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A continuous one-dimensional fluid as the limit of a lattice fluid

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Abstract. The basic model treated is a linear fluid in which each molecule has a hard core of length a and there is an interaction energy $\epsilon(r)$ when the hard cores of two molecules are separated by a distance r , for $r < a$. In the lattice version the hard core of each molecule occupies n sites and there is an interaction energy ϵ_q when there are q vacant sites between the hard cores of two neighbouring molecules, for $q < n$. The constant-pressure partition function is constructed for a general value of n and the equation of state deduced. It is shown that, with the ϵ_q appropriately related to the function $\epsilon(r)$, the equation of state of the lattice fluid tends to that of the continuous fluid when the mesh of the lattice becomes infinitely fine ($n \rightarrow \infty$), with the hard-core length kept constant. For rectangular-well interactions it is shown that the difference between the equation of state of the continuous fluid and that of the lattice fluid for any value of n depends solely on hard-core effects.

Three models displaying the water-like property of a maximum on density isobars in a low-pressure range are treated. Density isobars for lattice models with various values of n are compared with those of the continuous fluid. The relative magnitude of hard-core and attractive interaction effects in the lattice 'error' is considered for a parabolic well fluid.

1. Introduction

Although lattice fluid models (sometimes called lattice gases) and continuum fluid models are concerned with the same type of physical system, detailed comparison between them is rather rare. However the lattice model can be regarded as a kind of 'finite difference' approximation to the continuous case and it seems likely that, as the mesh of the lattice is reduced for molecules of a given size, results for the lattice fluid will approach those for the corresponding continuous fluid. A convenient measure of mesh fineness is n , where a pair of molecules at closest approach have their centres on n th-neighbour sites of the lattice. The lattice fluid equivalent to the Ising model corresponds to $n = 1$, first-neighbour exclusion models to $n = 2$, and so on. There have been a number of treatments with $n > 1$, both for molecules with hard-core repulsion only and for molecules with an interaction energy at closest approach. The lattices have been mainly two-dimensional and either series or matrix methods have been used (see the review by Runnels 1972). Kaye and Burley (1974a, b) have discussed a two-dimensional first-neighbour exclusion lattice model with more extended attractive interactions. However, for two- and three-dimensional systems the methods used for $n > 1$ are approximate and it is prohibitively difficult to consider more than a small value of n . Again, there are no exact results for the corresponding continuous models. Accordingly it seemed interesting to investigate a one-dimensional lattice model where

exact results can be obtained for any value of n and the approach to the continuous fluid for large n considered. This is the subject of the present paper. It should be mentioned that Hoover *et al* (1964) discussed a non-interacting gas on a one-dimensional lattice for general n and also compared the $n = 1$ case for a lattice fluid with a square-well interaction with the corresponding continuous fluid for Boltzmann factor values 0.1 and 10.

In § 2 of the present paper a one-dimensional lattice fluid with a hard core occupying n sites and an interaction field extending over a further n sites is treated. A constant-pressure partition function is derived for a general value of n and an equation of state giving the length of the assembly as a function of the (one-dimensional) pressure and temperature is deduced. (An Appendix gives an alternative method based on a combinatorial formula and the canonical ensemble.) In § 3 a Takahashi continuous fluid with a hard core of length a and an interaction field extending over a further distance a is introduced and a method of approximating by a lattice model described. It is shown that, as n tends to infinity and the lattice site separation to zero in such a way that the core and interaction lengths remain constant, the lattice equation of state tends to that of the continuous fluid. In § 4 it is shown that for a rectangular-well interaction the difference between the lattice and continuous expressions for assembly length at given pressure and temperature depends only on hard-core effects. It is also shown that this result can be generalised to a multiple rectangular-well interaction provided that n is chosen appropriately.

Although there are no phase transitions in a one-dimensional system with short-range interaction it is possible to represent cooperative phenomena depending on short-range order, such as the anomalous density maximum in water. To obtain water-like behaviour there must be a low density configuration which has lower energy than any denser configurations, leading to regions of open structure stable at low pressures. In § 5 three models having this characteristic, but with different forms of interaction energy, are considered. Lattice approximations for different values of n are compared numerically with continuous fluid results for all three models. In the third (parabolic well) model the contributions to the difference between the assembly lengths for the continuous and $n = 2$ lattice cases from the hard-core repulsion and the attractive 'well' interaction respectively are compared. Bell (1969) has previously compared water-like one-dimensional lattice and continuous models but the lattice model was confined to $n = 1$ and did not represent a first approximant to the continuous fluid in the sense of the present paper.

2. Hard-core lattice fluid with interaction of limited range

One-dimensional lattice and continuous fluids have been reviewed by Thompson (1972), but in the lattice case explicit solutions are given only when the interactions are confined to pairs of molecules on adjacent sites. In the present section an equation of state will be derived for a one-dimensional lattice fluid where each molecule has a hard core occupying n sites and a potential field extending over a number of further sites. Two molecules with no other molecule between them will be termed 'neighbouring'. It will be supposed that interaction is confined to neighbouring pairs and that such a pair has interaction energy ϵ_q when there are q vacant sites between the two molecules. Let us denote the distance between two adjacent lattice sites by b and the hard-core length nb by a . Then, if attention is focused on the centres of neighbouring molecules, the

foregoing assumptions imply that the interaction energy is infinite when the centres are separated by a distance of less than a and equal to ϵ_q when they are at a distance $a + qb$ for $q \geq 0$.

