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LETTER TO THE EDITOR

Lattice and continuous one-dimensional fluid models with a triple point

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Abstract. One-dimensional fluid models with a hard core, a short-range repulsion and a long-range attraction are considered. For certain parameter ranges there is a triple point where vapour, liquid and close-packed phases meet. Results for a lattice model are compared with results for the corresponding continuous model and are found to be qualitatively similar. However, the symmetry with respect to density in the lattice model is absent in the continuous model and the temperature and pressure at the triple point are much higher in the former than in the latter.

We consider a one-dimensional lattice model and the corresponding continuous model, both of which display a triple point for certain parameter ranges when a hard-core interaction, a short-range repulsion and a long-range attraction are present. Since one-dimensional models cannot develop long-range order the place of the solid state in experimental phase diagrams is taken in the theoretical phase diagrams by a close-packed fluid state. The other two phases present will be referred to as liquid and vapour respectively. Runnels (1972) has reviewed the effect on the phase diagram of changing the lattice mesh size in two- and three-dimensional fluid models while Hall and Stell (1973) and Kaye and Burley (1974) have derived phase diagrams for two-dimensional models with a hard core extending over several lattice spacings and a long-range attraction. The present simple model has the advantage that, apart from making the range of the potential infinite, no approximations need be introduced and it is possible to compare a coarse lattice mesh with an infinitely fine mesh (i.e. with the continuous case.)

Introduce a density ρ scaled so that the maximum possible value of ρ is 1. Let the length occupied by each molecule when $\rho = 1$ be a . (In the lattice model a is the lattice spacing while in the continuous model it is the hard-core length.) Denote the configurational free energy per length a in a reference model without long-range interaction by $f_c^*(\rho, T)$, T being the absolute temperature. Then the pressure p^* and the configurational chemical potential μ_c^* in the reference model are given by

$$p^*a = \rho\mu_c^* - f_c^*, \quad \mu_c^* = \partial f_c^* / \partial \rho. \quad (1)$$

With a long-range attraction the configurational free energy is given by

$$f_c(\rho, T) = f_c^*(\rho, T) - K\rho^2, \quad K > 0. \quad (2)$$

Lebowitz and Penrose (1966) showed that the convex envelope of the function (2) at

constant T represents the limiting free energy when the attractive interaction between a pair of molecules becomes infinitely small at each point, but of infinitely long range. The parameter K is proportional to an integral over d -dimensional space where $d = 1$ in the present case. The corresponding forms of pressure and chemical potential are given by

$$pa = p^*a - K\rho^2, \quad \mu_c = \mu_c^* - 2K\rho. \quad (3)$$

In the lattice model it is supposed that nearest-neighbour molecules have a repulsive interaction energy $\epsilon > 0$. Using the transfer matrix method for the grand partition function, the relation between chemical potential and pressure in the reference model is

$$\begin{vmatrix} ze^{-\beta\epsilon} - x & z^{1/2} \\ z^{1/2} & 1 - x \end{vmatrix} = 0, \quad (4)$$

where

$$x = \exp(\beta p^*a), \quad z = \exp(\beta\mu_c^*), \quad \beta = (kT)^{-1}, \quad (5)$$

k being Boltzmann's constant. If a variable Ω defined by

$$\Omega = (x/z) \exp(\beta\epsilon) \quad (6)$$

is introduced, equation (4) takes the form

$$(\Omega - 1)(x - 1) = \exp(\beta\epsilon). \quad (7)$$

The chemical potential μ_c^* can be derived as a function of p^* and T from (6) and (7). The density is then given by the relations

$$\frac{1-\rho}{\rho} = \frac{\bar{l}}{a} - 1 = \frac{1}{a} \frac{\partial \mu_c^*}{\partial p^*} - 1 = \frac{x(\Omega - 1)}{\Omega(x - 1)}, \quad (8)$$

where \bar{l} is the mean length per molecule. Once we have the density ρ in the reference model for a pair of values of p^* and μ_c^* the corresponding values p and μ_c for the model with long-range interaction can be derived from (3). Then phase equilibrium can be obtained by plotting μ_c against p .

