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An approximate variational method for improved thermodynamics of molecular fluids

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For a certain class of thermodynamic perturbation theories, a generalization of the Gibbs–Bogoliubov inequality holds through second order of perturbation theory and for a subset of terms the inequality is true to infinite order. Using this approximate variational principle, a perturbation theory is chosen for which the Helmholtz free energy of the reference system is minimized under the constraint that the first order term is identically zero. We apply these ideas to the determination of effective spherical potentials that accurately reproduce the thermodynamics of nonspherical molecular potentials. For a diatomic-Lennard-Jones (DLJ) potential with $l/\sigma = 0.793$, the resulting spherical reference potential is identical to the median average over angles for the repulsive part of the potential, but differs in the attractive well. The variational effective spherical potential leads to more accurate thermodynamics than the median, however, particularly in the triple point region.

I. INTRODUCTION

The Gibbs–Bogoliubov inequality^{1–10} gives a rigorous upper bound to the Helmholtz free energy of one system in terms of the properties of a reference system. It has been used in practice by finding the lowest upper bound from a class of reference systems that are well described by available methods, e.g., the hard sphere system^{11,12} and the soft sphere system.^{13,14} Recent work by Goldman and Kumar¹⁵ has been directed toward using the rigorous Gibbs–Bogoliubov inequality in an approximate manner to choose a thermodynamic perturbation theory. We have taken a different approach whereby an approximate inequality is derived and implemented as though it were rigorous. The effective spherical potential thereby obtained is surprisingly accurate in reproducing the thermodynamics of the diatomic-Lennard-Jones (DLJ) potential with $l^* = l/\sigma = 0.793$, where l^* is the reduced bond length between the two LJ centers on each molecule.

II. VARIATIONAL METHOD

Thermodynamic perturbation theories arise from choosing a parametric path in a single variable from a reference potential ϕ_0 to the potential of interest ϕ , and expanding the Helmholtz free energy as a Taylor series in that parameter. Because of numerical complications and limited knowledge of the reference system, the Taylor series is usually truncated after first or second order. Therefore, the choice of ϕ_0 and the path of ϕ strongly influence the accuracy of the truncated Taylor series.

In previous work^{16–19} we have used a formulation of general perturbation theories based on Smith *et al.*²⁰ and have restricted the class of perturbation theories considered. One can characterize this class of perturbation theories by a function R which determines the path by

$$R(\phi_\gamma - \phi_0) = \gamma R(\phi - \phi_0). \quad (1)$$

Here R is any odd invertible function, γ is the path parameter, and ϕ_γ is the potential along the path from ϕ_0 to ϕ at the parameter value of γ . Note that at $\gamma = 0$, $\phi_\gamma = \phi_0$, and at

$\gamma = 1$, $\phi_\gamma = \phi$. The choice $R(x) = x$ gives the familiar λ expansion.²¹ One can easily determine ϕ_γ and its derivatives as

$$\phi_\gamma = \phi_0 + R^{-1}[\gamma R(\phi - \phi_0)] \quad (2)$$

and

$$\left. \frac{d^n \phi_\gamma}{d\gamma^n} \right|_{\gamma=0} = \left. \frac{d^n R^{-1}(x)}{dx^n} \right|_{x=0} [R(\phi - \phi_0)]^n. \quad (3)$$

Since R is odd, all even derivatives of ϕ_γ are zero at $\gamma = 0$. Then we can write

$$\phi_\gamma - \phi_0 = \gamma \phi^{(1)} + \frac{\gamma^3}{3!} \phi^{(3)} + \frac{\gamma^5}{5!} \phi^{(5)} + \dots, \quad (4)$$

where $\phi^{(n)}$ denotes $d^n \phi_\gamma / d\gamma^n|_{\gamma=0}$. For a two-body potential, the total energy of a configuration of particles is $U = \frac{1}{2} \sum_{i \neq j} \phi_{ij}$, and consequently

$$U_\gamma - U_0 = \gamma U^{(1)} + \frac{\gamma^3}{3!} U^{(3)} + \dots, \quad (5)$$

where $U^{(n)} \equiv \frac{1}{2} \sum_{i \neq j} \phi_{ij}^{(n)}$.