The constant-pressure partition function for the one-dimensional lattice fluid will now be derived. We denote the number of molecules in the assembly by M and the number of vacant sites between the r th and $(r + 1)$ th molecules in order along the lattice by q_r . The numbers of vacant sites between the first and M th molecules respectively and the boundaries are denoted by q_0 and q_M . There is assumed to be no interaction energy between these molecules and the boundaries. Then the configuration energy E_c and the length L of the assembly for given values of $q_0, q_1, \dots, q_{M-1}, q_M$ are given by

$$E_c = \sum_{r=1}^{M-1} \epsilon_{q_r}, \quad L = Mnb + \sum_{r=0}^M q_r b = Ma + \sum_{r=0}^M q_r b. \quad (1)$$

The constant-pressure partition function for the assembly of M molecules at absolute temperature T and (one-dimensional) pressure p is then

$$\Phi = \Phi(M, T, p) = \sum_L e^{-\beta p L} \sum_c e^{-\beta E_c}, \quad (2)$$

$(kT)^{-1}$ being denoted by β where k is Boltzmann's constant. Here the inner summation is over all possible positions of the molecules in length L . It is now useful to define

$$\xi = e^{-\beta p b} = e^{-\beta p a / n}. \quad (3)$$

Then, using (1), equation (2) may be written in the form

$$\Phi = \xi^{Mn} \sum_L \sum_c \xi^{q_0 + q_M} \prod_{r=1}^{M-1} \xi^{q_r} \exp(-\beta \epsilon_{q_r}). \quad (4)$$

However, the sum over all configurations and over all values of L may also be effected by summing over all values of each q_r ($r = 0, \dots, M$) from 0 to ∞ . We can then write

$$\Phi = \xi^n (1 - \xi)^{-2} \phi^{M-1}, \quad \phi = \xi^n \sum_{q=0}^{\infty} \xi^q e^{-\beta \epsilon_q}. \quad (5)$$

The two factors $(1 - \xi)^{-1}$ in ϕ result from summation from 0 to ∞ over the possible numbers of vacant sites between an end molecule and a boundary. The summation in each factor ϕ is over the possible numbers of vacant sites between the molecules of a neighbouring pair.

We shall now suppose that $\epsilon_q = 0$ for $q \geq n$. There is thus no interaction between molecules with centres at distance $2a$ or greater, where a is the hard-core length. Since two molecules with another molecule between them must have their centres at least $2a$ apart, the restriction of interaction to neighbouring molecules becomes automatic and our assumptions are self-consistent. For $q \geq n$, the terms in ϕ become a geometrical progression and

$$\phi = \xi^n \left(\sum_{q=0}^{n-1} \xi^q e^{-\beta \epsilon_q} + \xi^n (1 - \xi)^{-1} \right). \quad (6)$$

The mean length occupied by the assembly at temperature T and (one-dimensional) pressure p is given by

$$\bar{L} = \sum_L L e^{-\beta p L} \sum_c e^{-\beta E_c} / \Phi = -\beta^{-1} \partial \ln \Phi / \partial p. \quad (7)$$

A mean length per molecule is defined by

$$l_n = \bar{L}/M \quad (8)$$

where the subscript n represents the number of lattice sites occupied by each hard core and is a measure of the closeness of the lattice mesh. In the thermodynamic limit, when $M \rightarrow \infty$, the contribution of the boundary terms in Φ to l_n becomes negligible and substitution of (5) in (7) yields

$$l_n = -\beta^{-1} \partial \ln \phi / \partial p = b \xi \partial \ln \phi / \partial \xi, \quad (9)$$

using the definition (3) of ξ . Substituting (6) in (9),

$$l_n = a + b \frac{n \xi^n (1 - \xi)^{-1} + \xi^{n+1} (1 - \xi)^{-2} + \sum_{q=0}^{n-1} q \xi^q e^{-\beta \epsilon_q}}{\xi^n (1 - \xi)^{-1} + \sum_{q=0}^{n-1} \xi^q e^{-\beta \epsilon_q}} \quad (10)$$

where $a = nb$ is the hard-core length and it can be seen that $l_n \rightarrow a$ as $p \rightarrow \infty$ ($\xi \rightarrow 0$). This is the required equation of state giving l_n in terms of T and p . A little manipulation yields the useful alternative form

$$l_n = a + \frac{b \xi}{1 - \xi} + b \frac{\sum_{q=0}^{n-1} [q - (q+1)\xi] \xi^q (e^{-\beta \epsilon_q} - 1)}{1 + (1 - \xi) \sum_{q=0}^{n-1} \xi^q (e^{-\beta \epsilon_q} - 1)}. \quad (11)$$

Instead of the Boltzmann factors $e^{-\beta \epsilon_q}$ we now have Mayer factors $e^{-\beta \epsilon_q} - 1$ and when $\epsilon_q = 0$ for all q the third term on the right-hand side of (11) disappears. Hence the first two terms give the mean length per molecule for a lattice gas with hard-core repulsion only. It is useful to define a number density ρ by

$$\rho = Ma/\bar{L} = a/l_n. \quad (12)$$

Hence ρ is the ratio of the number of molecules on a lattice of given length \bar{L} to the number \bar{L}/a present at closest packing ($p = \infty$) and the largest value of ρ is 1, attained at closest packing.

An alternative combinatorial method of deriving the equation of state is given in the Appendix.

3. The continuous one-dimensional (Takahashi) fluid as a limit

We now consider an assembly of rod-like molecules of length a , which can be placed on a line in any way, provided that no rods overlap. Two rods with centres at a distance $a + r$ apart have interaction energy $\epsilon(r)$, where $\epsilon(r) = 0$ for $r \geq a$. The last condition ensures that the interaction is confined to neighbouring molecules. (As in the previous section, a pair of molecules is termed 'neighbouring' if there is no other molecule between them.) The function $\epsilon(r)$ is bounded in the domain $0 \leq r < a$ and is also continuous, except possibly at a finite number of points. If $r = c$ is a point of discontinuity it is assumed that the limits $\epsilon(c - 0)$ and $\epsilon(c + 0)$ both exist. The equation of state of such an assembly can be approximated by that of a lattice model like that of the previous section with each hard core occupying n sites and distance $b = a/n$ between adjacent sites. The interaction energies ϵ_q between neighbouring molecules separated by q vacant lattice sites will be prescribed by the relation

$$\epsilon_q = \frac{1}{b} \int_{qb}^{(q+1)b} \epsilon(r) dr \quad q = 0, 1, \dots, n-1. \quad (13)$$

