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The Percus-Yevick Theory and the Equation of State of the 6:12 Fluid*

Abstract: The Percus-Yevick theory can be used to calculate the pair distribution function and from this the equation of state. The conventional method is to calculate the pressure of compressibility directly, unfortunately yielding poor results for the 6:12 fluid at low temperatures. In this paper results are obtained using an indirect method, in which the energy is calculated from the pair distribution function, and the equation of state is obtained by thermodynamic identities. These results are virtually in exact agreement with the machine calculation results for the 6:12 potential and with experimental results for argon.

Introduction

Previous attempts to apply the theory of Percus and Yevick[1] to the fluid state have been successful at high temperatures but were not satsifactory at low temperatures. In the present paper we will show a new computational method, based on the energy equation, for obtaining the equation of state for the 6:12 potential with excellent accuracy over a wide range of temperatures and densities.

Consider a fluid of N molecules at a temperature T and occupying a volume V. If the total potential energy, Φ, results solely from the additive contributions of a pair potential, $u(R)$, i.e.,

$$\Phi(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \sum_{i<j} u(R_{ij}), \tag{1}$$

where the $\mathbf{r}_\lambda$ are the positions of the molecules and $R_{ij} = |r_i - \mathbf{r}_j|$, then the thermodynamic properties of the fluid can be calculated from either

$$\frac{pV}{NkT} = 1 - \frac{2\pi\rho}{3kT}\int_0^\infty \frac{du}{dR}\, g(R)R^3 dR, \tag{2}$$

$$kT\left(\frac{\partial\rho}{\partial p}\right)_T = 1 + 4\pi\rho\int_0^\infty [g(R) - 1]R^2 dR, \tag{3}$$

or

$$U = \tfrac{3}{2}NkT + 2\pi N\rho\int_0^\infty u(R)g(R)R^2 dR. \tag{4}$$

In the above equations, k is Boltzmann's constant, $\rho = N/V$, and p and U are the pressure and energy of the fluid. The function $g(R)$ is called the *radial distribution function* and is proportional to the probability of finding two molecules separated by a distance R. The constant of proportionality is chosen so that $g(R) \to 1$ as $R \to \infty$.

We call (2), (3) and (4) the *pressure*, *compressibility* and *energy equations*, respectively.

In this paper we assume that $u(R)$ is given by the 6:12 potential:

$$u(R) = 4\epsilon\left\{\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right\}. \tag{5}$$

There is now considerable evidence,[2] for a real system such as argon, that (1) is not valid and that the 6:12 potential is not a close approximation to $u(R)$. Thus, the most meaningful comparison of theoretical results based on (5) is not with experimental results but with the quasi-experimental direct simulation (Monte Carlo and molecular dynamics) results.[3-5] If the experimental results for argon are reduced by means of the parameters $\epsilon/k = 119.8$ K and $\sigma = 3.405$ Å then the simulation results and the experimental results are, in general, in good agreement for both liquid and solid argon. This is to some extent accidental and does not imply that $u(R)$ is an accurate pair potential. However, it does provide a justification for making comparisons with experimental results for argon. We will consider more accurate pair potentials in later publications.

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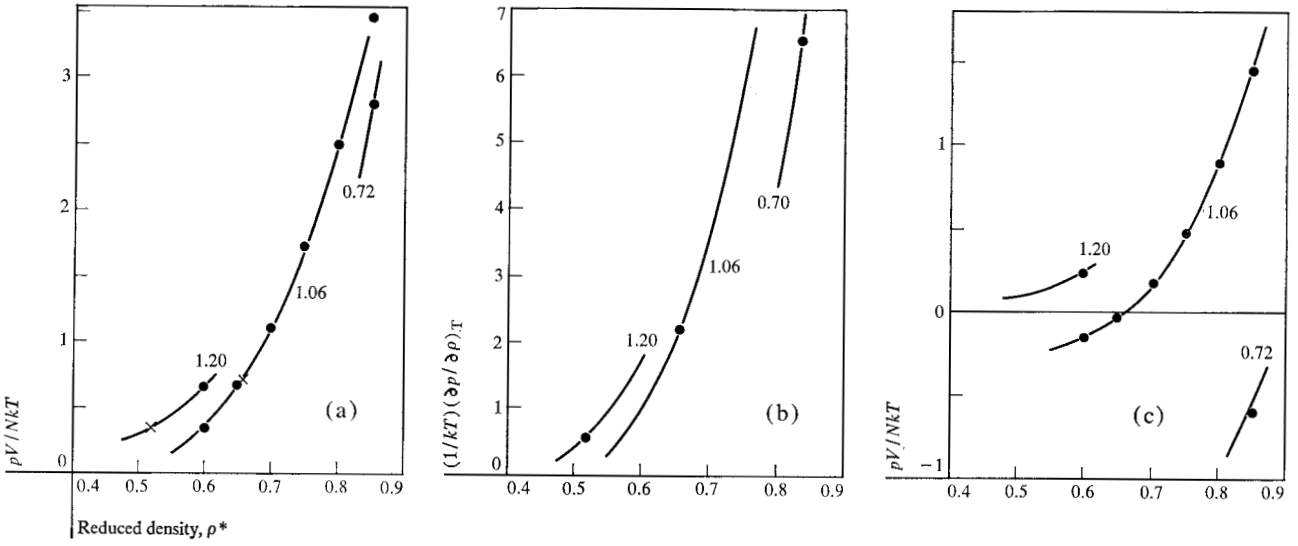


Figure 1 Pressure and compressibility curves giving results of our calculations. The curves are isotherms labelled with the appropriate reduced temperatures. (a) Pressure, calculated from Eq. (2). The points given by × and ● give the results of Levesque (Ref. 9) and Mandel et al. (Ref. 11), respectively, also calculated from Eq. (2). (b) Compressibility from Eq. (3). Points give results of Levesque (Ref. 9), also calculated from Eq. (3). (c) Pressure calculated from Eq. (10). Points are results of Mandel et al. (Ref. 11), also calculated from Eq. (10).

