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Variational limits on the Helmholtz free energy of simple fluids

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Accurate radial-distribution functions obtained from a thermodynamically consistent integral equation are used to calculate upper and lower bounds to the Helmholtz free energies of several inverse-power potential fluids and the Lennard-Jones fluid. Comparisons with results from Monte Carlo simulations indicate that the true free energies are tightly bracketed by the variational bounds. In addition, the simulations agree with the arithmetic mean of the limits near melt to within about $0.03Nk_BT$ for inverse power fluids and about $0.06Nk_BT$ for Lennard-Jones fluids. These results indicate that it is possible to obtain accurate free energies very efficiently by the variational method.

I. INTRODUCTION

Variational perturbation theories for the thermodynamic properties of fluids have been widely used over the past two decades.[1-3] Most of these theories are based upon the Gibbs-Bogolyubov inequality which places an upper bound on the excess Helmholtz free energy A of a fluid interacting through the pair potential $u(r)$ in terms of the excess free energy A_0 of a reference fluid interacting according to the pair potential $u_0(r)$:

$$\frac{A}{Nk_BT} \le \frac{A_0}{Nk_BT} + \frac{\rho}{2k_BT}\int d^3r[u(r)-u_0(r)]g_0(r) \ . \quad (1)$$

Here $g_0(r)$ is the radial-distribution function for the reference fluid, T is the temperature, and ρ is the number density. Historically, the most popular reference fluid has been hard spheres,[1-3] although both the one-component plasma (OCP)[4,5] and inverse 12th-power fluids (I12) (Refs. 6 and 7) have also been used.

Of course, the inequality is also valid when the roles of the reference and actual fluids are reversed. Interchanging the subscripted and nonsubscripted quantities in Eq. (1) and rearranging yields a lower bound for the free energy:[8]

$$\frac{A}{Nk_BT} \ge \frac{A_0}{Nk_BT} + \frac{\rho}{2k_BT}\int d^3r[u(r)-u_0(r)]g(r) \ . \quad (2)$$

This second form of the inequality has received little attention because its evaluation requires knowledge of the $g(r)$ for the fluid under consideration, which until recently was difficult to obtain. In addition, if one uses the hard-sphere fluid as a reference, Eq. (2) yields the trivial result $A \ge -\infty$ for any positive sphere diameter.

Very recently, Lai[9] has used Monte Carlo (MC) $g(r)$'s and an OCP reference fluid to place upper and lower bounds on the free energy of liquid metals near melt. In this paper we will use the I12 fluid for our reference, and we will obtain $g(r)$'s from the thermodynamically consistent integral equations developed by Rogers and Young (RY)[10] and Zerah and Hansen (ZH).[11] The RY integral equation is an interpolation between the Percus-Yevick (PY) and hypernetted-chain (HNC) equations in which the interpolation parameter is chosen to ensure the equality of the virial and compressibility equations of state. It provides highly accurate $g(r)$'s for repulsive potentials. Zerah and Hansen improved this equation to include attractive potential tails by interpolating between the mean spherical approximation (MSA) and the HNC equations. We employ their method to obtain $g(r)$'s for the Lennard-Jones (LJ) fluid.

In Sec. II we describe our methods for finding the variational limits in Eqs. (1) and (2). In Sec. III we compare our results against simulation data for r^{-n} potentials, and in Sec. IV we present results for the LJ potential. In Sec. V we discuss our results.

II. VARIATIONAL METHODS

Fluids interacting through inverse power potentials of the form

$$u(r)=u_n(r)=\varepsilon\left[\frac{\sigma}{r}\right]^n \quad (3)$$

are parametrized by the dimensionless quantity

$$z_n=\frac{\rho\sigma^3}{\sqrt{2}}\left[\frac{\varepsilon}{k_BT}\right]^{3/n} , \quad (4)$$

or equivalently by the coupling constant

$$\Gamma_n=\frac{\varepsilon}{k_BT}\left[\frac{\sigma}{a}\right]^n=\left[\frac{4\pi\sqrt{2}}{3}z_n\right]^{n/3} , \quad (5)$$

where $a=(3/4\pi\rho)^{1/3}$ is the ion-sphere radius. The LJ potential is

$$u(r)=u_{\mathrm{LJ}}(r)=4\varepsilon\left[\left[\frac{\sigma}{r}\right]^{12}-\left[\frac{\sigma}{r}\right]^6\right] , \quad (6)$$

and is parametrized by $T^*=k_BT/\varepsilon$ and $\rho^*=\rho\sigma^3$.