It will now be shown that as $n \rightarrow \infty$ (i.e. $b \rightarrow 0$), for fixed length a , the equation of state for the lattice fluid tends to that for the continuous fluid. First, introduce a set of quantities ϵ'_q where $\epsilon'_q = \epsilon(qb)$ if $\epsilon(r)$ is continuous at $r = qb$ and $\epsilon'_q = \epsilon(qb + 0)$ if $\epsilon(r)$ is not continuous at $r = qb$. Now, from the definition (13), $e^{-\beta\epsilon_q}$ lies between the greatest and least values of $e^{-\beta\epsilon(r)}$ in the interval $qb \leq r \leq qb + b$. Also, in any range where $\epsilon(r)$ is continuous, $e^{-\beta\epsilon(r)}$ is also continuous and hence uniformly continuous. Now the domain in which $\epsilon(r) \neq 0$ can be divided into a finite number of ranges where $\epsilon(r)$ is continuous, separated by points of discontinuity. Hence for any value of δ , however small, a value of b can be found such that

$$|e^{-\beta\epsilon_q} - e^{-\beta\epsilon'_q}| < \delta \tag{14}$$

for all q except where there is a discontinuity in the interval $qb \leq r \leq qb + b$. For an interval where there is a discontinuity the left-hand side of (14) is bounded since we have assumed that $\epsilon(r)$ is bounded. Hence, since the number of discontinuities is finite and $b \rightarrow 0$ as $n \rightarrow \infty$,

$$\begin{aligned} \lim_{n \rightarrow \infty} b^2 \sum_{q=0}^{n-1} q \xi^q e^{-\beta\epsilon_q} &= \lim_{n \rightarrow \infty} b^2 \sum_{q=0}^{n-1} q \xi^q e^{-\beta\epsilon'_q} \\ &= \int_0^a r e^{-\beta pr} e^{-\beta\epsilon(r)} dr \end{aligned} \tag{15}$$

where the last relation of (15) is a consequence of the standard theory of the Riemann integral. Similarly

$$\lim_{n \rightarrow \infty} b \sum_{q=0}^{n-1} \xi^q e^{-\beta\epsilon_q} = \int_0^a e^{-\beta pr} e^{-\beta\epsilon(r)} dr \tag{16}$$

and it is easy to show that

$$\lim_{b \rightarrow 0} \frac{1 - \xi}{b} = \lim_{b \rightarrow 0} \frac{1 - e^{-\beta pb}}{b} = \beta p. \tag{17}$$

Hence, from (10) above, keeping $nb = a$ fixed as n increases, we have

$$\lim_{n \rightarrow \infty} l_n = l_c = a + \frac{e^{-\beta pa}(1 + \beta pa) + (\beta p)^2 \int_0^a r e^{-\beta pr} e^{-\beta\epsilon(r)} dr}{\beta p \{e^{-\beta pa} + \beta p \int_0^a e^{-\beta pr} e^{-\beta\epsilon(r)} dr\}}. \tag{18}$$

This is the required result since l_c in (18) is the length per molecule for the continuous model introduced at the beginning of this section. The expression for l_c can be obtained from that given by Lieb and Mattis (1966) or by Bell (1969) for a Takahashi gas, if the interaction between neighbouring molecules is restricted to a range equal to the hard-core length. It may be transformed to

$$l_c = a + \frac{1}{\beta p} + \frac{\int_0^a (\beta pr - 1) e^{-\beta pr} (e^{-\beta\epsilon(r)} - 1) dr}{1 + \beta p \int_0^a e^{-\beta pr} (e^{-\beta\epsilon(r)} - 1) dr} \tag{19}$$

which is the limit of the form given for l_n in equation (11) above as $n \rightarrow \infty$, with $nb = a$ kept fixed as n increases.

The same limit would be attained as $n \rightarrow \infty$ and the proof of limiting properties would be easier if the ϵ'_q were used instead of the ϵ_q defined by (13) as interaction energies in the lattice approximation to the continuous fluid. However, for certain cases the approximation would be much worse for small n values. It may be noted that, while

the restriction of the interaction range to $r < a$ is physically self-consistent in that it automatically prevents interaction between pairs of molecules with a third molecule between them, it is possible to have an interaction of range $h > a$ and to postulate that it acts only between nearest neighbours. It is then necessary to replace a by h in the integrals of (19). To derive lattice approximations the formalism of § 2 above up to and including equation (5) could be applied. A corresponding result to equation (11) would be obtained with the summations taken from $q = 0$ to $q = n_1$ where $n_1 b$ is the smallest multiple of b greater than or equal to h . The continuous case would again be the limit of the lattice approximation as $b \rightarrow 0$ with a fixed. With interactions of infinite range the limiting arguments would be rather more complicated. Falk (1974a, b) has considered a continuous fluid of Ising spins with a neighbouring pair interaction of infinite range.

It is useful to define the difference

$$\Delta l_n(T, p) = l_c(T, p) - l_n(T, p), \quad (20)$$

where we have shown that $\Delta l_n \rightarrow 0$ as $n \rightarrow \infty$. For a continuous fluid with hard-core repulsion only, $\epsilon(r) = 0$ for $r > 0$ and the last term on the right-hand side of (19) vanishes. Similarly, for a lattice fluid with hard-core repulsion only, the last term on the right-hand side of (11) vanishes. Then

$$\Delta l_n = \Delta l_n^{(\text{hc})} = \frac{1}{\beta p} - \frac{\xi b}{(1-\xi)} = \frac{1}{\beta p} - \frac{a}{n(e^{\beta p a/n} - 1)}, \quad (21)$$

using the definition (3) of ξ . For the general model,

$$\Delta l_n = \Delta l_n^{(\text{hc})} + \Delta l_n^{(\text{int})} \quad (22)$$

where $\Delta l_n^{(\text{hc})}$ is given by (21) and $\Delta l_n^{(\text{int})}$ is the contribution of the interaction field outside the hard core and is the difference between the last terms on the right-hand sides of equations (19) and (11) respectively.