The most widely used theory for obtaining $g(R)$ is that of Percus and Yevick[1] (PY). In the PY theory, $g(R)$ satisfies the integral equation:

$$y(12) = 1 + \rho \int f(13)y(13)[e(23)y(23) - 1]\, d\mathbf{r}_3, \quad (6)$$

where $e(R) = \exp\{-\beta u(R)\}, \qquad (\beta = 1/kT)$ (7)

$$f(R) = e(R) - 1, \text{ and} \quad (8)$$

$$y(R) = g(R)/e(R). \quad (9)$$

For convenience we use the notation $y(12) \equiv y(R_{12})$ etc. At this point we might mention that, if exact results for $g(R)$ are used, then (2), (3) and (4) will yield the same exact equation of state. However, the PY $g(R)$ is not exact and, as a result, the consistency of these equations is lost.

Previously, several authors[6–13] have solved (6) for $g(R)$ assuming Eq. (5) and then used (2) and (3) to calculate the equation of state. At high temperatures, the results obtained from (2) and (3) are consistent and are in good agreement with the simulation and experimental results. However, at the low temperatures characteristic of the liquid phase, (2) and (3) yield results which differ widely from each other and which are in poor agreement with the simulation and experimental results.[9,11,13] As a result the PY theory has come to be regarded as an unsatisfactory theory of the liquid state.

This view is no longer justified. Recently, Chen et al.,[14] as a result of considerations based on the perturbation theory of liquids,[15] have shown that the PY values for $g(R)$ may be used with (4) to obtain values for the equation of state. This method involves more computation than the conventional method based on (2) and (3), because it involves a temperature integration to evaluate the free energy from the energy. The PY equation is then solved for many temperatures. However, the method leads to excellent results. In this paper we present the results of our calculations, based on the energy equation, for the 6:12 potential. A preliminary account of these results has appeared elsewhere.[16]

Solution of PY equation

Rather than solve (6) directly we have used the method developed by Baxter.[17] Our procedure is the same as that described by Watts[12] except that we follow his most recent procedure[13] and do not truncate $u(R)$ until $R > 6\sigma$. In addition, since $y(R)$ varies much less rapidly than either $u(R)$ or $e(R)$, we have interpolated additional values of $y(R)$ before calculating the thermodynamic properties from (2), (3) or (4).

Inasmuch as our method, which is based on the energy equation, involves numerical integrations and differentiations to obtain the thermodynamic properties, we need as much accuracy as possible. In this regard it is of interest to compare our results with those of other investigators since one measure of the accuracy of both our computational procedures and those of the other investigators is the degree of consistency of the different results. Thus, we have compared our results, calculated from (2) and (3), with those of Levesque[9] and Mandel et al.,[11] in Figs. 1(a) and 1(b). The agreement is good.

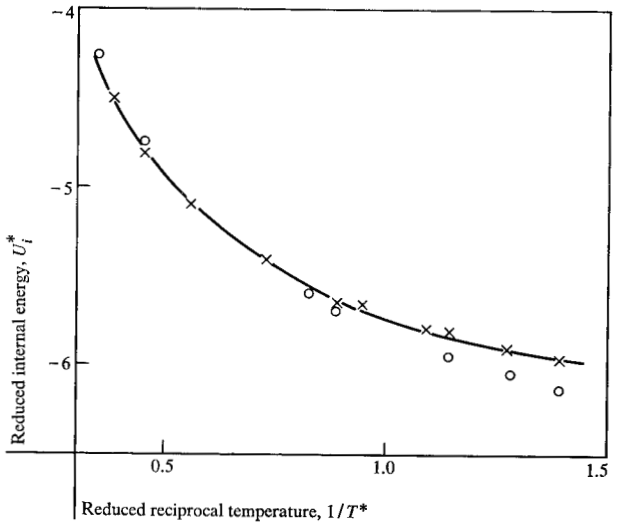
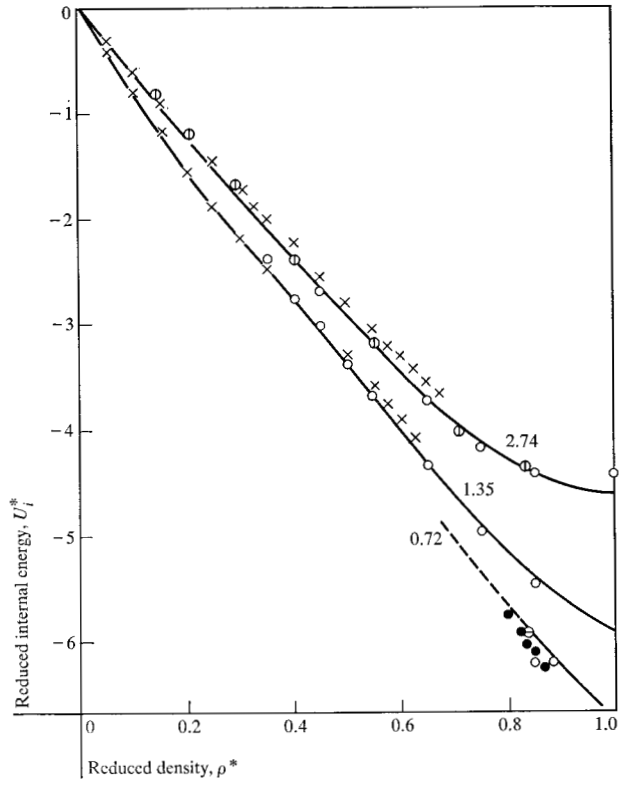


Figure 2(a) Internal energy calculated from Eq. (4). The curve gives the results of our calculations for $\rho^* = 0.85$. The points given by × give the results of the calculations of Mandel et al. (Ref. 11), also calculated from Eq. (4), and points given by ○ give the simulation results of Verlet (Ref. 5).