One can easily show (see, e.g., Mansoori and Canfield¹²) that the ratio of partition functions for the two systems may be written as

$$Q_\gamma / Q_0 = \langle \exp[-\beta(U_\gamma - U_0)] \rangle_0, \quad (6)$$

where $\langle \rangle_0$ represents the expectation value over the probability distribution function in the reference system. If $Q_\gamma / Q_0 > 1$, then the corresponding Helmholtz free energies, $A = -kT \ln Q$, have the property that $A_\gamma < A_0$. By writing the exponential as a Taylor series and inserting Eq. (5), we have

$$\begin{aligned} \frac{Q_\gamma}{Q_0} = & \left\langle 1 - \beta(\gamma U^{(1)} + \frac{\gamma^3}{3!} U^{(3)} + \dots) \right. \\ & + \frac{\beta^2}{2!} (\gamma U^{(1)} + \frac{\gamma^3}{3!} U^{(3)} + \dots)^2 \\ & - \frac{\beta^3}{3!} (\gamma U^{(1)} + \frac{\gamma^3}{3!} U^{(3)} + \dots)^3 \\ & \left. + \dots \right\rangle_0. \quad (7) \end{aligned}$$

One can collect the terms involving only $(\gamma U^{(1)})^n$ and sum them to get $\exp(-\beta\gamma U^{(1)})$, and the first terms that are ignored are third order in the perturbation theory. So we have

$$Q_\gamma/Q_0 = \langle \exp(-\beta\gamma U^{(1)}) + O(\gamma^3) \rangle_0. \quad (8)$$

If the terms $\langle O(\gamma^3) \rangle_0$ are small and we use a special case of the Jensen inequality²² $\langle e^x \rangle \geq e^{\langle x \rangle}$, then for $\gamma = 1$ we get

$$A \leq A_0 + \langle U^{(1)} \rangle_0. \quad (9)$$

For $R(x) = x$, the terms $O(\gamma^3)$ are identically zero and we recover the Gibbs–Bogoliubov inequality. In fact, one can prove the Gibbs–Bogoliubov inequality by applying the Jensen inequality directly to Eq. (6). For this more general class of perturbation theories, the inequality is approximate with some third and higher order contributions neglected. The extra freedom from the choice of R allows us to find upper bounds that are lower than with the Gibbs–Bogoliubov inequality provided the neglect of the terms $O(\gamma^3)$ is a good approximation.

As an aside, it may be helpful at this point to compare the terms in Eq. (7) with the more standard perturbation expansion of excess Helmholtz free energy A^{ex} . We will show that the terms $\langle O(\gamma^3) \rangle_0$ which we dropped to get Eq. (9) are also of third and higher order in the general Smith *et al.*²⁰ formulation for A^{ex} . From the definition

$$A_\gamma^{\text{ex}} = -(1/\beta) \ln Q_\gamma^{\text{ex}},$$

Eq. (7), and the fact that the ideal contribution to Q is independent of γ , we have

$$\left. \frac{\partial A_\gamma^{\text{ex}}}{\partial \gamma} \right|_{\gamma=0} = -\frac{1}{\beta} \frac{1}{Q_0} \left. \frac{\partial Q_\gamma}{\partial \gamma} \right|_{\gamma=0} = \langle U^{(1)} \rangle_0. \quad (10)$$

