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Integral equation and perturbation theory in the calculation of pressure for a Lennard-Jones liquid

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The pressure of a classical simple fluid, assumed to be represented by a Lennard-Jones 6-12 potential function, is computed as a function of density at a temperature approximately midway between the triple- and critical-point temperatures. The method employs a parametric integral equation to compute radial distribution functions for a reference potential and these functions are then used in a first-order perturbation equation to obtain the Helmholtz function for the system, and consequently the pressure. The Lennard-Jones potential function is separated into the sum of two parts, a reference potential and a perturbing potential which includes a parameter which varies the "strength" of the perturbation. In this paper we are particularly interested in how the final results depend upon the perturbation parameter: that is, upon how the potential function is separated. We find that there is some dependence of the final answer upon how the potential is separated, but that there is a range of the parameter for which the results are reasonably constant and show good agreement with "exact" calculations.

I. INTRODUCTION

In this paper I present the results of a study of integral equation and perturbation techniques[1] for the calculation of the pressure of a simple classical liquid. More specifically, I separate the pair-potential function into the sum of a reference part and perturbing part, and study the effect of separating the potential in different ways. I examine the Lennard-Jones potential because it approximately represents real fluids and because many theoretical methods have been applied to it and these provide a basis for evaluating new results.

This integral equation has proven to be very good for repulsive potentials and for potentials with attractive wells at high temperatures, but very poor in the liquid region. By combining the integral equation with first-order perturbation theory it now appears that the usefulness of the integral equation can be extended over the complete temperature and density range of the simple classical fluid.

II. COMPUTATIONAL METHOD

We assume that we have a simple classical system of particles interacting pairwise according to the pair-potential function

$$\phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^{6}], \tag{1}$$

where ϕ is the pair potential, r is the separation distance of the particles, and σ and ϵ are parameters adjusted to fit the type of fluid being described. It is usual to work with the dimensionless quantities

$$\chi = r/\sigma , \tag{2}$$

$$n^* = n\sigma^3 , \tag{3}$$

$$T^* = kT/\epsilon , \tag{4}$$

where n is the number of particles (N) divided by the volume (V), k is Boltzmann's constant, and T is the absolute temperature. The potential function now becomes

$$\beta\phi = \phi/kT = (4/T^*)(X^{-12} - X^{-6}). \tag{5}$$

Similar to Chandler and Weeks[2] we separate the potential into a reference part (ϕ_r) and a perturbing part (ϕ_p) in the following way:

$$\phi = \phi_r + \phi_p , \tag{6}$$

$$\beta\phi_r = (4/T^*)(X^{-12} - X^{-6}) + (\alpha/T^*), \quad X < 2^{1/6}, \tag{7}$$

$$\beta\phi_r = (1-\alpha)(4/T^*)(X^{-12} - X^{-6}), \quad X \geqslant 2^{1/6} , \tag{8}$$

$$\beta\phi_p = -(\alpha/T^*) \quad X < 2^{1/6} , \tag{9}$$

$$\beta\phi_p = (4\alpha/T^*)(X^{-12} - X^{-6}), \quad X \geqslant 2^{1/6} , \tag{10}$$

where α is a parameter which can be varied to change the "strength" of the perturbation. Note that when $\alpha = 0$, there is no perturbation and the reference potential becomes just the Lennard-Jones potential.

We use the parametric integral equation[3]

$$g(r) = 1 + c(r) + n \int [g(\vec{s}) - 1] c(|\vec{s} - \vec{r}|)\, d\vec{s}, \tag{11}$$

$$c = g - 1 - a^{-1} \ln[a g \exp(\beta\phi) - a + 1], \tag{12}$$

to calculate the radial distribution function g corresponding to the reference potential. In the above equations $\vec{r}$ and $\vec{s}$ are position vectors, c is called the direct correlation function, and a is a parameter. Previous calculations[3] have shown that the