By scaling distances to a, $x=r/a$, and replacing the subscript 0 with subscript 12 to explicitly indicate our use of the I12 fluid as a reference, Eq. (1) becomes

$$\frac{A}{Nk_BT} \le \frac{A_{12}(z_{12})}{Nk_BT} + \tfrac{3}{2}\int_0^\infty dx\, x^2 \left[\frac{u(ax)}{k_BT} - \frac{\Gamma_{12}}{x^{12}}\right] g_{12}(x,z_{12}) \ . \quad (7)$$

The minimum of the right-hand side of Eq. (7) with respect to z_{12} is obtained using a simple Newton-Raphson code previously developed and described in Ref. 7.

Using the same reduced variables, Eq. (2) may be reexpressed as

$$\frac{A-U}{Nk_BT} = -\frac{S}{Nk_B} \ge \frac{A_{12}(z_{12})}{Nk_BT} - \Gamma_{12}I_{12} \ , \quad (8)$$

where U is the excess internal energy for the actual fluid,

$$U = \tfrac{3}{2}\int_0^\infty dx\, x^2 u(ax) g(ax) \ , \quad (9)$$

and

$$I_{12} \equiv \tfrac{3}{2}\int_0^\infty dx\, x^2 \frac{1}{x^{12}} g(ax) \ . \quad (10)$$

We note that because it is the "true" $g(r)$ appearing in Eqs. (9) and (10), the right-hand side of Eq. (8) is a simple algebraic expression whose maximum can be found much more easily than the minimum can be found in Eq. (7).

Recently Wallace[12] has used the first term in a correlation expansion[13–15] to obtain a closed-form approximation to the excess entropy which depends only upon $g(r)$:

$$\frac{S_{\text{ex}}}{Nk_B} + 1 \approx \frac{S_2}{Nk_B} = -\frac{\rho}{2}\int d^3r\, g(r)\ln g(r) \ . \quad (11)$$

Combining Eqs. (9) and (11) gives an approximate expression for the excess free energy,

$$\frac{A}{Nk_BT} \approx \frac{A_2}{Nk_BT} = \frac{U-TS_2}{Nk_BT} + 1 \ . \quad (12)$$

It has long been known that the contributions of higher correlations to the entropy are important,[16] but they are expected to be less significant for high densities than for low densities.[12] Since Eq. (12) is quite easy to evaluate once the RY and ZH radial distribution functions are available, we examine its validity for the softer repulsive potentials and the LJ potential.

In order to evaluate the variational free energies in either Eq. (7) or Eq. (8), one needs to know the free energy of the I12 fluid. There are extensive MC data[17] for the excess pressure for this fluid which can be accurately fit by a virial series:[7]

$$\frac{pV}{Nk_BT} - 1 = B_2z + B_3z^2 + B_4z^3 + B_5z^4 + B_6z^5 \ . \quad (13)$$

The coefficients B_2 through B_5 are computed from first principles[17] and have the values $B_2 = 3.6296$, $B_3 = 7.5816$, $B_4 = 9.9792$, and $B_5 = 8.4520$. The last coefficient, $B_6 = 4.4$, is a fit to the difference between the MC data and the four-term series.[7] Integration of the virial series gives the expression for the reference free energy used here,

$$\frac{A_{12}}{Nk_BT} = \sum_{j=2}^{6} \frac{B_j}{j-1} z_{12}^{j-1} \ . \quad (14)$$

Our approach will be to use $g(r)$'s obtained from the RY and ZH integral equations in Eqs. (7) and (8) to evaluate variational limits on the free energy with the reference free energy given by Eq. (14). In order to test the usefulness of these limits we compare them to the MC free energies for other fluids in Secs. III and IV.