That is, the first order term in A^{ex} comes from the first order term in Q/Q_0 . By the n th order term in A^{ex} , we mean the term

$$\frac{1}{n!} \left. \frac{\partial^n A_\gamma^{\text{ex}}}{\partial \gamma^n} \right|_{\gamma=0}$$

in the Taylor expansion of A_γ^{ex} ,

$$A_{\gamma=1}^{\text{ex}} = A_0^{\text{ex}} + \left. \frac{\partial A_\gamma^{\text{ex}}}{\partial \gamma} \right|_{\gamma=0} + \frac{1}{2!} \left. \frac{\partial^2 A_\gamma^{\text{ex}}}{\partial \gamma^2} \right|_{\gamma=0} + \dots \quad (11)$$

and similarly for Q/Q_0 . This is in accordance with the usual terminology for the order of a term in a perturbation expansion of the excess Helmholtz free energy. The second order term is given by

$$\begin{aligned} \frac{1}{2} \left. \frac{\partial^2 A_\gamma^{\text{ex}}}{\partial \gamma^2} \right|_{\gamma=0} &= -\frac{1}{2\beta} \left[\frac{1}{Q_0} \left. \frac{\partial^2 Q_\gamma}{\partial \gamma^2} \right|_{\gamma=0} - \left(\frac{1}{Q_0} \left. \frac{\partial Q_\gamma}{\partial \gamma} \right|_{\gamma=0} \right)^2 \right] \\ &= \frac{1}{2} \beta [-\langle (U^{(1)})^2 \rangle_0 + (\langle U^{(1)} \rangle_0)^2]. \quad (12) \end{aligned}$$

The second order term in A^{ex} has contributions from the first and second order terms in Q/Q_0 . In general, the n th order term in A^{ex} will be a function of the first through n th order terms in Q/Q_0 .

We now return to the main development. We will restrict our study to those cases where U_0 and R are related in such a way that $\langle U^{(1)} \rangle_0 = 0$, and therefore $A \leq A_0$. We further specialize to the case of effective spherical potentials for molecular systems. The choice $\langle U^{(1)} \rangle_0 = 0$ is numerical-

ly convenient in that a spherical ϕ_0 may be chosen from the condition¹⁷

$$\int R [\phi(r, \Omega) - \phi_0(r)] d\Omega = 0. \quad (13)$$

Then $\langle U^{(1)} \rangle_0$ becomes zero and A_0 is evaluated for a spherical potential, for which many accurate methods are available. Also, by choosing the first order term to be zero, one hopes that the higher order terms would be small, which is essential for Eq. (9) to be useful.

III. GENERALIZATION TO r DEPENDENT PERTURBATION THEORIES

One usually considers perturbation theories in which R is a simple function of one variable. However, there is no necessity for such a restriction on R . All that is required is that a parametric path from ϕ_0 to ϕ be specified. We will consider here a choice of R that also depends on the center of mass separation r of a nonspherical potential $\phi(r, \Omega)$. That is, for each r , ϕ_r is chosen from

$$R [\phi_r(r, \Omega) - \phi_0(r); r] = \gamma R [\phi(r, \Omega) - \phi_0(r); r]. \quad (14)$$

Note that we still have a well-defined path from $\phi_0(r)$ to $\phi(r, \Omega)$ as a function of γ .

The reason for choosing this form is to permit the determination of the lowest allowed $\phi_0(r)$ at each value of r . If we choose two potentials $\phi_A(r)$ and $\phi_B(r)$ such that $\phi_A(r) \geq \phi_B(r)$ for all r , then for an arbitrary configuration of particles

$$U_A = \frac{1}{2} \sum_{i \neq j} \phi_A(r_{ij}) \geq U_B = \frac{1}{2} \sum_{i \neq j} \phi_B(r_{ij}).$$

From the definition of the partition function, we then have that $Q_A \leq Q_B$ and consequently $A_A \geq A_B$. Therefore, the lowest choice of $\phi_0(r)$ allowed by Eq. (13) gives for this class of perturbation theories the best choice of A_0 , provided the error in Eq. (9) is small.