Figure 2(b) Internal energy calculated from Eq. (4). The curves are isotherms and are labelled with the appropriate reduced temperatures. The broken portion of the lowest temperature isotherm lies inside the two-phase region of the energy equation of state. The points given by ⦶, ●, and ○ are simulation results taken from Refs. 3, 4 and 5, respectively. The point given by ⊖ was calculated from experimental data in Refs. 20 and 21 and the points given by × are experimental results taken from Ref. 23.



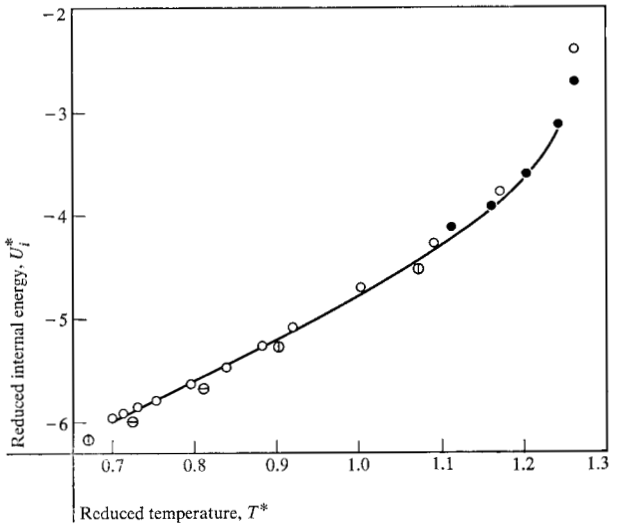


Figure 2(c) Internal energy at saturated vapor pressures. The curve gives the results calculated from Eq. (4) using the *experimental* argon densities. The points given by ⊖ and ⦶ are simulation results taken from Refs. 4 and 5, respectively. The points given by ○ were calculated from experimental data in Refs. 20 and 21 and the points given by ● are experimental results taken from Ref. 22.

The reduced temperature and density are $T^* = kT/\epsilon$ and $\rho^* = \rho\sigma^3$, respectively.

At low temperatures there is, for a given temperature, a range of densities for which (6) has no solution. Thus, the compressibility-equation pressures cannot be obtained by a simple numerical integration of the compressibilities obtained from (3). However, Baxter[18] has shown that if the pressure is calculated from

$$\frac{pV}{NkT} = 1 + 2\pi\rho \int_0^\infty R^2 c(R)\{g(R) - 2\}dR + (2\pi^2\rho)^{-1} \int_0^\infty q^2\{\ln [1 - \rho\tilde{c}(q)] + \rho\tilde{c}(q)\}dq, \quad (10)$$

where $c(R)$ is the direct correlation function which is given, in the PY theory, by

$$c(R) = f(R)y(R), \quad (11)$$

and the Fourier transform of $c(R)$ and is given by

$$\tilde{c}(q) = \frac{4\pi}{q} \int_0^\infty Rc(R) \sin qRdR, \quad (12)$$

then the compressibility obtained from these pressures is identical to those given by (3). The results which we have obtained using (10) are in good agreement with those of Mandel et al.[11] This agreement may be seen in Fig. 1(c).

Finally in Fig. 2(a) we compare our results for the energy, calculated from Eq. (4), with those calculated by

Mandel et al.[11] The reduced internal energy is defined as

$$U_i^* = U/N\epsilon - \tfrac{3}{2}T^* \tag{13}$$

The agreement is good.

From these comparisons we see that all the calculations of the PY thermodynamic properties are in good agreement. Khan's results[7] are an exception and appear to be seriously in error.[9]

Energy and heat capacity

We have calculated U_i^* from (4) for $0.69 < T^* \leq 2.74$ in steps of 0.01 in $(T^*)^{-1}$ and for $0.05 \leq \rho^* \leq 1.00$ in steps of 0.025. This wide range of temperatures and densities includes the entire liquid state and most of the gaseous state for which simulation results or experimental results[19-25] are available.

In Figs. 2(a), (b), and (c) we have shown the results of our calculations for the energy. The agreement with the simulation and the reduced experimental results for argon is excellent. We have obtained the reduced internal heat capacity at constant density,

$$C_i^* = C_v/Nk - \tfrac{3}{2}, \tag{14}$$

by means of a three-point numerical differentiation. These results are shown in Figs. 3(a) and (b) and are seen to be in good agreement with the simulation and the reduced experimental results for argon.

The most interesting feature of our calculations of the PY heat capacity is that the heat capacity becomes large in the critical region. It is difficult to reach definitive conclusions since we have only numerical results. The heat capacity, however, appears to be infinite at the compressibility equation critical point. This conjecture is supported by the fact that Baxter has found the heat capacity to be a system of adhesive hard spheres, for which analytic calculations can be made in the PY approximation, to be infinite at the critical point in the compressibility equation.

As we have already mentioned, the singularity in the heat capacity occurs at the compressibility equation critical point and, as we shall see, not at the energy equation critical point. This inconsistency in the PY theory does not seem too important when one considers that the PY theory is, to our knowledge, the first approximate theory to predict an infinity in the heat capacity at constant density of a liquid at the critical point.