III. NUMERICAL RESULTS FOR INVERSE-POWER POTENTIALS

A. Soft potentials ($4 \le n < 12$)

In addition to the very extensive MC data available for the I12 fluid, there is also data[18] for inverse-power potentials with $n = 4$, 6, and 9. We will compare the free-energy bounds predicted by Eqs. (7) and (8) to free energies obtained from fits to the MC pressure data for these fluids. Young and Rogers[7] provide virial coefficients to be used in an expansion like Eq. (14) for $n = 4$, 6, and 9. Unlike their coefficients for the I12 system, all of the B_j's for these other systems are obtained from fits to the MC data. For $n = 6$ and $n = 9$ the values of B_2 and B_3 are very nearly the exact, first-principles values. But for $n = 4$ the B_2 obtained from the fit is about 7% larger than its exact value. Hence the fits for $n = 6$ and 9 can be expected to give reliable results for all values of z_n, but for $n = 4$ we expect that the fit will give free energies which are too large at low density.

This last difficulty is illustrated in Table I which shows the limits placed by Eqs. (7) and (8) on the free energy for $n = 4$ and compares them to the MC fit. For low z_4 the free energies from the fit are too large. However, if one calculates the free energy from the virial expansion using the exact values[18,19] of B_2, B_3, and B_4, the values shown in parentheses are obtained. These values are "in bounds" indicating that any apparent difficulties at low

TABLE I. Excess free-energy comparisons for $n = 4$. A_{max} is the upper limit determined from Eq. (7), A_{min} is the lower limit determined from Eq. (8), and A_{MC} is the fit due to Young and Rogers in Ref. 7. A_2 is the correlation expansion prediction of Eq. (12). The figures in parentheses are obtained from the first three terms in the exact virial expression (see text).

z_4	$\frac{A_{\text{max}}}{Nk_BT}$	$\frac{A_{\text{min}}}{Nk_BT}$	$\frac{A_{\text{MC}}}{Nk_BT}$		$\frac{A_2}{Nk_BT}$
0.030	0.3356	0.3098	(0.3299)	0.3506	1.125
0.050	0.5718	0.5267	(0.5596)	0.5893	1.277
0.10	1.188	1.010	(1.164)	1.203	1.755
0.25	3.181	3.021	(3.001)	3.228	3.530
0.50	6.927	6.709		6.893	7.055
1.0	15.60	15.34		15.53	15.46
1.5	25.48	25.18		25.40	25.17
2.0	36.31	36.00		36.22	35.91
2.5	47.93	47.62		47.83	46.51
3.0	60.25	59.95		60.14	59.85
3.5	73.21	72.90		73.09	72.84
4.0	86.74	86.43		86.62	86.44

TABLE II. Same as Table I, but for $n=6$.

z_6	$\frac{A_{\text{max}}}{Nk_BT}$	$\frac{A_{\text{min}}}{Nk_BT}$	$\frac{A_{\text{MC}}}{Nk_BT}$	$\frac{A_2}{Nk_BT}$
0.025	0.1366	0.1293	0.1337	1.0211
0.05	0.2800	0.2662	0.2747	1.0756
0.10	0.5952	0.5626	0.5792	1.2513
0.25	1.706	1.638	1.673	2.097
0.50	4.169	4.066	4.121	4.259
1.00	11.50	11.36	11.44	11.30
1.50	22.13	21.98	22.07	22.06

TABLE III. Same as Table I, but for $n=9$.

z_9	$\frac{A_{\text{max}}}{Nk_BT}$	$\frac{A_{\text{min}}}{Nk_BT}$	$\frac{A_{\text{MC}}}{Nk_BT}$	$\frac{A_2}{Nk_BT}$
0.025	0.1030	0.1022	0.1029	1.0122
0.050	0.2121	0.2102	0.2115	1.0420
0.10	0.4495	0.4444	0.4459	1.1500
0.25	1.330	1.318	1.320	1.7477
0.50	3.548	3.528	3.535	3.623
1.00	12.35	12.32	12.36	12.69

density for $n=4$ are due to the fit to A_4 and not the variational methods. For $z_4 \geq 0.5$, the MC fit to A_4 lies between the variational limits whose difference initially increases with z_4 but seems to saturate at about $0.3Nk_BT$. For all values of z_4, the arithmetic mean of the limits, $\overline{A}=(A_{\text{max}}+A_{\text{min}})/2$ is in good agreement with the fit. At $z_4=4$ (melt is at $z_4=3.94$), $A_4=86.62Nk_BT$ while $\overline{A}=86.59Nk_BT$. The difference between these numbers is within the uncertainty in the MC data itself.

