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Phase diagrams of Lennard-Jones fluids

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Phase diagrams of Lennard-Jones fluids

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Smit and Frenkel¹ have shown that the phase diagram of the two-dimensional Lennard-Jones fluid depends largely on the details of the truncation of the potential. In this Note, Gibbs-ensemble calculations are reported for the three-dimensional Lennard-Jones fluid. As expected, the phase diagram for this system also depends significantly on the details of the truncation.

The Lennard-Jones potential is defined by

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (1)$$

where r is the distance between two particles. In a Monte Carlo simulation the potential is usually truncated at a distance $r = R^c$. Simulations are performed with this truncated potential. The influence of the tail of the potential is usually estimated analytically, by assuming that $g(r) = 1$ for distances greater than the cut-off radius. If one is interested in interfacial properties, this tail correction cannot be added straightforwardly. The simulations are then performed with a truncated potential

$$\Phi(r) = \begin{cases} \phi(r) & r \leq R^c \\ 0 & r > R^c \end{cases}. \quad (2)$$

The cut-off radius is usually set to $R^c = 2.5\sigma$.

Similarly, in a molecular dynamics simulation the forces are truncated at the cut-off radius.² It is important to note that in a molecular dynamics simulation, Eq. (2) is *not* the potential that is simulated. Differentiating Eq. (2) gives a delta function at $r = R^c$ which is inconvenient in a molecular dynamics simulation. Therefore in a molecular dynamics simulation the potential is not only truncated but shifted as well

$$\Phi(r) = \begin{cases} \phi(r) - \phi(R^c) & r \leq R^c \\ 0 & r > R^c \end{cases}. \quad (3)$$

It turns out that the phase diagram of the Lennard-Jones fluids modeled with potentials (1), (2), or (3) is different in each case. These differences are by no means small.

The Gibbs ensemble technique^{3,4} is used to calculate the vapor-liquid curve of the Lennard-Jones fluids modeled with potentials (1) and (3).⁵

The results for the full Lennard-Jones potential together with the results of Refs. 3, 4, and 6 are shown in Fig. 1 and are compared with the results of conventional N , V , T simulations [represented by the equation of state (EOS) of Nicolas *et al.*⁷].

To estimate the critical point we have fitted our results to the scaling law for the density and law of rectilinear

diameters, using the three-dimensional Ising critical exponent, $\beta = 0.32$, which gives $T_c = 1.316 \pm 0.006$ and $\rho_c = 0.304 \pm 0.006$. This estimate of the critical temperature is significantly lower than the estimate obtained from the conventional simulations ($T_c = 1.35$,⁸). In Ref. 4 it is argued that the Gibbs ensemble yields a better estimate of the critical temperature than the conventional simulations. It is interesting to note that our estimate of the critical temperature is in good agreement with the estimate, $T_c = 1.31$, of Sung and Chandler.⁹

The results for the truncated and shifted Lennard-Jones potential [Eq. (3), with $R^c = 2.5\sigma$] are given in Fig. 2. The estimated critical point is $T_c = 1.085 \pm 0.005$ and $\rho_c = 0.317 \pm 0.006$, showing that the truncation has a large effect on the phase behavior.

The phase diagram of the truncated ($R^c = 2.5$), but *not* shifted Lennard-Jones potential [Eq. (2)] has been calculated by Finn and Monson,¹⁰ who have used the EOS of Nicolas *et al.*⁷ (p_{LJ}) for the full Lennard-Jones potential and corrected this equation for the absence of the long tail and the discontinuity in the potential at R^c , so

$$p_{tr} = p_{LJ}(T, \rho) + (8/3)\pi\rho^2(R^c)^{-3}, \quad (4)$$

where p_{tr} is the pressure of the Lennard-Jones fluid with truncated potential. For $T = 0.88$ they showed that this equation is in excellent agreement with Gibbs ensemble calculations.

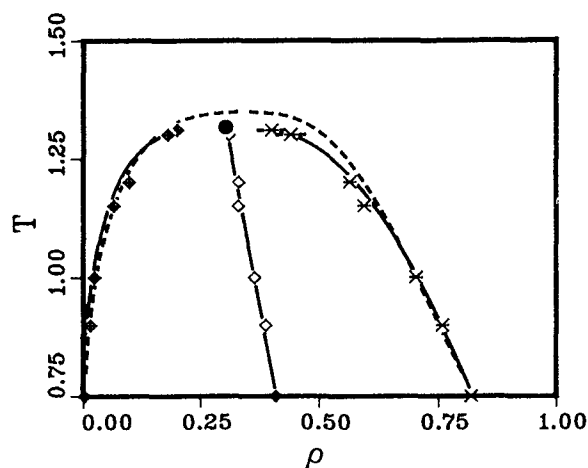


FIG. 1. Phase diagram of the Lennard-Jones fluid, Eq. (1). The solid lines are the fits to the scaling law and the rectilinear law. The dashed line is the EOS of Nicolas (Ref. 7). The points are the simulation results of Refs. 3, 4, and 6, ● is the estimate of the critical point.