The general procedure may therefore be summarized as follows. We require that ϕ_0 and R are related by Eq. (13), so that $\langle U^{(1)} \rangle_0 = 0$ and Eq. (9) reduces to $A \leq A_0$. We then minimize A_0 with respect to the remaining freedom in ϕ_0 and R , which is equivalent to minimizing $\phi_0(r)$ itself at each point r subject to the constraint of Eq. (13). This minimization simultaneously determines ϕ_0 and R , but only the former is of interest so the latter is not explicitly determined.

The development by which we have arrived at this procedure is totally dependent on the neglect of terms which cannot be readily calculated. For sufficiently small anisotropy, these terms will also be small. Lacking a criterion for what is "sufficiently small," there is no *a priori* basis for expecting it to work as well as it does. The real justification for the procedure lies in the accuracy of the results to which it leads; see Sec. V.

IV. DETERMINATION OF THE BEST $\phi_0(r)$

Now that we have a general procedure, it is necessary to find an efficient numerical method for the determination of the lowest allowed $\phi_0(r)$. We want to minimize $\phi_0(r)$ at each r subject to the constraint of Eq. (13) with R in the class of

perturbation theories giving Eq. (9), i.e., R an odd invertible function or the limit of such. We can rewrite Eq. (13) in terms of the probability density

$$\rho(E) = \int \delta[\phi(r, \Omega) - E] d\Omega / \int d\Omega$$

of an orientation having potential energy E at a given value of r :

$$\int_{-\infty}^{\infty} \rho(E) R(E - E_0) dE = 0, \quad (15)$$

where E_0 is just $\phi_0(r)$ for the given value of intermolecular separation r . We then look for the function R that leads to the lowest value of E_0 . Conversely, we may determine the lowest value of E_0 for which a nontrivial function R satisfying Eq. (15) exists, and this is how we actually proceed in practice. Integrating by parts, we obtain

$$s(E)R(E - E_0) \Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} s(E)R'(E - E_0) dE = 0, \quad (16)$$

where

$$s(E) = \int_{-\infty}^E \rho(x) dx. \quad (17)$$

From the definition of $\rho(E)$, $s(E)$ is the cumulative distribution function; i.e., the fraction of orientations Ω with $\phi(r, \Omega) \leq E$ for a given r . Clearly, $s(x) = 0$ for $x < a$ and $s(x) = 1$ for $x > b$, where a is the lowest value of $\phi(r, \Omega)$ and b is the highest value of $\phi(r, \Omega)$ at the given value of r . Equation (16) can be rewritten as

$$\int_0^{\infty} R'(y) \{1 - [s(E_0 + y) + s(E_0 - y)]\} dy = 0, \quad (18)$$

since $R(0) = 0$ from our restriction to odd functions. We note that $R'(y) > 0$ for all y because R is odd and invertible. Now define the function

$$f(y, E_0) = 1 - [s(E_0 + y) + s(E_0 - y)], \quad (19)$$

which is determined solely by the probability density $\rho(E)$. Note that $f(y, E_0) = 0$ for $y > \max(b - E_0, E_0 - a)$. Now if E_0 is too small, then $f(y, E_0)$ is strictly positive for $0 < y < \max(b - E_0, E_0 - a)$, and it is then impossible to satisfy Eq. (18) with a nontrivial $R(y)$. For example, let $E_0 = a$ and $b \neq a$. Then $s(E_0 - y) = 0$ for all $y > 0$. For the interval $0 < y < b - a$, $s(E_0 + y) < 1$ and therefore $f(y, E_0) > 0$ for the same interval. Also, note that $f(y, E_0)$ is monotonically decreasing with E_0 for fixed y , because $s(x)$ is monotonically increasing. In order for Eq. (18) to be satisfied, $f(y, E_0)$ must clearly be zero somewhere in the interval $0 < y < \max(b - E_0, E_0 - a)$. There will be some critical value of E_0 , such that $f(y, E_0)$ is zero at one or more values of y and positive elsewhere in this interval. This value of E_0 depends only on the function $s(y)$ which in turn depends on r . It is the smallest E_0 for which Eq. (18) can be satisfied, and thus just what we wish to determine. For values of E_0 slightly larger than this critical value, the required R' will be sharply peaked in the vicinity of a small region of slightly negative f . In the limit as E_0 approaches its minimum value from above, $R'(y)$ approaches a delta function and $R(y)$ becomes a step function, with the step occurring at the point in the interval

$0 < y < \max(b - E_0, E_0 - a)$ where $f(y, E_0)$ just touches zero.