4. Multiple rectangular-well models

It will now be shown that there is a class of models where $\Delta l_n^{(\text{int})}$, as defined by equation (22), is zero although there are interactions in addition to the hard-core repulsion. It is convenient to list some preliminary results. Using integration by parts for the second relation it is easy to show that

$$\beta p \int_c^d e^{-\beta p r} dr = e^{-\beta p c} - e^{-\beta p d}, \quad \int_c^d (\beta p r - 1) e^{-\beta p r} dr = c e^{-\beta p c} - d e^{-\beta p d}. \quad (23)$$

The corresponding lattice sums are

$$(1-\xi) \sum_{q=s}^t \xi^q = \xi^s - \xi^{t+1} = e^{-\beta s a/n} - e^{-\beta(t+1)a/n} \quad (24)$$

$$\sum_{q=s}^t [q - (q+1)\xi] \xi^q = s \xi^s - (t+1) \xi^{t+1} = s e^{-\beta s a/n} - (t+1) e^{-\beta(t+1)a/n}.$$

The first relation of (24) is just the summation of a geometrical progression while the second can easily be obtained by writing

$$[q - (q+1)\xi] \xi^q = q \xi^q - (q+1) \xi^{q+1}.$$

Now introduce a rectangular-well model defined for the continuous case by

$$\epsilon(r) = -u \quad (0 \leq r < a), \quad \epsilon(r) = 0 \quad (a \leq r), \quad (25)$$

where u is a constant. Substitution into (19) and the use of (23) with $c = 0$ and $d = a$ immediately gives

$$l_c = a + \frac{1}{\beta p} - a \frac{(e^{\beta u} - 1) e^{-\beta p a}}{1 + (e^{\beta u} - 1)(1 - e^{-\beta p a})}. \quad (26)$$

In the lattice approximation (13) gives

$$\epsilon_q = -u \quad (q = 0, 1, \dots, n - 1); \quad \epsilon_q = 0 \quad (q \geq n). \quad (27)$$

Substitution into (11) and the use of (24) with $s = 0$, $t = n - 1$ together with the definition (3) of ξ and the relation $bn = a$ gives

$$l_n = a + \frac{a}{n(e^{\beta p a/n} - 1)} - a \frac{(e^{\beta u} - 1) e^{-\beta p a}}{1 + (e^{\beta u} - 1)(1 - e^{-\beta p a})}. \quad (28)$$

Comparison with (26) shows that for the rectangular-well model there is no contribution to Δl_n from interactions apart from the hard-core repulsion and thus

$$\Delta l_n = \Delta l_n^{(hc)}, \quad \Delta l_n^{(int)} = 0, \quad (29)$$

where the hard-core contribution $\Delta l_n^{(hc)}$ is given by equation (21) above.

The foregoing result can be generalised to a multiple-well model where, in the continuous case,

$$\begin{aligned} \epsilon(r) &= -u_1, 0 \leq r < c_1; & \epsilon(r) &= -u_2, c_1 \leq r < c_2; \\ \dots & & \epsilon(r) &= -u_m, c_{m-1} \leq r < a \end{aligned} \quad (30)$$

where u_1, \dots, u_m are constants. Substitution into (19) and the use of (23) for each energy interval yields

$$l_c = a + \frac{1}{\beta p} - \frac{\sum_{k=1}^m (e^{\beta u_k} - 1)(c_k e^{-\beta p c_k} - c_{k-1} e^{-\beta p c_{k-1}})}{1 + \sum_{k=1}^m (e^{\beta u_k} - 1)(e^{-\beta p c_{k-1}} - e^{-\beta p c_k})} \quad (31)$$

where, in the summations, c_0 and c_m are identified with 0 and a respectively. Now suppose that the ratios between the intervals c_1, c_2, \dots, c_m are rational (e.g. $m = 2$, $c_1 = \frac{1}{2}a$, $c_2 = a$). Then we can put

$$c_k = (\nu_k / \nu) a, \quad \nu = \nu_m \quad (32)$$

where $\nu_1, \nu_2, \dots, \nu_m$ are a set of integers with no common factor. The continuous model can now be approximated by a lattice model if we put $n = \nu n_0$ where n_0 is a positive integer. Then (13) yields

$$\begin{aligned} \epsilon_q &= -u_k \quad (\nu_{k-1} n_0 \leq q < \nu_k n_0, k = 1, \dots, m); \\ \epsilon_q &= 0 \quad (q \geq n) \end{aligned} \quad (33)$$

where ν_0 is defined as 0. Substitution into (11) now yields an expression for l_n with the same third term as in the expression for l_c given by (31). Hence equation (29) is applicable in the multiple-well model. In fact, the single-well model treated at the beginning of this section is just the particular case $m = 1$.

Although we have used the term 'multiple rectangular well' to give a 'picture' of the interaction potential the foregoing derivation is not affected if some or all of the u_k are negative in sign. Change of sign of any u_k changes the sign of the corresponding Mayer factor.

5. Water-like models

We now consider models where, in certain temperature ranges, the density increases with temperature at constant pressure. For such water-like behaviour the interactions between the molecules in the model must simulate hydrogen bonding in real water by giving rise to configurations of low density which have lower energy than closer-packed configurations. Hence regions of open structure are stable at low temperatures and pressures but are progressively broken down by thermal motion as the temperature increases. This counteracts the usual increase of volume with temperature and leads to the phenomenon of negative thermal expansion. At high enough temperatures the regions of open structure have largely disappeared and the thermal behaviour becomes normal. Thus there are density maxima on certain isobars. Previous work (for instance Bell 1969, 1972, Bell and Lavis 1970a, b, Perram 1971, Bell and Sallouta 1975) confirms that anomalous thermal behaviour is confined to isobars in the pressure range where the open structure is stable at $T = 0$. The three models to be discussed are as follows.