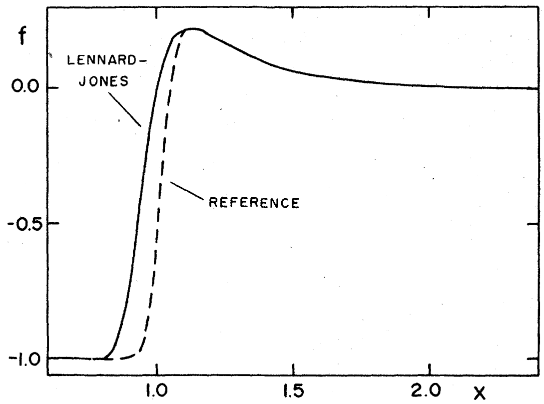

FIG. 1. The Mayer f functions $[f=\exp(-\beta\phi)-1]$ are plotted for the reference potential at $T^*=1.0$, $\alpha=0.8$ ($T_H^*=5.0$), and for the Lennard-Jones potential at $T^*=5.0$.

integral equation works well when applied to purely repulsive potentials and to potentials with wells at high temperatures. In the case of the Lennard-Jones potential the integral equation works quite well for temperatures above $T^*=2.0$, but for temperatures around the critical temperature ($T^*\simeq 1.35$) and below, the approximate integral equation gives poor results at high densities. By separating the potential as previously discussed, for proper choices of α the reference potential has a shallow well and one would expect the integral equation to be accurate. Note that small values of α deepen the reference potential well and make the integral equation less reliable. If we let

$$\alpha=1-(T^*/T_H^*)\,, \tag{13}$$

then $\beta\phi_r(T^*)$ has the same minimum value as $\beta\phi(T_H^*)$ and furthermore, the two Mayer f functions are similar in shape (see Fig. 1). This result is useful in determining the parameter a, for we then select a to fit the Lennard-Jones result for T_H^* as determined by previous calculations.[3]

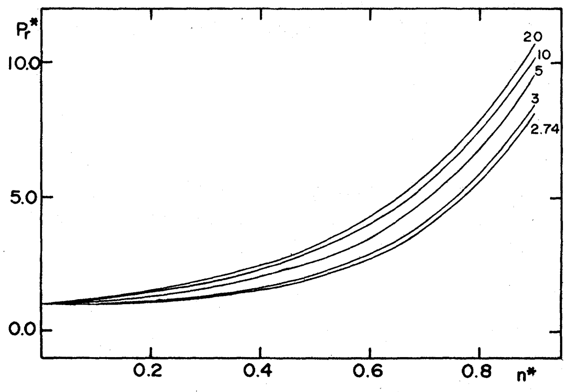

FIG. 2. The pressure (P_r^*) for the reference system is plotted as a function of density (n^*) for $T^*=1.0$. The numbers labeling the curves are values of T_H^*.

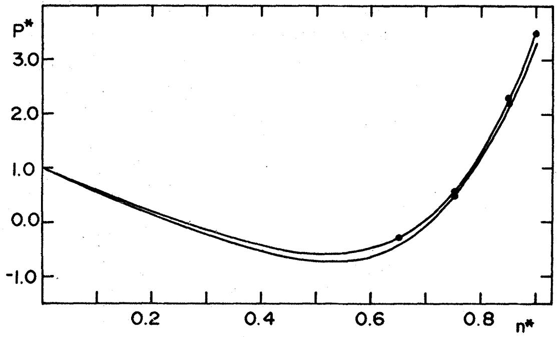

FIG. 3. The pressure (P^*), for the Lennard-Jones fluid at $T^*=1.0$, is plotted as a function of n^*. The lines border the values obtained with integral equation—perturbation theory for values of T_H^* ranging from 2.74 to 20.0. The points are the molecular simulation results obtained by Verlet and Levesque and by McDonald and Singer.

Once the radial distribution function for ϕ_r has been obtained, the corresponding pressure P_r can be computed from the equation[4]

$$\begin{aligned} P_r^*=\frac{P_rV}{NkT}&=1-\frac{2\pi N}{3VkT}\int_0^\infty \frac{d\phi_r}{dr}\,r^3g\,dr\\ &=1-\frac{16\pi n^*}{T^*}\int_0^{2^{1/6}} g(X^{-4}-2X^{-10})\,dX\\ &\quad-\frac{16\pi n^*(1-\alpha)}{T^*}\int_{2^{1/6}}^\infty g(X^{-4}-2X^{-10})\,dX\,. \end{aligned} \tag{14}$$