For the lattice model, however, it is better to make use of certain symmetry properties in deriving the phase diagram. First, note that from (3) and (5)

$$pa = kT \ln x - K\rho^2 \quad (9)$$

and then define the quantity P by

$$Pa = kT \ln \Omega - K(1 - \rho)^2 = pa - \mu_c + \epsilon - K. \quad (10)$$

Equations (6), (9) and (3) were used in deriving the last expression. Now, from (7) it is possible to interchange values of x and Ω . It follows from (8) that ρ and $1 - \rho$ are then interchanged and from (9) and (10) that p and P are also interchanged. Hence if P is plotted against p at a given temperature the curve will be symmetrical about the line $P = p$. Any self-intersection of this curve implies phases with different densities but equal values of p and μ_c and corresponds to phase equilibrium. If the intersection lies on the line $P = p$ the conjugate phases have densities ρ and $1 - \rho$. Any self-intersection which is off the line $P = p$ has a 'twin' placed symmetrically on the other side of this line. Hence if phases with densities ρ_1 and ρ_2 , where $\rho_1 \neq 1 - \rho_2$ are in equilibrium then there is another pair of conjugate phases at the same temperature with densities $1 - \rho_1$ and $1 - \rho_2$.

For $\frac{1}{2} > \epsilon/K > 0.317$ there is vapour/close-packed equilibrium between $T = 0$ and the triple point, where the liquid phase appears. Above the triple point there are liquid/close-packed and vapour/liquid equilibrium lines which, because of the symmetry properties, terminate in critical points at the same temperature (see figure 1). In the (T, ρ) plane the phase diagram is symmetrical about the line $\rho = \frac{1}{2}$ (see figure 3). For $\epsilon/K > \frac{1}{2}$ the short-range repulsion is too large for the close-packed phase to occur at low pressures and there are non-intersecting liquid/close-packed and vapour/liquid equilibrium lines in the (T, p) plane. These leave the p axis at the origin and the point $pa = \epsilon - \frac{1}{2}K$ respectively and terminate at the same temperature. For $0.317 > \epsilon/K$ there is only one equilibrium line.

The lattice fluid can be transformed into a magnetic model which was treated by Nagle (Nagle 1970, Bonner and Nagle 1971). The molecules and 'holes' are equivalent to 'up' and 'down' dipoles with an antiferromagnetic short-range exchange energy parameter $J = \frac{1}{4}\epsilon$ and a long-range interaction energy $-\frac{1}{4}Km^2$ per site, where $m = 2\rho - 1$ is the relative magnetization. The dipoles are acted on by an external field H , where $Hd = \frac{1}{2}(\mu_c - \epsilon + K)$, d being the dipole strength. The relation between the grand partition function for the fluid and the partition function $(PF)_M$ for the magnet is given by

$$\exp[\beta N(pa - \frac{1}{2}\mu_c)] = \exp[\frac{1}{4}\beta N(K - \epsilon)](PF)_M,$$

N being the number of sites. The symmetry properties of the fluid are related to the field-reversal symmetry of the magnet. They can be deduced from the invariance of $(PF)_M$ with respect to change of sign of H .

We now consider the corresponding continuous fluid. The short-range interaction energy between two molecules with centres at distance r is given by

$$v(r) = \begin{cases} \infty & 0 \leq r < a \\ \epsilon & a \leq r < 2a \\ 0 & 2a \leq r. \end{cases} \quad (11)$$

Thus the 'hard core' of each molecule is of length a and two molecules can have non-zero short-range interaction energy only when no other molecule is situated between them. Thus the reference model is a Takahashi gas (see, for instance, Thompson 1972). The relation between μ_c^* and p^* can be obtained from a constant-pressure partition function and is given by

$$\begin{aligned} \exp(-\beta\mu_c^*) &= \frac{1}{a} \int_0^\infty \exp[-\beta(v(r) + p^*r)] dr \\ &= \frac{\exp(-\beta p^*a)}{\beta p^*a} \{ \exp(-\beta\epsilon)[1 - \exp(-\beta p^*a)] + \exp(-\beta p^*a) \}. \end{aligned} \quad (12)$$

The constant factor a^{-1} makes the right-hand side dimensionless. By using the thermodynamic relation expressed by the first three members of equation (8) we then have

$$\frac{1-\rho}{\rho} = \frac{1}{\beta p^*a} + \frac{\exp(\beta\epsilon) - 1}{\exp(\beta\epsilon) - 1 + \exp(\beta p^*a)}. \quad (13)$$

This gives a relation between p^* and ρ and equation (3) is now used to plot μ_c against p for the continuous model with long-range interaction and hence derive the phase equilibria. It is found that there is a triple point when the parameters lie in the range $\frac{1}{2} > \epsilon/K > 0.225$.