5.1. Hard-shoulder model

For the continuous case the interaction energy in this model is defined by: $\epsilon(r) = w > 0, 0 \leq r < a; \epsilon(r) = 0, r > a$. In addition to the hard-core repulsion there is thus an additional finite repulsive energy w for molecules whose centres are separated by distances between a and $2a$. By considering the enthalpy per molecule at $T = 0$ it can be shown that an open structure in which the neighbouring molecular centres are separated by distance $2a$ is stable when $pa < w$. The equation of state for the continuous case is (26), with u replaced by $-w$. Lattice approximations are possible for all values of n and the equation of state is (28), again with u replaced by $-w$. It is not difficult to show that for both the continuous and lattice models $l \rightarrow 2a$ ($\rho \rightarrow \frac{1}{2}$) as $T \rightarrow 0$ for $pa < w$ while $l \rightarrow a$ ($\rho \rightarrow 1$) as $T \rightarrow 0$ for $pa > w$.

The model is an extremely simple one, but rather unsatisfactory in that maxima appear on isobars only in the upper part of the 'open structure' pressure range, just below $p = w/a$. In figures 1 and 2 lattice approximation density isobars are compared with the continuous case for $pa = 0.9w$ and $pa = 1.1w$ respectively. At the lower pressure negative thermal expansion can be seen but at the pressure greater than w/a thermal behaviour is normal.

5.2. Double-well model

For the continuous case the interaction energy in this model is defined by: $\epsilon(r) = -u_1, 0 \leq r < \frac{1}{2}a; \epsilon(r) = -u_2, \frac{1}{2}a \leq r < a; \epsilon(r) = 0, a \leq r$ where $u_2 > u_1 > 0$. The 'bonding' which results in the open structure is represented by the deeper part of the well, which gives an interaction energy of $-u_2$ to pairs of molecules with centres at distances between $\frac{3}{2}a$ and $2a$. From enthalpy considerations it can be shown that at $T = 0$ an open

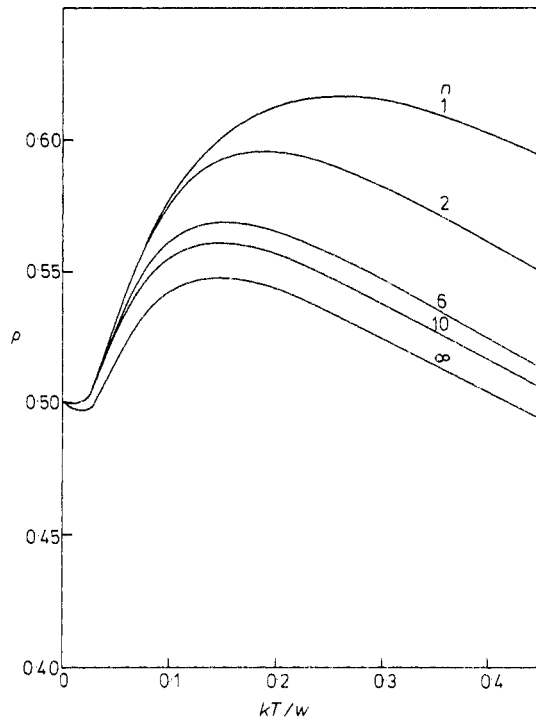


Figure 1. Hard-shoulder model: density/reduced temperature isobars for reduced pressure $pa/w = 0.9$. n denotes number of sites occupied by the hard core of one molecule; the continuous fluid corresponds to $n = \infty$.

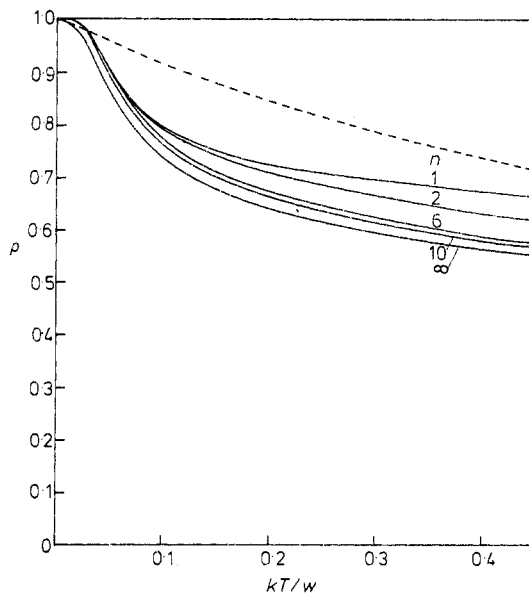


Figure 2. As figure 1 for $pa/w = 1.1$. The broken curve represents the continuous hard-rod fluid without interaction.

structure with the centres of neighbouring molecules at a distance of $\frac{3}{2}a$ is stable for $pa < 2(u_2 - u_1)$. This is a model of the type discussed in § 4 above and the equation of state for the continuous case is given by (31) with $m = 2$, $c_1 = \frac{1}{2}a$, $c_2 = a$. Lattice approximations are possible for even values of n and the equation of state is given by (29) in conjunction with (31). For both the continuous and lattice cases $l \rightarrow \frac{3}{2}a$ ($\rho \rightarrow \frac{2}{3}$) as $T \rightarrow 0$ for $pa < 2(u_2 - u_1)$ while $l \rightarrow a$ ($\rho \rightarrow 1$) as $T \rightarrow 0$ for $pa > 2(u_2 - u_1)$.

Although the open structure must be of lower energy than the close-packed structure for water-like behaviour to occur (i.e. in the present case $u_2 > u_1$) results are more satisfactory for models in which the gap is not too large (Bell and Sallouta 1975). Accordingly the ratio $u_1/u_2 = \frac{3}{4}$ was chosen for calculation, which gives a pressure range $(0, \frac{1}{2}u_2/a)$ for stability of the open structure at $T = 0$. Maxima occur on density/temperature isobars over a larger fraction of this range than is the case for the hard-shoulder model. In figure 3 lattice approximation isobars are compared with the continuous model for $pa = 0.3u_2$ and a range of negative thermal expansion can be seen in all cases.