Thus, the minimum E_0 for which Eq. (18) can be satisfied is simply the smallest value of E_0 for which $f(y, E_0)$ goes to zero at some point in the range $0 < y < \max(b - E_0, E_0 - a)$. To find this E_0 we first invert the function $s(y)$ to obtain $y(s)$, the value of the potential such that a fraction s of the orientations are lower in energy. That is,

$$\int \theta[y(s) - \phi(r, \Omega)] d\Omega / \int d\Omega = s,$$

where $\theta(x) = 1$ for $x \geq 0$ and $\theta(x) = 0$ otherwise. Clearly then, $y(0) = a$, $y(1) = b$, and $y(1/2)$ is the median. In terms of $y(s)$, the condition $f(y, E_0) = 0$ becomes $E_0 = \frac{1}{2}[y(s) + y(1 - s)]$. We then simply vary s from 0 to 1/2; the smallest value of $\frac{1}{2}[y(s) + y(1 - s)]$ encountered in doing so is the desired minimal E_0 , which is in turn the optimal choice for $\phi_0(r)$ at that value of r . If the minimal E_0 occurs at $s = 1/2$, then $\phi_0(r)$ is the median average over angles. If the minimal E_0 occurs at $s = 0$, then $\phi_0(r)$ is the midpoint between a and b . For the DLJ potential studied in the next section, we will see that for almost all values of r one of these two values is the minimum.

In order to evaluate the required quantities numerically, we have constructed an approximate probability density at fixed r from the weights w_i and values ϵ_i used in a Gauss-Legendre quadrature in the angular coordinates. The set of (w_i, ϵ_i) was reordered in ascending order of ϵ_i 's. The probability density was taken to be piecewise constant with the value

$$\frac{1}{2} \frac{(w_i + w_{i-1})}{\epsilon_i - \epsilon_{i-1}} \quad \text{for } \epsilon_{i-1} < \epsilon < \epsilon_i.$$

This leads to an $s(y)$ such that

$$s(\epsilon_i) = \frac{1}{2} w_i + \sum_{j=1}^{i-1} w_j,$$

with $s(y)$ for intermediate y obtained by linear interpolation. A table of $y(s)$ was then constructed for regular increments in s from 0 to 1. For this study Δs was taken to be 0.01. Finally, $\phi_0(r)$ at r was determined by the minimum value of $\frac{1}{2}[y(s) + y(1 - s)]$ in the table. The order of quadrature used was systematically increased until the fluctuations in E_0 were significantly less than 1%.

Thermodynamic quantities for $\phi_0(r)$ were calculated using the perturbation theory developed by Ross¹³ based on earlier work by Rasaiah and Stell¹¹ and Mansoori and Canfield.¹²

V. RESULTS

For comparison with a simulation of anisotropic potentials we have chosen a DLJ potential with $l/\sigma = 0.793$. This corresponds roughly to CO_2 and is the same potential used in previous analytical work by MacGowan *et al.*^{23,24} and in MD simulations by Singer *et al.*²⁵ For significantly smaller values of l/σ , the median^{16,26} gives good thermodynamics²³ and will be nearly identical to our variational $\phi_0(r)$. Figure 1 shows a plot of $\frac{1}{2}[y(s) + y(1 - s)]$ as a function of s for values of r where $s = 1/2$ (the median) was minimal, where