It should be kept in mind that, for the system of adhesive hard spheres, the PY critical exponent for the heat capacity singularity is not in good agreement with the experimental value for real liquids. No doubt the PY critical exponents for the 6:12 potential are also not reliable.

At first sight it may seem unrealistic to use Baxter's adhesive hard sphere model to support our conjectures

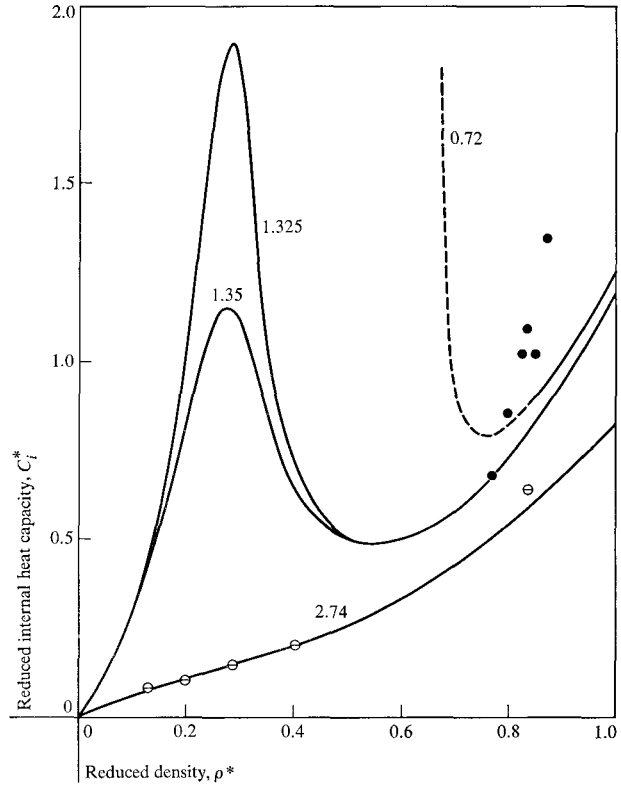
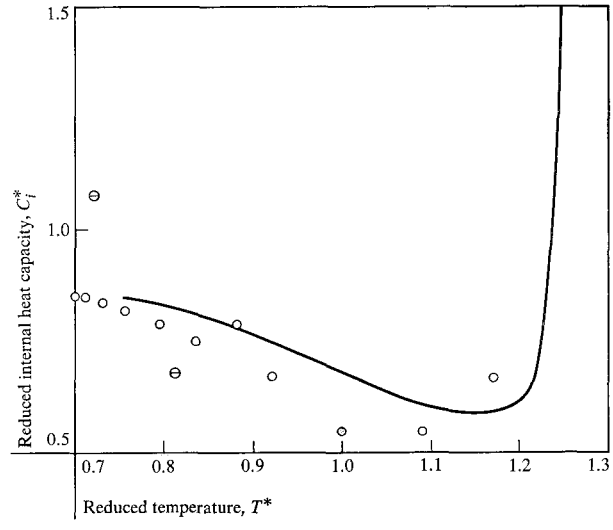


Figure 3(a) Internal heat capacity calculated from Eq. (4). The curves are isotherms and are labelled with the appropriate reduced temperatures. The broken part of the lowest temperature isotherm lies inside the two-phase region of the energy equation of state. The points given by ⊖ and ● are simulation results taken from Refs. 3 and 4, respectively.

Figure 3(b) Internal heat capacity at saturated vapor pressures. The curve gives the results calculated from Eq. (4) using the *experimental* argon densities. The points given by ⊖ are simulation results taken from Ref. 4 and the points given by ○ are experimental results taken from Ref. 21.



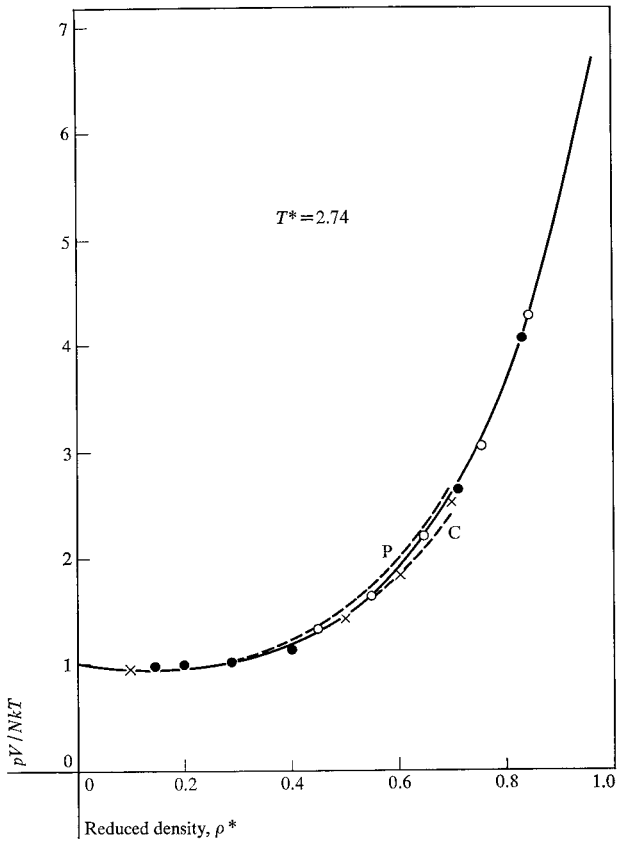


Figure 4(a) Equation of state of 6:12 fluid at $T^* = 2.74$. The solid curve gives the perturbation theory results which are used to obtain A_0, and the broken curves marked P and C give the PY pressure and compressibility results. The points given by ● and ○ are simulation results taken from Refs. 3 and 5, respectively. The points given by × are experimental results taken from Ref. 23.

