J. Phys.: Condens. Matter 1 (1989) 7735–7739. Printed in the UK

LETTER TO THE EDITOR

Computer simulation of solid–liquid coexistence in binary hard-sphere mixtures

W G T Kranendonk and D Frenkel
FOM Institute for Atomic and Molecular Physics, PO Box 41883, 1009 DB Amsterdam, The Netherlands

Received 16 August 1989

Abstract. We report the first numerical simulation of the melting curve of a binary mixture. The melting curves of binary hard-sphere mixtures with diameter ratios $\alpha = 0.95$ and 0.90 were obtained by Monte Carlo simulation. For $\alpha = 0.95$ the phase diagram is found to be spindle-like; for $\alpha = 0.90$ it exhibits an azeotrope. We compare these findings with predictions based on density-functional theory.

One of the key problems in statistical mechanics is that of obtaining a simple, yet reliable estimate of the melting point of an atomic or molecular solid for which the intermolecular potential is known.

In recent years, several authors have applied density-functional theory to compute the melting point of atomic solids (for a review, see [1]). On the whole it appears that density-functional theory is quite successful (although not entirely without flaws) in describing the melting of atomic systems. A case where density-functional theory has been applied with considerable success is in the description of the melting transition of the hard-sphere system. For the latter system, second-order density-functional theory predicts [2] that at coexistence $\eta_f = 0.51$, $\eta_s = 0.56$ and $PV_0/NkT = 11.2$, which should be compared with the simulation results of Hoover and Ree [3]: $\eta_f = 0.494$, $\eta_s = 0.545$ and $PV_0/NkT = 8.27\ (\pm 0.13)$. N/V_0 is the density of regular close packing of the hard-sphere solid, η is the volume fraction occupied by the spheres and the subscripts s and f refer to the solid and fluid phase respectively.

Encouraged by the good results obtained with density-functional theory for the pure (monodisperse) hard-sphere system, several authors have recently considered extensions of the second-order theory to polydisperse systems. In particular, the phase diagram for binary mixtures of nearly monodisperse hard spheres has been calculated by Barrat, Baus and Hansen [4] and by Smithline and Haymet [5]. Barrat *et al* [4] only considered the melting behaviour of substitutionally disordered FCC lattices. Rick and Haymet [5] also considered crystalline phases with long-range substitutional order, but found these to be only metastable. The calculations of [4] and [5] suggest that a change in the diameter ratio α of the spheres of only 15% has a dramatic effect on the phase diagram. In particular, the melting curve changes from spindle-like close to $\alpha = 1$ through azeotropic below $\alpha = 0.94$ to eutectic for $\alpha < 0.92$. Throughout the present paper α denotes the ratio of the diameter of the smaller spheres to that of the larger ones, while X is defined as the molar fraction of the large particles.

0953-8984/89/417735 + 05 $02.50

The first numerical study of the melting point of a monodisperse three-dimensional solid was published over 20 years ago [3]. Surprisingly enough, no simulation study has (to our knowledge) yet been reported on the melting of binary mixtures, even though fluid binary mixtures have been studied extensively by simulation. In the simulations of binary hard-sphere mixtures by Jackson, Rowlinson and van Swol [6] spontaneous solidification was observed, but no attempt was made either to determine the structure of the resulting phase or to locate the coexistence point.

Below we present the first numerical determination of the melting curve of a binary system, namely a mixture of hard spheres. The results obtained in these simulations allow us to test the quality of the corresponding predictions of density-functional theory. We have carried out simulations for two diameter ratios in the range that is of most interest for a comparison with density-functional theory—that is, $\alpha = 0.95$ and $\alpha = 0.9$.