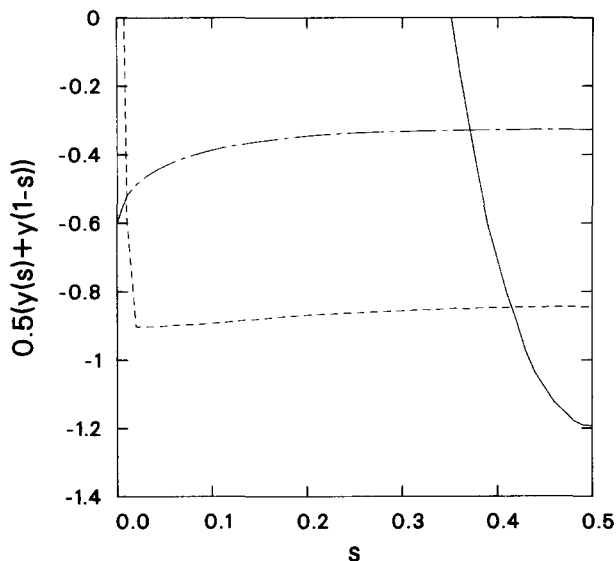


FIG. 1. The function $\frac{1}{2}[y(s) + y(1-s)]$ is plotted vs s . The minimum value of the function is the variational choice for the potential. — is for $r^* = 1.3$ and the median ($s = 0.5$) is minimum. - - - is for $r^* = 1.7$, and neither the median nor the midpoint is minimum. - · - · is for $r^* = 2.0$ and the midpoint ($s = 0.0$) is minimum.

some intermediate s was minimal, and where $s = 0$ (the midpoint) was minimal.

Figure 2 shows the variational minimum potential $\phi_0(r)$ as well as the median, the midpoint, the unweighted average, and two extreme orientations in the attractive well. In the repulsive region, $\phi_0(r)$ is always the median for this potential and is therefore not shown. All quantities are shown in reduced units; $r^* = r/\sigma$ and $\phi^*(r^*) = \phi(r/\sigma)/\epsilon$.

Figure 3 compares the reduced pressure $P^* = P\sigma^3/\epsilon$ vs reduced density $\rho^* = \rho\sigma^3$ for $\phi_0(r)$, the median, and fits to

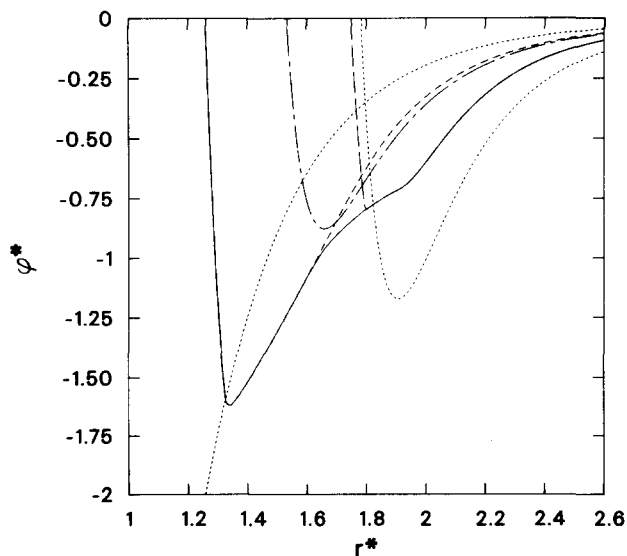


FIG. 2. Various potentials, ϕ^* , are plotted vs the radius, r^* . — is the variational potential. - - - is the potential median. - · - · is the unweighted angular average. ···· is the midpoint. ···· is for two extreme orientations of the anisotropic potential. For $r^* \leq 1.6$ the variational potential and the potential median are identical. For $r^* \geq 1.8$ the variational potential and the midpoint are identical.