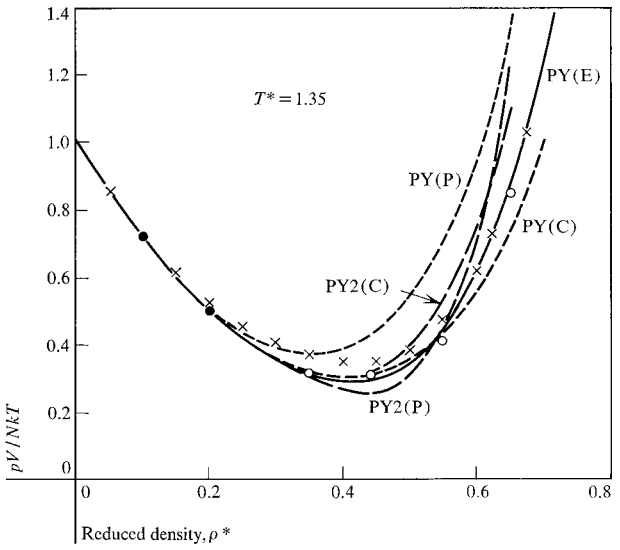
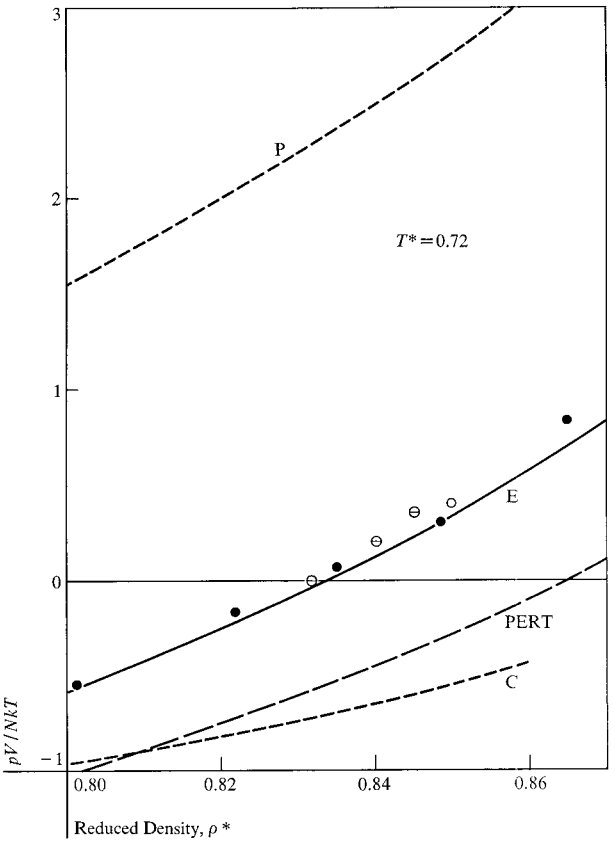


Figure 4(b) Equation of state of 6:12 fluid at $T^* = 1.35$. The curves give the theoretical results. The points given by ○ and ● give the simulation results taken from Refs. 5 and 37, respectively, and the points given by × give experimental results taken from Ref. 23.

Figure 4(c) Equation of state of 6:12 fluid at $T^* = 0.72$. The curves give the theoretical results. The points given by ● and ○ give the simulation results taken from Refs. 4 and 5, respectively, and the points given by ⊖ are experimental results taken from Ref. 24.



concerning the infinity in the heat capacity at the critical point, but critical exponents appear not to depend strongly on the nature of the system.

Baxter's calculation, however, must be considered as providing only weak support for the above conjecture because a potential of Baxter's type is somewhat unphysical. It is possible that his model may not answer delicate questions about C_v correctly. Also, as Baxter points out, there are unresolved difficulties in taking the limit that must be taken preparatory to calculating C_v. Thus the question as to whether the PY value for C_v at the critical point is still open.

Bearman et al.[26] have investigated the extrema in the heat capacity and found good agreement with experiment away from the critical point. Thus one heretofore unknown success of the PY theory is its ability to give good results for the heat capacity away from the critical point and to give results for the heat capacity at the critical point that are better than those of other approximate theories of liquids.

Energy equation of state

Our procedure is to integrate (4) with respect to $1/T$ to obtain the Helmholtz free energy:

$$\frac{A - A_0}{NkT} = -\tfrac{1}{2}\rho \int_{\beta_0\epsilon}^{\beta\epsilon} G d(\beta\epsilon), \tag{15}$$

where

$$\epsilon G(T, \rho) = -4\pi \int_0^\infty g(R)u(R)R^2 dR \tag{16}$$

and A_0 is the Helmholtz free energy at the reference temperature $\beta_0\epsilon$. The pressure may be obtained by differentiating (15) with respect to ρ. For the reference temperature we chose $\beta_0\epsilon = 1/2.74$, which is high enough so that the PY theory is reliable. This may be seen from Fig. 4(a). At $T^* = (\beta\epsilon)^{-1} = 2.74$ both the pressure and compressibility isotherms are in good agreement with the simulation and experimental argon results. We could use either the PY pressure or compressibility isotherm to provide A_0. However, we chose to use perturbation theory to obtain A_0. In Fig. 4(a) we see that the perturbation theory result is virtually in exact agreement with the simulation and experimental results.

