compare our values for the hard-sphere diameter with Barker and Henderson's choice.

As $\rho^* \to 0$ we see from (3.4) and (3.8) that $I_{\mathrm{A}}(d^*) \to -\frac{8}{9}$ and $I_{\mathrm{B}}(d^*) \to \frac{4}{9}$ which agrees to within 0·014 of the zero density limit implied in the least-squares fit of Kozak and Rice. Using the PY equation to obtain the hard-sphere contributions to $O(d^*)$ in $F^{\mathrm{ex}}/\rho kT$, we have for small ρ^*:

$$\psi(c, \rho^*, T^*) \to \frac{2\pi d^*}{3} + \frac{2\pi d^*}{T^* c^6}\left[-\frac{12}{9} + \frac{4}{9c^6}\right]. \tag{3.11}$$

On minimizing ψ with respect to c, a quadratic expression in c^6 is obtained:

$$T^* c^{12} + 4c^6 - 4 = 0, \tag{3.12}$$

which has only one positive root given by:-

$$c_0{}^6 = \frac{2}{T^*}\left[-1 + (1+T^*)^{1/2}\right]. \tag{3.13}$$

As $T^* \to 0, c_0 \to 1$ which corresponds to a hard-sphere diameter of σ. In figure 3 the low density limit of $c_0\sigma$ is compared with the hard-sphere diameters that are appropriate to the perturbation scheme of Barker and Henderson. For small ρ^* the upper bound on the free energy follows from (3.11) on substituting c_0 for c.

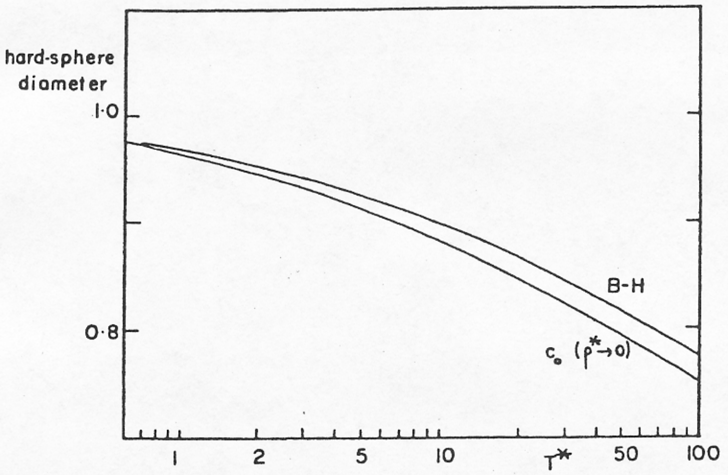

Figure 3. Comparison of the hard-sphere diameter (in units of σ) as a function of T^* in the Barker and Henderson [4] perturbation theory with c_0 of the present theory in the limit of low density.

Throughout the whole range of densities that correspond to a stable fluid, a good estimate of our upper bound on the free energy can be obtained directly from the extremum value (or values) of the function ψ given by (3.3). Numerical analysis showed only one minimum for ψ as a function of c, in contrast to two minima for the total free energy as a function of the hard-sphere diameter which Kozak and Rice obtained from their variational procedure. Our numerical estimates of the upper bounds for the free energy are compared in figure 4 with recent Monte-Carlo results of Levesque, Hansen and Verlet [14, 15] for the Lennard-Jones potential. We note in passing that the bounds obtained for the free energies of Lennard-Jones molecules also apply to the same molecules with point dipoles embedded at their centres since the term of $O(1/T)$ from the dipole contribution to $F/\rho kT$ is identically zero. To enable comparison of our bounds with the first-order terms in the perturbation theory of Barker and Henderson and others as they become available, the results for $T^* = 0{\cdot}75$, 1·35, 1·15 and 2·74 are also presented in table 2. For a given T^*, the ρ^* dependence of c_0 is also given in the same table, and it is seen that c_0 is relatively insensitive to charges in ρ^* compared to changes in T^*. In figure 5 we illustrate the sensitivity of $F/\rho kT$ to the choice of $c\sigma$. It is evident that when $c\sigma$ is within 0·01 of its optimum value $c_0\sigma$, the error in $F/\rho kT$ is small in comparison with the difference between the exact Monte-Carlo results and our bounds at the temperatures and densities that we consider.