We now describe the simulations. Equation-of-state data for the hard-sphere mixtures were obtained by both constant-pressure Monte Carlo (NPT MC) and by conventional molecular dynamics (MD) simulations. To improve the sampling over the configuration space, we included Monte Carlo trial moves in which an attempt was made to permute a large and a small particle chosen at random. These particle permutations were done both in the MC (typically, once every cycle) and in the MD runs (typically, one permutation per 100 collisions). Clearly, these particle-swapping moves make our MD simulations non-deterministic. For our purpose this was not serious as we did not attempt to compute transport properties.

Because the diameter ratio α is always close to unity, the acceptance of particle-swapping moves is relatively high. For example, at a density $\rho = 1.1$, a molar fraction $X = 0.5$ and a diameter ratio $\alpha = 0.90$, 45% of all attempted particle swaps in the solid were accepted.

Particle-swapping moves are particularly important for simulations of crystalline solids where diffusion is negligible. Without particle interchanges, the initial distribution of large and small particles over the lattice would effectively be frozen for the entire duration of the simulation.

In our simulations of the solid phase, we initially prepare the system in a face-centred cubic (FCC) lattice without defects or vacancies: the large and small particles are initially distributed randomly over the lattice sites. However, during the equilibration run correlations in the particle positions may build up. Cubic periodic boundary conditions were used in all simulations. If we consider this system as a sample drawn from an infinite lattice, we may then view the process of interchanging particles as a technique that allows us to take different samples from the infinite lattice. However, since we keep the total the number of small and large spheres in the simulation box constant we do neglect concentration fluctuations with a wavelength larger than the box size.

The equation-of-state data for both the liquid and the solid mixtures were obtained in simulations on a system containing 108 particles. In the MC simulations the system was equilibrated for some $(0.5\text{–}1) \times 10^4$ cycles (i.e. trial moves per particle). The actual production runs took some 1.5×10^4 MC cycles. During the MD simulations the system was equilibrated during $(0.6\text{–}1) \times 10^5$ collisions. The thermodynamic data of interest were collected over the next $(3\text{–}4) \times 10^5$ collisions. In all cases, the initial configuration for a simulation was the final, well equilibrated, configuration of a previous run at an adjacent state point. More details will be given in a subsequent publication [7].

For the hard-sphere mixture with a diameter ratio $\alpha = 0.95$ we computed the equation of state of the fluid at six different compositions ($X = 0\,(=1), 0.2, 0.4, 0.5, 0.6$ and 0.8). The fluid branch for $\alpha = 0.90$ was computed at seven different compositions:

$X = 0(=1), 0.1, 0.2, 0.4, 0.5, 0.6$ and 0.8. The equation of state of the solid was computed at six (nine) different compositions for $\alpha = 0.95$ (0.90). Typically we computed some ten to twelve points on every solid branch and fifteen points per fluid branch.

The second step in the determination of the phase diagrams is the calculation of the Gibbs free enthalpy in both the liquid and the solid. The basic idea is that we always want to construct a reversible path between a reference state, for which we know the value of the (excess) Gibbs free enthalpy, and the thermodynamic state, for which we want to know this enthalpy. For the liquid we can directly apply thermodynamic integration [8]. For the solid state accurate values of the free energy for the monodisperse FCC lattice have been calculated by Frenkel and Ladd [9] at two different densities. We have employed two independent methods to relate the free energy of a FCC solid solution at an arbitrary composition X to that of the monodisperse solid. The first technique is a particle-swapping method, similar in spirit to the Widom particle-insertion method [8, 10]. The difference in free energy between a system of N_1 small particles and N_2 large particles and a system of $N_1 - 1$ small particles and $N_2 + 1$ large particles at the same volume fraction follows from the ratio of the acceptance of virtual trial moves that transform the former system into the latter to the acceptance of the reverse trial moves. The second method for measuring the free energy of a solid solution uses a direct thermodynamic integration scheme. In this method we start with a solid solution of equal-sized particles at composition X. We thereupon compute the reversible work needed to change the diameter ratio of the particles from 1 to α. The 'force' conjugate to a change in α is easily computed in a MD simulation. Again, more details will be given in [7].