In Fig. 2(a) we have plotted the internal energy as a function of $1/T^*$ for $\rho^* = 0.85$. The function is smooth and thus there is no difficulty in performing the numerical integration. For comparison we have plotted the simulation results. The PY results lie somewhat higher than the simulation results at the lower temperatures. This might lead one to anticipate that poor results would be obtained from (15) at low temperatures. However, the area between the PY and simulation is small and, as we will see, does not cause any appreciable errors.

In Figs. 4(b) and (c) we have compared the PY results obtained from the pressure, compressibility and energy equations with virial expansion,[28] simulation and argon experimental results. As the temperature is lowered the pressure (and, to a lesser extent, the compressibility) results become seriously in error. On the other hand the energy equation results are virtually in exact agreement with the simulation and experimental results.

In fact, as may be seen from Fig. 4(b), the PY energy results are better than the pressure or compressibility results obtained from the more complex second-order PY2 theory.[27,29] In Fig. 4(c) we have included the perturbation theory results (using the exact second-order term) for $T^* = 0.72$. Although the perturbation theory result is better than the PY pressure or compressibility results, it is inferior to the PY energy result. One might be tempted to generalize and conjecture that the PY energy equation is superior to perturbation theory. We feel that this is a premature conclusion because we have some indication, based on calculations using other potentials, that the relative merits of the PY theory and perturbation theory may vary somewhat with the potential used.

One further virtue of this approach based on the energy equation is that we obtain results for the free energy. The free energy cannot be calculated directly from the pressure or compressibility equations because such a calculation of the free energy involves a density integration. This presents no problem at high temperatures. However, at low temperatures there is a range of densities for which the PY equation has no solution. As a result the density integration cannot be performed. Thus, we can calculate the properties of the 6:12 liquid in equilibrium with its vapor. These results are shown in Figs. 5(a), (b), and (c). The PY energy results are virtually in exact agreement with the machine results—even in the critical region. Since the simulation calculations are made for finite systems, they do not take account adequately of the long-range correlations characteristic of the critical region. Thus, the critical point of the 6:12 fluid is almost certainly at a lower temperature than the machine calculations indicate. Hence, the PY energy estimates of the critical point are almost certainly in error. However, it is interesting that they are as accurate as the simulation results. This may be seen from Table 1. We have included the PY pressure critical constants in Table 1. Since these constants are determined by extrapolation into the region where the PY theory has no solution, we do not regard the numbers as having much meaning. However, we do include them because they are widely quoted.

We have calculated the entropy from the energy equation and (15). In Figs. 6(a) and (b) we have plotted the results for the internal entropy defined by

$$S_i^* = S_i/Nk$$
$$= S/Nk - \tfrac{5}{2} - \tfrac{3}{2} \ln\left(\frac{2\pi mkT}{h^2}\right) - \ln \rho. \tag{17}$$

The agreement with the simulation and experimental results is excellent.

Finally, we have considered the solidification of the 6:12 fluid for which simulation results[30] and experimental results are available.[31] The PY theory, as formulated in (6), assumes the fluid to be isotropic and thus is not able to treat solidification. However, we can adopt the procedure of Henderson and Barker[32] and use a separate theory to calculate the free energy of the solid phase. As may be seen from Table 2, if the cell model[33] is used for the 6:12 solid, reasonable results are obtained for the triple-point properties. If simulation results[34] for the 6:12 solid are used, excellent results are obtained.

Discussion

In this paper we have shown that the PY theory is an excellent theory of the liquid state when used with the

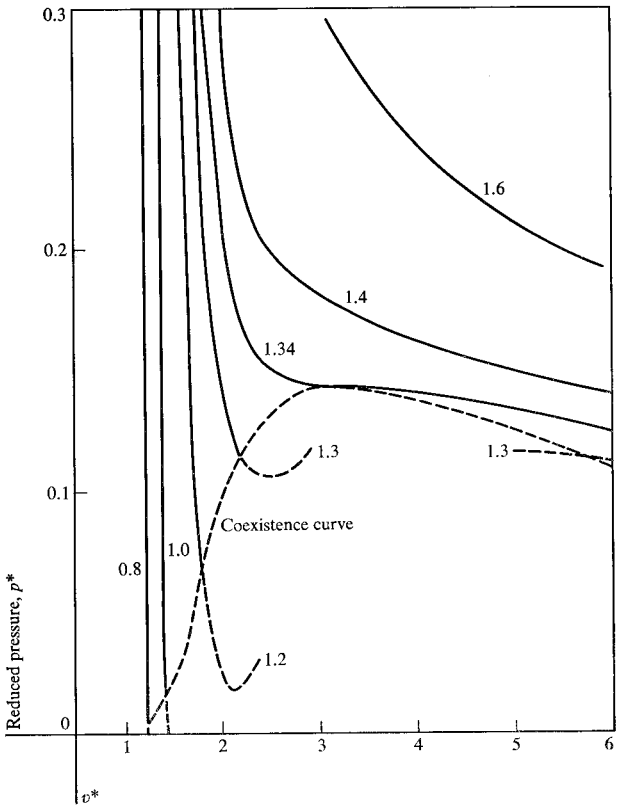


Figure 5(a) Equation of state of 6:12 fluid. The solid curves are isotherms calculated from Eq. (15) and are labelled with the appropriate reduced temperatures. The reduced volume is $v^* = V/N\sigma^3$.