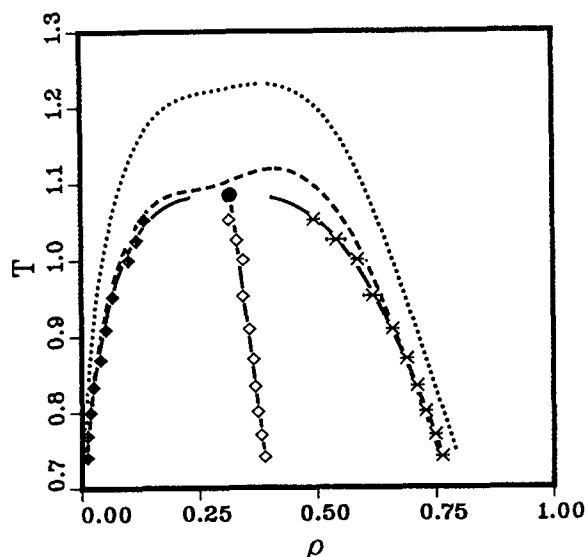


FIG. 2. Phase diagram of the truncated and shifted Lennard-Jones fluid, Eq. (3). The dashed line is the corrected EOS of Nicolas (5). The dotted line is the phase diagram of the truncated but not shifted Lennard-Jones fluid, Eq. (2), as estimated by Eq. (4). See also the caption to Fig. 1.

For the truncated and shifted Lennard-Jones potential there is no discontinuity in the potential, so the only correction to the Nicolas EOS comes from the absence of the long tail in the potential. In this case

$$p_{tr} = p_{LJ}(T, \rho) + (16/3)\pi\rho^2(R^c)^{-3}. \quad (5)$$

Comparison of the predictions of Eq. (5) with the results of the Gibbs ensemble simulations (see Fig. 2) shows that below $T = 0.9$ there is good agreement. However, as can be expected, the agreement is less good close to the critical temperature. Furthermore, close to the critical temperature the phase diagram calculated by Eq. (4) has a strange hump. This is probably due to the extrapolation of the Nicolas equation. Since this EOS contains 32 parameters which have been fitted to simulation data for the full Lennard-Jones potential, its range of validity does not go far beyond the range of the simulation data. Close to the critical temperature of the truncated and shifted Lennard-Jones potential, the full Lennard-Jones potential is metastable and therefore the validity of the Nicolas EOS at those conditions is questionable.

The effect of shifting the Lennard-Jones potential on the phase diagram is also demonstrated in Fig. 2, which

shows that the shift in the potential lowers the critical temperature significantly.

Nijmeijer *et al.* studied¹¹ the effect of the tail of the Lennard-Jones potential on the interfacial tension, using the molecular dynamics technique. Nijmeijer *et al.* observed that including this tail increased the surface tension (γ) by a factor of 2.8 ($T = 0.92$ for both cases), namely $\gamma = 0.24 \pm 0.02$ for $R^c = 2.5$ and $\gamma = 0.63 \pm 0.02$ for $R^c = 7.33$. Nijmeijer *et al.* attributed this effect to the omission of the tail. This study shows that including the tail also influences the phase diagram significantly. When we use the scaling law for the surface tension to estimate the surface tension for $R^c = 7.33$ at the same distance from the critical point, we obtain $\gamma \approx 0.27$. This shows that the increase of the surface tension is mainly due to a shift of the phase diagram. It is therefore unlikely that the discrepancy between simulation results with $R^c = 2.5$ and the measured surface tension of noble gases can be attributed to the omission of the tail, as is suggested in Ref. 11.

To summarize, in this Note the phase diagrams of Lennard-Jones fluids that are often used in simulations are calculated. It is shown that the phase diagram depends largely on the details of the truncation of the potential. These differences are by no means small and must be taken into account when different studies are compared.

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¹ B. Smit and D. Frenkel, *J. Chem. Phys.* **94**, 5663 (1991).

² In some studies the discontinuity of the first derivative of the force is also removed by introducing $\alpha r^2 + \beta$ as an extra term in the potential.

³ A. Z. Panagiotopoulos, *Mol. Phys.* **61**, 813 (1987); A. Z. Panagiotopoulos, N. Quirke, M. Stapleton, and D. J. Tildesley, *ibid.* **63**, 527 (1988).

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⁵ These simulations concern the (approximated) full Lennard-Jones potential (1). The tail corrections are estimated analytically. The cutoff is set equal to half the box size. Note that in the Gibbs ensemble these tail corrections need to be added during a simulation.

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⁷ J. J. Nicolas, K. E. Gubbins, W. B. Streett, and D. J. Tildesley, *Mol. Phys.* **37**, 1429 (1979).

⁸ Note that in this EOS the critical temperature is fixed at $T_c = 1.35$.

⁹ S. H. Sung and D. Chandler, *Phys. Rev. A* **9**, 1688 (1974).

¹⁰ J. E. Finn and P. A. Monson, *Phys. Rev. A* **39**, 6402 (1989); *ibid.* **42**, 2458 (1990).

¹¹ M. J. P. Nijmeijer, A. F. Bakker, C. Bruin, and J. H. Sikkenk, *J. Chem. Phys.* **89**, 3789 (1988).