First-order perturbation theory[5] gives for the Helmholtz function (F)

$$F=F_r+F_p\,, \tag{15}$$

$$F_p=\frac{N^2}{2V}\int_0^\infty g(r)\phi_p(r)4\pi r^2\,dr\,, \tag{16}$$

or for this particular problem

$$\begin{aligned} F_p^*=\frac{2F_p}{3NkT}&=-\frac{4\pi n^*\alpha}{3T^*}\int_0^{2^{1/6}} gX^2\,dX\\ &\quad+\frac{16\pi n^*\alpha}{3T^*}\int_{2^{1/6}}^\infty g(X^{-10}-X^{-4})\,dX\,. \end{aligned} \tag{17}$$

The pressure for the Lennard-Jones system is then given by

$$P^*=P_r^*+\frac{3n^*}{2}\left(\frac{\partial F_p^*}{\partial n^*}\right)_{T^*}\,. \tag{18}$$

To summarize the computation process: (i) The desired density (n^*), temperature (T^*), and separ-

TABLE I. The pressure (P^*) for a Lennard-Jones fluid for a temperature (T^*) of 1.0. The first five columns of pressure are the results obtained in this work by changing the value of T_H^*. For comparison the final column lists the molecular simulation results of Verlet and Levesque and of McDonald and Singer.

	P^*					
n^*	$T_H^*=2.74$ $a=0.12$	$T_H^*=3.0$ $a=0.15$	$T_H^*=5.0$ $a=0.248$	$T_H^*=10.0$ $a=0.28$	$T_H^*=20.0$ $a=0.32$	Molecular simulation
0.05	0.78	0.79	0.80	0.81	0.81	
0.10	0.58	0.58	0.60	0.61	0.62	
0.15	0.38	0.38	0.40	0.40	0.41	
0.20	0.19	0.19	0.19	0.20	0.20	
0.25	0.00	0.00	0.00	−0.01	−0.01	
0.30	−0.17	−0.17	−0.19	−0.21	−0.21	
0.35	−0.32	−0.33	−0.36	−0.39	−0.40	
0.40	−0.45	−0.46	−0.51	−0.54	−0.56	
0.45	−0.55	−0.56	−0.62	−0.66	−0.68	
0.50	−0.60	−0.61	−0.68	−0.73	−0.74	
0.55	−0.58	−0.60	−0.66	−0.72	−0.73	
0.60	−0.49	−0.50	−0.56	−0.62	−0.63	
0.65	−0.29	−0.30	−0.35	−0.41	−0.42	−0.25
0.70	0.04	0.03	−0.01	−0.06	−0.05	
0.75	0.53	0.52	0.51	0.46	0.49	0.58; 0.48
0.80	1.20	1.21	1.24	1.19	1.24	
0.85	2.10	2.13	2.21	2.18	2.26	2.27; 2.23
0.90	3.29	3.33	3.47	3.47	3.58	≃3.50

ation parameter (α) were chosen. (ii) T_H^* was computed from Eq. (13) and the parameter a was selected on the basis of previous calculations[3] for a high-temperature Lennard-Jones gas. (iii) The integral equation, Eqs. (11) and (12), was solved for the g corresponding to ϕ_r. (iv) The pressure (P_r^*) was obtained using Eq. (14). (v) The Helmholtz energy (F_r^*) was obtained using Eq. (17). (vi) The pressure (P^*) was obtained using Eq. (18).

III. DISCUSSION OF RESULTS

We chose to work with the value of $T^*=1.0$ since this puts us into the liquid region and this particular isotherm has been extensively studied by other theories. Figure 2 shows P_r^* as a function of n^* for different values of T_H^*. Figure 3 shows the envelope of curves of P^* as a function of n^* along with "exact" results. Table I lists P^* as a function of n^* for different values of T_H^* and for comparison the molecular simulation results[6] of Verlet and Levesque and of McDonald and Singer.

If the integral equation were exact and if we did not limit our calculations to only the first term in the perturbation series, then the final pressures should not depend upon T_H^*. From Fig. 3 and Table I we see that there are differences. A small value of T_H^* decreases the reliability of the integral equation and a large value increases the "strength" of the perturbation and presumably the contribution of higher-order perturbation terms. If we are interested in the liquid region, we are interested in densities greater than $n^*=0.7$ and we see that for T_H^* equal to or greater than 5, the differences in pressure are quite small and further are in good agreement with the "exact" results. These results suggest that the thermodynamic equations of state of a Lennard-Jones liquid can be calculated with reasonable accuracy using this technique with a value of $T_H^*=5.0$ and $a=0.248$.

ACKNOWLEDGMENT

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