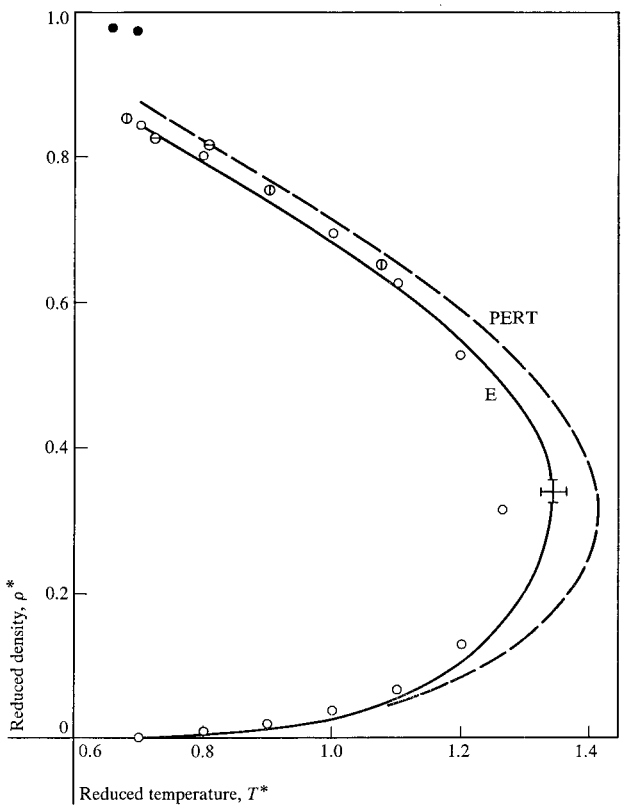
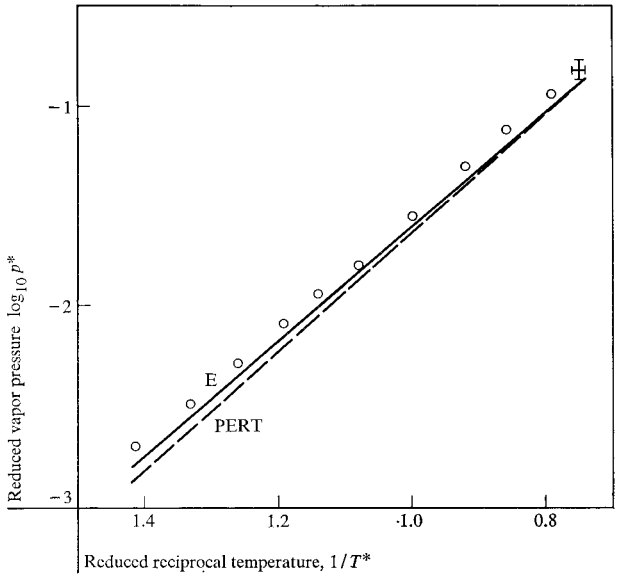


Figure 5(b) Densities of coexisting phases of 6:12 fluid. The solid curve gives the theoretical results calculated from Eq. (15) and the broken curve gives the perturbation theory results calculated using the exact second-order term. The points given by ⊖ and ⓘ are machine calculation results taken from Refs. 4 and 5, respectively, and the points given by ○ and ● are experimental results for liquid and solid argon and are taken from Refs. 19 and 20, respectively. The large cross gives the machine calculation estimate, together with error bounds, of the critical point and is taken from Ref. 5.

Figure 5(c) Reduced vapor pressures for 6:12 fluid. The solid curve gives results calculated from (15) and the broken curve gives perturbation theory results calculated using the exact second-order term. The points are reduced experimental values for Ar (Ref. 21) and the large cross gives the simulation estimate, together with error bounds, of the critical point (Ref. 5).



energy equation. Insight into why the energy equation is the preferred route to thermodynamics may be found by using perturbation theory.[15] If a perturbational expansion of $g(R)$, using hard spheres as the reference system, is undertaken then it can easily be established[14] that the nth order perturbation term for $g(R)$ gives rise to the nth order perturbation term in the thermodynamic properties if either the pressure or compressibility equation is used. However, if the energy equation is used then the nth order perturbation term in $g(R)$ gives rise to the $(n+1)$th order perturbation term in the thermodynamic properties.

The success of perturbation theory, not only in our formulation[15] but also alternative formulations,[35,36] has shown that the structure of a dense fluid is determined primarily by the repulsive forces, which are well represented by a hard-sphere potential, with the attractive forces merely providing the "internal pressure" which

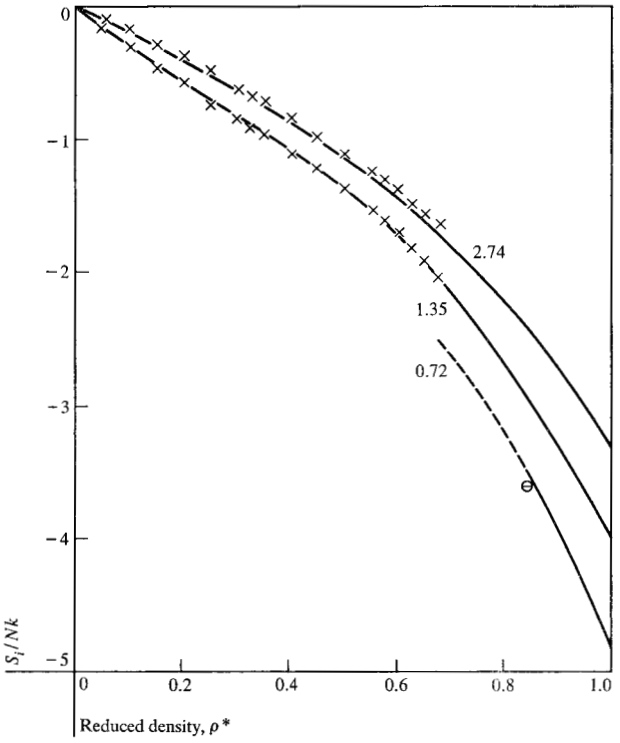


Figure 6(a) Internal entropy calculated from Eq. (15). The curves are isotherms and are labelled with the appropriate reduced temperatures. The broken portion of the lowest temperature isotherm lies inside the two-phase region of the energy equation of state. The points given by × are experimental results taken from Ref. 23 and the point given by ⊖ was calculated from experimental data in Refs. 20 and 21.