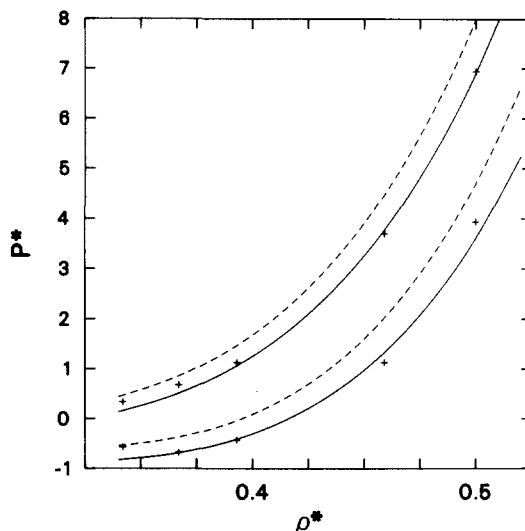


FIG. 3. Reduced pressure, P^* , vs reduced density, ρ^* . — is calculated from the variational potential. - - - is from the potential median. + are from MD simulations as noted in the text. $T^* = 1.9$ for the upper grouping and $T^* = 1.3$ for the lower grouping.

the MD simulations of Singer *et al.*²⁵ The reduced temperature $T^* = T/\epsilon$ is 1.9 for the upper grouping of calculations and 1.3 for the lower grouping. In Fig. 4 the reduced internal energy $E^* = E/N\epsilon = U^* + \frac{3}{2}T^*$ (where U^* is the reduced configurational energy) is plotted vs ρ^* for the same values of T^* . For $\rho^* = 0.5$ and $T^* = 1.9$, the accuracy of the fit to MD was questionable because this point was apparently outside the range of the data used for the fit. We have therefore recalculated it using MD as described in Johnson *et al.*,¹⁷ with the results $P^* = 6.94$ and $E^* = -6.47$. The results for $\phi_0(r)$ agree with the DLJ simulations to about the accuracy of the Ross procedure itself. Some *ad hoc* modifications of the median by MacGowan²⁴ lead to results for E^* roughly 3/4 of the way from that of the median to that of $\phi_0(r)$. Calculations with a radial median¹⁸ lead to similar improvement over the median, but less accurate than that obtained by using $\phi_0(r)$.

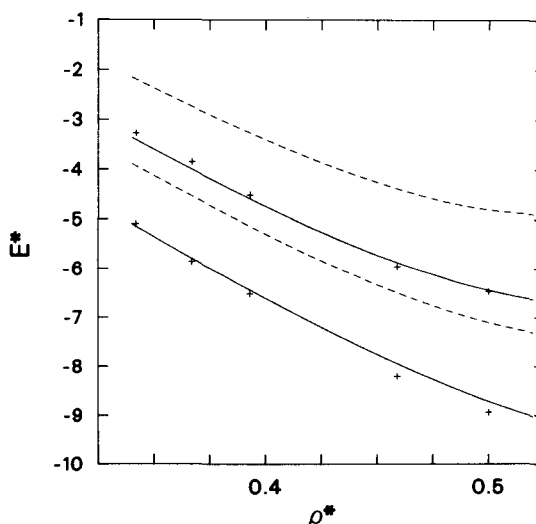


FIG. 4. Reduced energy, E^* vs reduced density, ρ^* . Symbols are the same as in Fig. 3.

VI. CONCLUSION

We have found an approximate variational method that leads to a significant improvement in accuracy over the median potential in the triple point region for a diatomic-Lennard-Jones potential with anisotropy comparable to CO₂. The resulting effective spherical potential is identical to the median for the repulsive part of the potential, which dominates in high-density, high-temperature regions where the median itself is very accurate,¹⁶⁻¹⁸ but differs in the attractive well. It will be interesting to see whether this procedure continues to be accurate for different types of anisotropic potentials where the median does not give good results.

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Note added in proof: See D. MacGowan, *J. Chem. Phys.* (to be published) for a comment pointing out a problem with Goldman and Kumar's method.

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