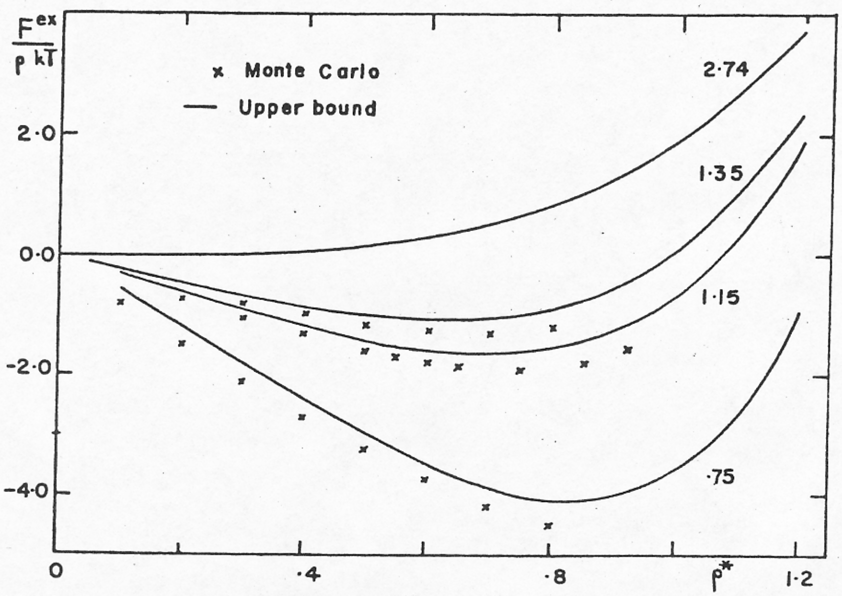

Figure 4. Comparison of the upper bounds for Lennard-Jones systems at $T^* = 2{\cdot}74$, 1·35, 1·15 and 0·75 with the Monte-Carlo results of Hansen and Verlet [15].

3.2. *Upper bounds for coulomb systems*

We have already noted that (2.7) provides a bound for coulomb systems in terms of the properties of an uncharged reference system. Here we shall consider instead the use of charged hard spheres to provide a bound for a charged system in which

ρ^*	c_0	$\frac{F}{\rho kT}$	$\frac{F}{\rho kT}$ (MC)	Percentage difference	c_0	$\frac{F}{\rho kT}$	$\frac{F}{\rho kT}$ (MC)	Percentage difference
$T^*=0\cdot75$					$T^*=1\cdot35$			
0·1	0·980	−3·869	−4·11	5·8	0·965	−3·526	−3·597	2·0
0·2	0·988	−3·764	−4·09	8·1	0·970	−3·052	−3·171	4·0
0·3	0·993	−3·965	−4·31	8·1	0·974	−2·856	−2·999	4·7
0·4	0·999	−4·287	−4·60	6·7	0·976	−2·756	−2·914	5·5
0·5	1·002	−4·650	−4·92	5·5	0·977	−2·681	−2·852	6·0
0·6	1·004	−4·988	−5·24	4·8	0·977	−2·579	−2·769	6·9
0·7	1·003	−5·232	−5·53	5·4	0·975	−2·402	−2·645	9·2
0·8	1·000	−5·300	−5·69	6·8	0·971	−2·102	−2·413	12·9
0·9	0·996	−5·099	—	—	0·967	−1·620	—	—
1·0	0·989	−4·520	—	—	0·961	−0·8946	—	—
$T^*=1\cdot15$					$T^*=2\cdot74$			
0·1	0·969	−3·600	−3·69	2·4	0·939	−3·316		
0·2	0·975	−3·205	−3·34	3·9	0·942	−2·619		
0·3	0·980	−3·094	−3·25	4·9	0·943	−2·188		
0·4	0·983	−3·084	−3·25	5·2	0·944	−1·844		
0·5	0·984	−3·100	−3·28	5·5	0·944	−1·524		
0·6	0·984	−3·088	−3·29	6·1	0·942	−1·189		
0·7	0·983	−2·997	—	—	0·939	−0·8053		
0·8	0·980	−2·768	—	—	0·935	−0·3441		
0·9	0·975	−2·337	—	—	0·931	0·2262		
1·0	0·969	−1·632	—	—	0·922	0·9426		

Table 2. Comparison of upper bounds for the free energy with Monte-Carlo results.

the perturbing potential is a square well defined by:

$$\begin{aligned} \lambda w_{ij} &= 0, \qquad && r < a_{ij} \\ &= d_{ij}, && a_{ij} < r < b_{ij} \\ &= 0, && b_{ij} < r. \end{aligned} \tag{3.14}$$