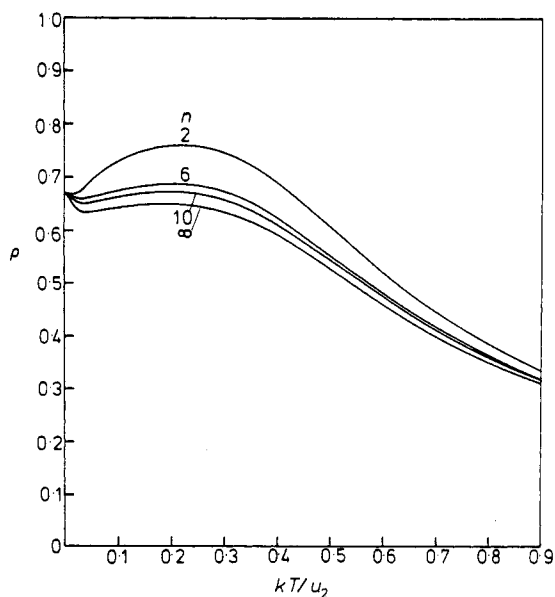


Figure 3. Double-well model; $u_1/u_2 = \frac{3}{4}$: density/reduced temperature isobars for reduced pressure $pa/u_2 = 0.3$. n denotes number of sites occupied by the hard core of one molecule; the continuous fluid corresponds to $n = \infty$.

5.3. Parabolic-well model

The continuous version of this model, in which bonding is represented by a parabolic well separated by a non-zero distance from the hard core, was introduced by Bell (1969). For the calculations performed here the interaction energy is given by: $\epsilon(r) = 0$, $0 \leq r \leq \frac{1}{2}a$, $a \leq r$; $\epsilon(r) = -(8v_0/a^2)(2r-a)(a-r)$, $\frac{1}{2}a \leq r \leq a$. The minimum energy is $-v_0$ at $r = \frac{3}{4}a$. Owing to the continuity of the potential function the behaviour of the system at $T = 0$ is more complicated than that of the two models described above. It can be deduced from equation (7.9) of Bell (1969) that an open structure is stable at $T = 0$ for $pa < 1.373v_0$. From equation (7.8) of Bell (1969), the distance between the centres

of neighbouring molecules in the open structure, which is the limit of l_c as $T \rightarrow 0$, varies from $1.75a$ at $p = 0$ to $1.707a$ at $p = 1.373v_0/a$. For $pa > 1.373v_0$ the molecules are close-packed with $l_c = a$ at $T = 0$. It can be shown that there is a maximum on all isotherms in the range $pa < 1.373v_0$. Lattice approximations are possible for even values of n but it should be noted that in this case it is essential to use the ϵ_q defined by equation (13) above rather than the ϵ'_q . There are differences between the ground states of lattice approximations and continuous fluid which are not present in the other two models. For instance, in the lattice approximation for $n = 2$, $\epsilon_1 = 0$ and $\epsilon_2 = -\frac{2}{3}v_0$, so that the distance between the centres of neighbouring molecules in the open structure is $\frac{3}{2}a$ and the latter is stable at $T = 0$ for $pa < \frac{4}{3}v_0$.

Density/temperature isobars derived from the lattice approximation for several values of n are compared with the continuous fluid isobar for $pa = v_0$ in figure 4 and for $pa = \frac{3}{2}v_0$ in figure 5. For $pa = v_0$ density maxima occur for both the lattice and continuous models but $pa = \frac{3}{2}v_0$ is above the pressure range for negative thermal expansion in all cases. The parabolic-well fluid is not of the 'rectangular-well' type discussed in § 4 above. Hence there is a non-zero contribution $\Delta l_n^{(\text{int})}$ from the attractive interaction in addition to the contribution $\Delta l_n^{(\text{hc})}$ from the hard-core repulsion to the difference Δl_n between the length per molecule l_c in the continuous model and the length l_n in the lattice approximation for given n . In table 1 l_c , Δl_2 and the ratio of the attractive contribution $\Delta l_2^{(\text{int})}$ to Δl_2 are given for a number of temperatures at the two pressures $pa = v_0$ and $pa = \frac{3}{2}v_0$.

6. Discussion

From the three models of water-like type studied it can be seen that in important respects results derived from lattice approximations are qualitatively similar to those from the continuous fluid. Negative thermal expansion occurs in a similar pressure

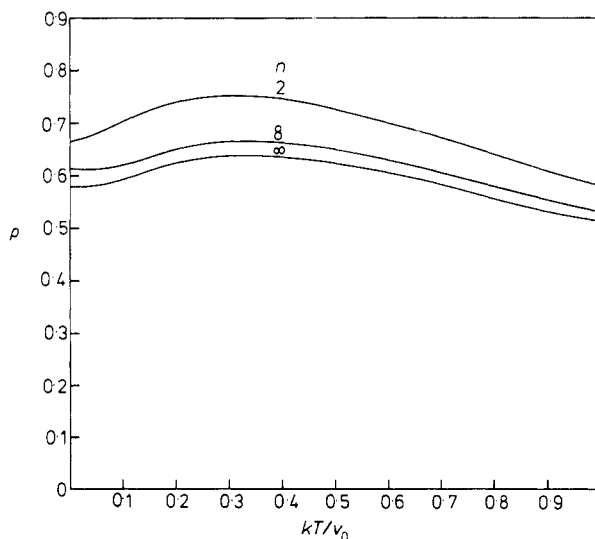


Figure 4. Parabolic-well model: density/reduced temperature isobars for reduced pressure $pa/v_0 = 1$. n denotes number of sites occupied by the hard core of one molecule; the continuous fluid corresponds to $n = \infty$.