The correlation expansion results obtained using Eq. (12) are also shown in Table I. They appear to be in worse agreement at lower densities than near melt, which is consistent with previous results for the hard-sphere fluid.[12]

The results for $n=6$ and 9 are shown in Tables II and III. The qualitative features are the same as for $n=4$. The separation between the limits gets larger with z_n for each n, but as n gets closer to the reference value of 12 the separation in the limits decreases. In both cases the MC fits lie between the limits, except for the highest value of z_9 for which the fit is very slightly too high. But once again suspicion lies with the fit and not the method. Nonetheless, in both cases the arithmetic mean of the limits agrees well with the MC fits for all densities and is within about $0.02Nk_BT$ of the MC estimate near melt. Again, A_2 is generally much more accurate at densities near melt.

B. The reference fluid ($n=12$)

If we put $n=12$ in Eqs. (7) and (8), we would expect to find $A_{\text{min}}=A_{\text{MC}}=A_{\text{max}}$, provided that $g_{12}(x,z_{12})$ and $A_{12}(z_{12})$ are exact and that the numerical calculations are done exactly. Hence any difference between A_{min} and A_{max} for $n=12$ will be a measure of the accuracy of the reference functions and the numerical calculations. In Table IV we list A_{max}/Nk_BT and A_{min}/Nk_BT, as well as the corresponding variational parameters z_{max} and z_{min}. The free-energy bounds are extremely close and equal to the MC results to within the MC accuracy. The only noticeable deviation from equality occurs at the freezing point, where $\Delta A/Nk_BT=0.002$. The variational z_{max} and z_{min} values show somewhat larger deviations from the actual z value, showing that the variational functions are very flat near the extreme values.

We believe that the numerical calculations have been done with high precision and that the deviations from perfect equality in the A and z values in Table IV are due to the RY approximation for $g_{12}(x,z_{12})$. At the melting point, for example, the RY pressure[10] deviates from MC by 2%, which implies errors in $g_{12}(x,z_{12})$. Overall, however, the small deviations from equality in Table IV show that the RY results are very accurate and suitable for variational calculations.

C. Hard potentials ($n>12$)

We conclude our study of purely repulsive potentials by evaluating the free-energy bounds for $n=20$ and 28. While there is no MC data for these systems, they are still of some physical interest. Very recently, Moriarty[20] has shown that electron shells with angular momentum l produce a repulsive potential that varies as r^{-n}, with $n=4(2l+1)$. Thus $n=4$, 12, 20, and 28 correspond, respectively, to s-, p-, d-, and f-shell electrons.

The results for these two cases are shown in Table V. As expected, the separation of the bounds increases with z in both cases and is in general larger for $n=28$ than for $n=20$. From our experience with the softer potentials we would expect that the arithmetic mean of the bounds will give a very accurate estimate of the free energies of these fluids.

TABLE IV. Variational bounds on the excess free energy for $n=12$. The variational z values for A_{max} and A_{min} are included.

z_{12}	z_{max}	z_{min}	$\frac{A_{\text{max}}}{Nk_BT}$	$\frac{A_{\text{min}}}{Nk_BT}$	$\frac{A_{\text{MC}}}{Nk_BT}$
0.025	0.0290	0.0249	0.093 03	0.093 16	0.093 16
0.05	0.0524	0.0499	0.191 38	0.191 38	0.191 4
0.10	0.100	0.100	0.404 41	0.404 38	0.404 4
0.25	0.250	0.250	1.205 4	1.205 4	1.205
0.50	0.497	0.502	3.337 7	3.337 9	3.338
0.813	0.805	0.820	8.478 6	8.480 6	8.480

TABLE V. Variational bounds on the excess free energy for $n=20$ and 28.