Here d_{ij} is positive for a mound and negative for a well. An upper bound for the excess free energy per unit volume is given by the multicomponent analogue of (2.1), which for this system can be written:

$$\frac{F^{\text{ex}}}{\rho kT} \leqslant \frac{F^{\text{ex},0}}{\rho kT} + \frac{2\pi}{\rho kT} \sum_{i,j} \rho_i \rho_j d_{ij} \int_{a_{ij}}^{b_{ij}} g_{ij}{}^0(r, \rho) r^2 \, dr \tag{3.15}$$

and the superscript zero in (3.15) refers to properties of the primitive model (charged hard-spheres). Accurate HNC computations for this model and for the square-well model are available. To estimate the upper bounds for F^{ex} we make use of published results [2] as well as some additional computations done at high concentrations especially for this study. Our bounds are compared with the 'exact' HNC results for the square-well model in table 3. It is obvious that the above scheme can be applied to other short-range potentials as well, and that the bounds for F^{ex} also provide the zeroth and first-order terms in a perturbation theory which uses the primitive model as the reference system. In particular,

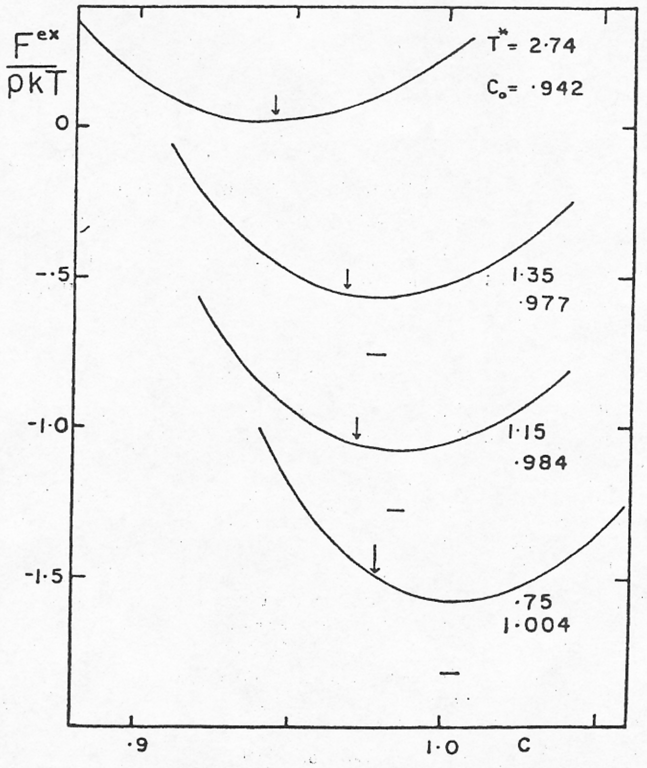

Figure 5. $F^{ex}/\rho kT$ as a function of c for a Lennard-Jones system at $\rho^* = 0{\cdot}6$ and $T^* = 2{\cdot}74$, 1·35, 1·15 and 0·75. The minimum gives the least upper bound on $F^{ex}/\rho kT$ and the optimum value of $c = c_0$. The arrows point to the hard sphere diameters (in units of σ) in Barker and Henderson's theory. They are 0·934, 0·967, 0·971 and 0·978 at $T^* = 2{\cdot}74$, 1·35, 1·15 and 0·75, respectively. The horizontal lines represent the exact Monte-Carlo results of Levesque, Hansen and Verlet at $T^* = 1{\cdot}35$, 1·15 and 0·75, respectively. The ordinate scale for $T^* = 2{\cdot}74$ has been lowered by 0·3. For $T^* = 1{\cdot}35$, 1·15 and 0·75 it has been raised by 0·5, 0·5 and 1·9 respectively.

Conc. (moles/litre)	$F^{ex}/\rho kT$		
	Upper bound	HNC	Percentage difference
0·1	−0·190	−0·192	1·0
0·4	−0·296	−0·301	1·6
0·7	−0·336	−0·343	2·0
1·0	−0·353	−0·362	2·5
1·2	−0·359	−0·368	2·4
1·6	−0·358	−0·370	3·2
2·0	−0·351	−0·363	3·3

The concentration is the stoichiometric molarity of the electrolyte. The model parameters are those necessary to obtain rough agreement with experiment for NaCl in H_2O at 25°c (Rasaiah and Friedman, 1968, *J. phys. Chem.*, 72, 3352).

Table 3. Upper bounds for the excess free energy in the charged square-well model for the parameters $a_{++} = 1{\cdot}90$, $a_{+-} = 2{\cdot}76$, $a_{--} = 3{\cdot}62$, $b_{+-} - a_{+-} = 2{\cdot}76$ Å, $d_{+-} = 0{\cdot}25kT$, $d_{++} = d_{--} = 0$.

effects due to changes in dielectric constant with distance between two ions, and other peculiarities of the short-range potential, could be investigated by this perturbation scheme.

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