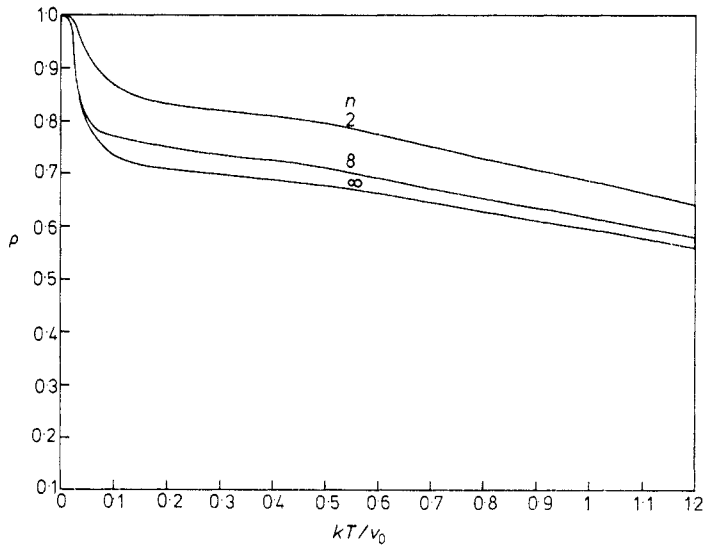


Figure 5. As figure 4 for $pa/v_0 = \frac{3}{2}$.

Table 1.

kT/v_0	$pa/v_0 = 1$			$pa/v_0 = \frac{3}{2}$		
	l_c/a	$\Delta l_2/a$	$\Delta l_2^{(int)}/\Delta l_2$	l_c/a	$\Delta l_2/a$	$\Delta l_2^{(int)}/\Delta l_2$
0.1	1.6893	0.2687	0.6405	1.3601	0.2089	0.6818
0.2	1.6088	0.2587	0.3998	1.4087	0.2098	0.4219
0.3	1.5718	0.2415	0.2399	1.4312	0.2123	0.2684
0.4	1.5729	0.2322	0.1422	1.4532	0.2161	0.1850
0.5	1.6010	0.2278	0.0823	1.4790	0.2191	0.1341
0.75	1.7460	0.2257	0.0145	1.5649	0.2217	0.0574
1.0	1.9487	0.2279	-0.0060	1.6802	0.2226	0.0159
1.5	2.4192	0.2333	-0.0124	1.9795	0.2407	0.0475
2.0	2.9171	0.2371	-0.0104	2.3260	0.2740	0.1444

range for the lattice and continuous models while above this range the density decreases monotonically with temperature along each isobar. Nevertheless it can be seen from figures 1–5 that there are considerable quantitative differences between lattice and continuous fluid isobars for small values of n where n is the number of sites occupied by the hard core in the lattice model. For the parabolic-well model, where away from the hard core the interaction energy is a continuous function of the molecular separation, the lattice and continuous model isobars resemble each other in shape but there is some shift along the density axis. In all three models lattice results for $n = 8$ or 10 are quite close to the continuous case.

For the ‘hard-shoulder’ and ‘double-well’ models the difference between lattice and continuous fluid values for the assembly size at given pressure and temperature is entirely due to hard-core terms. For the ‘parabolic-well’ model the situation is more complicated and the relative magnitudes of contributions to this difference from

hard-core repulsion and attractive interaction respectively varies strongly with temperature. In the neighbourhood of the density maximum the hard-core contribution is several times larger than that of the attractive interaction.

If a long-range attractive interaction of Van der Waals type is incorporated into a one-dimensional model phase transitions can occur. Wilson and Bell (1977) compared an $n = 1$ lattice model with a continuous model for a fluid with hard-core repulsion, a finite repulsive interaction outside the hard core and a long-range attraction. They found a triple point in both the lattice and continuous cases. It is hoped to present results on the convergence of the lattice approximation to the continuous case for one-dimensional fluids with long-range attraction in a further communication.

Appendix

We now develop an alternative method, based on a combinatorial formula, for treating the model of § 2 above. It is supposed that there are M molecules on the N_s sites of a linear lattice and for convenience the lattice is converted into a ring by supposing that the first and last sites are adjacent. Defining a 'neighbouring pair' as two molecules with no other molecule between them, there are then exactly M neighbouring pairs. The hard core of each molecule occupies n sites and, if $N_{MM}^{(q)}$ denotes the number of neighbouring pairs with q vacant sites between the hard cores, then, according to the assumptions of § 2, the interaction energy E_c and the total number of interacting pairs N_{MM} are given by

$$E_c = \sum_{q=0}^{n-1} N_{MM}^{(q)} \epsilon_q, \quad N_{MM} = \sum_{q=0}^{n-1} N_{MM}^{(q)}. \quad (\text{A.1})$$

The number of non-interacting neighbouring pairs (i.e. the number with n or more vacant sites between the hard cores) is then $M - N_{MM}$. Now denote the number of ways of placing the M molecules on the N_s lattice sites with given values of $N_{MM}^{(q)}$ for $q = 0, 1, \dots, n-1$ by $g(N_s, M, N_{MM}^{(q)})$. The given values of the $N_{MM}^{(q)}$ must satisfy the inequality

$$nM + \sum_{q=0}^{n-1} qN_{MM}^{(q)} + n(M - N_{MM}) \leq N_s \quad (\text{A.2})$$

since each hard core occupies n sites and there must be at least n vacant sites for each non-interacting pair. The difference between the two sides of the inequality (A.2) represents the number of 'free vacant sites' which can be placed between the molecules of any non-interacting pair. Accordingly we define

$$N_f = N_s - nM - \sum_{q=0}^{n-1} qN_{MM}^{(q)} - n(M - N_{MM}). \quad (\text{A.3})$$

The configuration number g will now be calculated by building up the required distribution in two steps. The first step is to place M molecules on a ring lattice of $N_s - N_f$ sites in such a way that, for $q = 0, 1, \dots, n-1$, there are a given number $N_{MM}^{(q)}$ of neighbouring pairs with q vacant sites between the two hard cores. From the definition (A.3) of N_f there must now be exactly n vacant sites between the two hard cores for each of the remaining $M - N_{MM}$ neighbouring pairs and all these pairs are thus

identical. Hence the number of ways of achieving a distribution of this type is

$$\frac{M!}{(M - N_{MM})! \prod_{q=0}^{n-1} N_{MM}^{(q)}!} \quad (\text{A.4})$$

The next step is to place the remaining N_f sites between the molecules of the $M - N_{MM}$ non-interacting pairs which can be done in

$$\frac{(N_f + M - N_{MM} - 1)!}{N_f! (M - N_{MM} - 1)!} \quad (\text{A.5})$$

ways. This is the number of ways of placing N_f indistinguishable objects into $M - N_{MM}$ compartments. Since M is assumed to be large and the logarithm of the configuration number will be used we can replace $M - N_{MM} - 1$ by $M - N_{MM}$ in (A.5). Then, forming the product of the expressions (A.4) and (A.5), we have

$$g(N_s, M, N_{MM}^{(q)}) = \frac{M! (N_f + M - N_{MM})!}{[(M - N_{MM})!]^2 N_f! \prod_{q=0}^{n-1} N_{MM}^{(q)}!} \quad (\text{A.6})$$

where N_{MM} and N_f are defined by equations (A.1) and (A.3) respectively.