In the figures results for the lattice and continuous model are compared for the short-range/long-range energy parameter ratio $\epsilon/K = 9/20$. Figure 1 gives the phase equilibrium diagram in the (T, p) plane for the lattice model, with the corresponding diagram for the continuous model shown by the broken curves. Figure 2 gives part of the (T, p) phase diagram, including the triple point, for the continuous model with the pressure scale enlarged. The critical point for liquid/close-packed equilibrium in the continuous model occurs at too high a pressure to be shown in either diagram: the critical values are $pa/\epsilon = 0.3509$, $kT/\epsilon = 0.3294$, $\rho = 0.6688$. Figure 3 compares phase

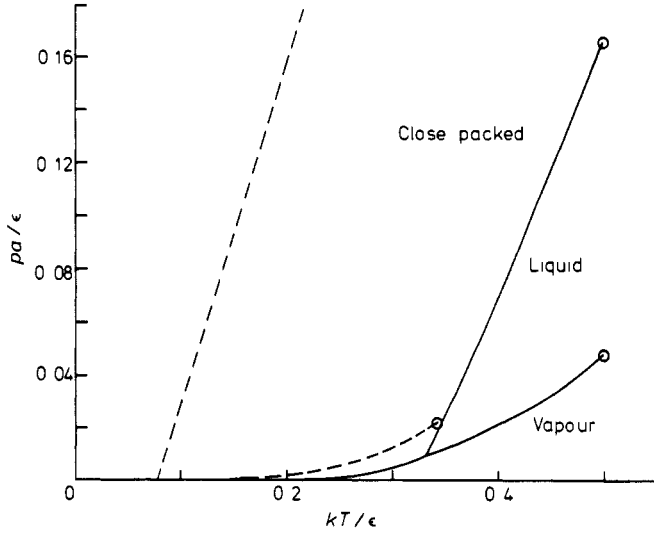


Figure 1. Phase equilibrium diagrams in the temperature–pressure plane for the lattice and continuous fluids (the broken curves represent the continuous case).

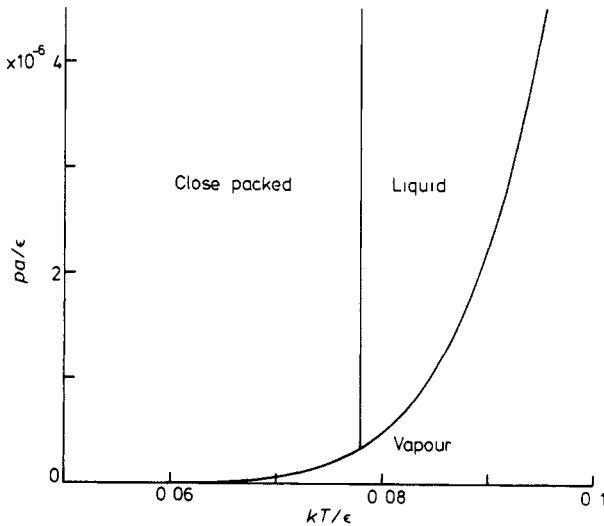


Figure 2. Part of phase equilibrium diagram in the temperature–pressure plane for the continuous fluid (the pressure scale is larger than in figure 1).

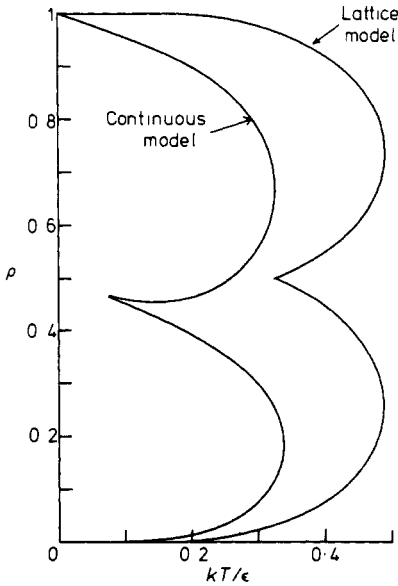


Figure 3. Phase equilibrium diagrams in the temperature–density plane for the lattice and continuous fluids.

diagrams in the (T, ρ) plane. In general the results show that the behaviour of the lattice and continuous models is qualitatively similar, except that the symmetry about $\rho = \frac{1}{2}$ is seen to be an artifact of the lattice model. Quantitatively there are considerable differences, particularly in the position of the triple point whose temperature and pressure are much higher for the lattice fluid than for the continuous one. It is of interest that a phase diagram so similar to the experimental vapour/liquid/solid diagram can be obtained in models where the close-packed state differs from the liquid state in the amount of work against repulsive forces needed to establish the phase but where long-range order is absent. However, in the present models there is a liquid/close-packed critical point although, particularly for the continuous fluid, its pressure is very much higher than that of the vapour/liquid critical point. In observed systems, on the other hand, no liquid/solid critical point has ever been found. The explanation is probably that in the absence of long-range order the close-packed and liquid phases in the models become indistinguishable at very high pressures. Experimentally, on the other hand, long-range order differentiates between the solid and liquid phases even at indefinitely high pressures.

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