	$n=20$		$n=28$	
z_n	$\frac{A_{\max}}{Nk_BT}$	$\frac{A_{\min}}{Nk_BT}$	$\frac{A_{\max}}{Nk_BT}$	$\frac{A_{\min}}{Nk_BT}$
0.05	0.1773	0.1714	0.1787	0.1629
0.10	0.3731	0.3614	0.3721	0.3430
0.20	0.8345	0.8106	0.8277	0.7675
0.30	1.418	1.379	1.404	1.304
0.40	2.165	2.111	2.139	1.998
0.50	3.139	3.070	3.108	2.917
0.60	4.437	4.351	4.412	4.167
0.70	6.193	6.090	6.227	5.921

IV. LENNARD-JONES FLUID

The preceding section indicates that the RY integral equation can be used to obtain useful limits on the free energy of inverse power fluids. Here we present results for the LJ fluid using the generalization of RY proposed by Zerah and Hansen.[11] Since the repulsive part of the LJ potential is identical to the I12 reference potential, we expect the free-energy bounds to be very close together, especially for high T^*. This expectation is borne out in Table VI, which shows the variational limits for several points near the LJ melting curve. "Exact" free energies for the LJ fluid can be obtained by integrating MC data from $T^*=\infty$ to the chosen T^* value. This is time consuming, and not many such numbers are available. The exact values (A_{ex}) quoted in Table VI are either MC or perturbation theory results from Hansen.[21] Accurate free energies at low temperatures are not available. The variational results are in reasonable agreement with the exact results, given the probable errors in the latter. From the table it seems that the correlation expansion results A_2 are somewhat worse for the LJ fluid than for the inverse-power fluids.

V. DISCUSSION

The thermodynamically consistent integral equations developed by Rogers and Young[10] and Zerah and Hansen[11] are efficient algorithms for obtaining accurate radial-distribution functions. In this paper we have used these functions in the Gibbs-Bogolyubov inequality to evaluate upper and lower variational bounds to the Helmholtz free energy of inverse-power potential fluids and the LJ fluid, with the I12 system acting as our reference.

The general trends indicated by the tabulated results are what would be expected. For the inverse-power potentials, the separation between the upper and lower bounds increases as the density increases and as n deviates more and more from the reference value of 12. For the LJ fluid the separation between the limits decreases with increasing T^*, since at high temperature only the repulsive r^{-12} part of the potential is important.

TABLE VI. Excess free energies of the LJ fluid near the melting curve. $A_{\max}$ and $A_{\min}$ are from Eqs. (7) and (8). A_2 is from Eq. (12), and the exact free energy A_{ex} is from Ref. 21. Accurate values of A_{ex} are unavailable at the lower-T^* values.

T^*	ρ^*	$\frac{A_{\max}}{Nk_BT}$	$\frac{A_{\min}}{Nk_BT}$	$\frac{A_{\text{ex}}}{Nk_BT}$	$\frac{A_2}{Nk_BT}$
0.786	0.85	-4.06	-4.22		-3.8
1.15	0.936	-1.44	-1.54		-1.1
2.74	1.1	2.33	2.29	2.31	2.7
5.0	1.279	4.21	4.19	4.26	4.6
20.0	1.765	6.46	6.46	6.49	6.9

The correlation expansion method[12] provides a very convenient form for the free energy in terms of the radial-distribution function. However, from the results presented here the correlation expansion method seems to be less consistently accurate than the mean of the variational limits. As expected, the method is also less accurate at low density than near melt.

In all of the cases we studied the variational limits were close enough together to provide a useful constraint on the actual free energy. Near melt, we found $\Delta A \le 0.3Nk_BT$. In addition, comparison with MC estimates of the free energy for $n=4$, 6, and 9 indicate that the arithmetic mean of the variational limits is always within about $0.06Nk_BT$ of the actual free energies and usually much closer. Near melt the mean is within about $0.03Nk_BT$. Since the uncertainty[18] in the MC data itself is at least of order $0.01Nk_BT$, such agreement is quite remarkable.

Assessing the utility of our method for the LJ fluid is more difficult due to lack of accurate free energies. Of the three exact values in Table VI, only the one corresponding to $T^*=2.74$ comes directly from MC data. The other two are perturbation theory results. Nevertheless, the overall agreement in Table VI is quite encouraging.

The use of the RY and ZH thermodynamically consistent integral equations in the Gibbs-Bogolyubov inequality seems to provide a very efficient method to obtain highly accurate free energies in simple fluids all the way up to melt. The results presented here for inverse-power repulsive potentials and the Lennard-Jones potential hold the promise that accurate free energies for fluids interacting through more realistic potentials can be calculated in the same manner.

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