By using (A.6) in equation (2) above and summing first over N_f and then over the $N_{MM}^{(q)}$ the constant-pressure partition function can be again obtained. However we shall instead use the canonical ensemble and the method of the maximum term. The partition function can be written

$$(\text{PF}) = \sum_{N_{MM}^{(q)}} \Psi(N_s, M, N_{MM}^{(0)} \dots N_{MM}^{(n-1)}) = \sum_{N_{MM}^{(q)}} g e^{-\beta E_c} \quad (\text{A.7})$$

Using (A.1), (A.6) and Stirling's formula

$$\ln \Psi = \ln g - \beta E_c$$

$$\begin{aligned} &= M \ln M + (N_f + M - N_{MM}) \ln (N_f + M - N_{MM}) - N_f \ln N_f \\ &\quad - 2(M - N_{MM}) \ln (M - N_{MM}) - \sum_{q=0}^{n-1} N_{MM}^{(q)} (\ln N_{MM}^{(q)} + \beta \epsilon_q). \end{aligned} \quad (\text{A.8})$$

The equilibrium values of $N_{MM}^{(q)}$, N_{MM} and N_f will be denoted by $\bar{N}_{MM}^{(q)}$, \bar{N}_{MM} and \bar{N}_f respectively and are obtained by maximising (A.6). Hence, noting (A.3) and the second relation of (A.1),

$$\begin{aligned} &\left(\frac{\partial \ln \Psi}{\partial N_{MM}^{(q)}} \right)_{N_{MM}^{(q)} = \bar{N}_{MM}^{(q)}} \\ &= -\beta \epsilon_q - \ln \bar{N}_{MM}^{(q)} - (n - q) \ln \bar{N}_f + (n - q - 1) \ln (\bar{N}_f + M - \bar{N}_{MM}) \\ &\quad + 2 \ln (M - \bar{N}_{MM}) = 0, \quad q = 0, 1, \dots, n - 1. \end{aligned} \quad (\text{A.9})$$

The configurational Helmholtz free energy F_c is given by

$$F_c(M, L, T) = -kT \ln \Psi(N_s, M, \bar{N}_{MM}^{(q)}) \quad (\text{A.10})$$

where $L = N_s b$ is the length of the system, b being the distance between adjacent lattice sites. The (one-dimensional) pressure p is then given by

$$p = - \left(\frac{\partial F_c}{\partial L} \right)_{M, T} = \frac{kT}{b} \left(\frac{\partial \ln \Psi}{\partial N_s} \right)_{\bar{N}_{MM}^{(q)}} = \frac{kT}{b} \ln \frac{\bar{N}_f + M - \bar{N}_{MM}}{\bar{N}_f}. \quad (\text{A.11})$$

From (A.11), using the definition of ξ given by equation (3) above,

$$\frac{\bar{N}_f}{M - \bar{N}_{MM}} = \frac{\xi}{1 - \xi}, \quad \frac{\bar{N}_f + M - \bar{N}_{MM}}{M - \bar{N}_{MM}} = \frac{1}{1 - \xi}. \quad (\text{A.12})$$

Substitution into (A.9) then gives the following result for the number $\bar{N}_{MM}^{(q)}$ of interacting pairs with centres separated by $n + q$ lattice spacings:

$$\bar{N}_{MM}^{(q)} = \xi^{-n} (1 - \xi) (M - \bar{N}_{MM}) \xi^q e^{-\beta \epsilon_a}. \quad (\text{A.13})$$

Summing (A.13) from $q = 0$ to $q = n - 1$ gives the relation

$$\bar{N}_{MM} = \xi^{-n} (1 - \xi) (M - \bar{N}_{MM}) \sum_{q=0}^{n-1} e^{-\beta \epsilon_a} \xi^q, \quad (\text{A.14})$$

from which it may be deduced that

$$M - \bar{N}_{MM} = \phi^{-1} (1 - \xi)^{-1} \xi^{2n} M \quad (\text{A.15})$$

where ϕ is the function defined in equation (6) of § 2 above. Substitution of (A.15) into (A.12) and (A.13) yields

$$\bar{N}_f = \phi^{-1} (1 - \xi)^{-2} \xi^{2n+1} M, \quad \bar{N}_{MM}^{(q)} = \phi^{-1} \xi^{n+q} e^{-\beta \epsilon_a} M. \quad (\text{A.16})$$

Equations (A.15) and (A.16) enable us to write the equation of state:

$$N_s = nM + n(M - \bar{N}_{MM}) + \bar{N}_f + \sum_{q=0}^{n-1} q \bar{N}_{MM}^{(q)} \\ = M \left(n + \phi^{-1} \left[n \xi^{2n} (1 - \xi)^{-1} + \xi^{2n+1} (1 - \xi)^{-2} + \xi^n \sum_{n=0}^{q-1} q \xi^q e^{-\beta \epsilon_a} \right] \right). \quad (\text{A.17})$$

Since the length per molecule l_n is equal to bN_s/M , equation (A.17) immediately yields equation (10) of § 2 above. Hence we have verified that the canonical ensemble, using combinatorial and maximum term methods, yields the same equation of state as the constant pressure ensemble.

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