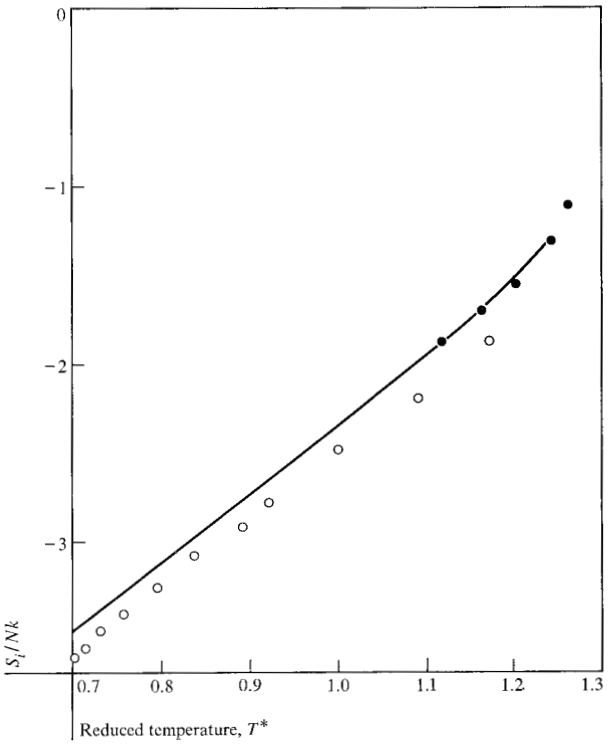


Figure 6(b) Internal entropy at saturated vapor pressures. The curve gives the results calculated from Eq. (4) using the *experimental* argon densities. The points given by ○ were calculated from experimental data in Refs. 20 and 21 and the points given by ● are experimental results taken from Ref. 22.

Table 1 Critical constants for 6:12 potential.

	T_c^*	ρ_c^*	p_c^*	p_cV_c/NkT_c
Expt	1.26	0.316	0.117	0.293
MD	1.32–1.36	0.32–0.36	0.13–0.17	0.30–0.36
Present	1.34	0.34	0.14	0.31
PY(P)	1.25[a]	0.29[a]	0.11[a]	0.30[a]
PY(C)	1.32	0.28	0.13	0.36
PY2(P)	1.36	0.36	0.15	0.31
PY2(C)	1.33	0.33	0.15	0.34
Pert	1.41	0.32	0.17	0.38

[a] Determined by extrapolation

Table 2 Triple-point properties for 6:12 potential.

	T_t^*	p_t^*
Expt	0.699	0.00163
Machine Calc	0.68 ± 0.02	
Present[a]	0.64	0.0006
Present[b]	0.704	0.0020

[a] Using cell model for solid phase
[b] Using machine calculation results for solid phase

maintains the high density. The PY theory is an excellent theory of hard spheres and thus gives a good value for the zeroth-order perturbation term in the expansion of $g(R)$. From this term, good estimates for the zeroth-order contributions to the thermodynamic properties will be obtained when the pressure and compressibility equations are used and a good estimate of the *first*-order contribution will be obtained when the energy equation is used. It is hard to comment on the higher-order terms in the expansion of $g(R)$. However, explicit calculations using the square-well potential indicate that they are not too accurately described by PY theory.[14] Thus if an accurate expression for A_0 is used in (15), the energy equation of state will be accurate in both the zeroth- and first-order perturbation terms, whereas the pressure and compressibility equations of state will be accurate only in zeroth order. This difference is highly significant because the zeroth- and first-order terms are important and of the

same order of magnitude, the second- and higher-order terms being small.[15,37] Thus the energy equation will yield more reliable results.

Furthermore, since the values of the integrals (2) and (3) are small residues resulting from differences in large quantities, small errors in $g(R)$ can cause large errors in thermodynamic quantities. On the other hand, the integrand in (4) is predominantly negative, so the (4) is less sensitive to errors in $g(R)$.

When used with the energy equation, the PY theory is at least comparable in accuracy to the perturbation theory of liquids. The reason we refrain from making the conclusion that the PY theory is more accurate than perturbation theory is that the reliability of a theory depends on the order to which it is taken. The PY theory is a first-order theory and there is some evidence [see Fig. 4(b)], that the PY2 theory will be less successful than the PY theory. The perturbation results we have shown are calculated including the effects of the second-order term. Had first-order perturbation results been displayed, perturbation theory would have been about as accurate as the PY theory. Perturbation theory has the virtue of being easier to use and of providing a simple physical picture. On the other hand the PY theory is, at least for the 6:12 fluid, more accurate and gives more informative results for the heat capacity.

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Note added in proof

Our recent work has supported our conjectures concerning the nature of critical point singularities in the PY theory. We have developed an analytical proof that at the critical density the PY heat capacity at constant density has the form

$$C_v = \frac{\text{constant}}{[T - T_c]^{\frac{1}{2}}}$$

near the critical point. In addition, we have made detailed numerical studies confirming the above result.

Also, our recent calculations of the second-order perturbation term using longer computer runs have shown our previous results to be somewhat in error at the highest densities. If the revised second-order term is used, the second-order perturbation equation of state is as good as the PY energy equation of state.

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