In order to locate the melting curve in a binary mixture of species 1 and 2, we must know the pressure and the chemical potentials of the individual species in both phases. The latter quantities are most easily determined from the molar Gibbs free enthalpy $G = X\mu_2 + (1 - X)\mu_1$ in combination with the relation:

$$\mu_2 - \mu_1 = (\partial G/\partial X)_{N_1+N_2,P,T} \tag{1}$$

The melting curve follows from the conditions $\mu_{1,s} = \mu_{1,f}$, $\mu_{2,s} = \mu_{2,f}$ and $P_s = P_f$.

We now go on to give the results. Figure 1 shows the phase diagram for a binary mixture of hard spheres with diameter ratio $\alpha = 0.95$ as obtained by the present simulations. Note that our results for the melting point of monodisperse hard spheres $\eta_s = 0.546$, $\eta_f = 0.493$, $PV_0/Nk_BT = 8.29$ (± 0.06) agree very well with the Hoover and Ree results.

In figure 1 we have also indicated the predictions of density-functional theory given in [4]. The qualitative agreement is quite striking. In particular, the computer simulations confirm the spindle-type phase diagram predicted theoretically. Moreover, theory and simulation are in agreement about the width of the spindle (i.e. about the composition of the coexisting phases). Note, however, that there is a large discrepancy between the coexistence pressure found in the simulations and the value predicted theoretically. Actually, this problem is not confined to *binary* systems: even for a monodisperse system, for the compressibility relation that was used in [4], the coexistence pressure was overestimated by some 30% [2]. More serious is the fact that the density-functional theory does not reproduce the behaviour of the density jump at melting that we find in the simulations. Density-functional theory predicts that the density jump for the mixtures is *larger* than for the pure systems. The simulations show exactly the opposite trend (see figure 2).

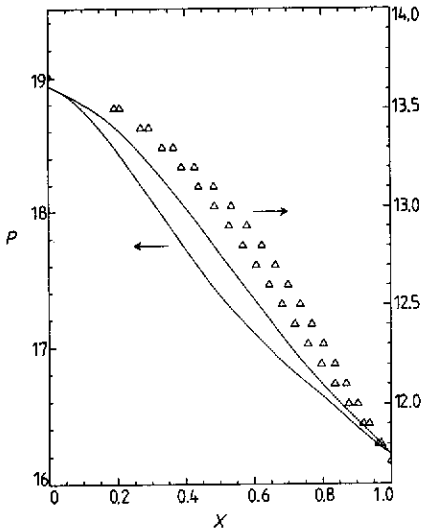

Figure 1. Phase diagram of a binary hard-sphere mixture for diameter ratio $\alpha = 0.95$. X is the molar fraction. Triangles represent the results obtained from the present computer experiments. The full curve gives the theoretical prediction [4]. Because of the large discrepancy between the melting pressure of monodisperse hard spheres obtained by computer simulation and density-functional theory (see text), the ordinate axis for the coexistence pressures predicted by density-functional theory (left) has been scaled and shifted with respect to the pressure axis of the simulation results (right). The pressure is expressed in units $k_B T/\sigma^3_2$, where σ_2 is the diameter of the larger sphere. The arrows in the figure indicate the labelling of the axes.

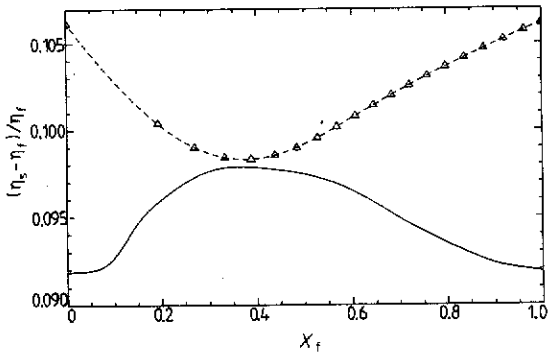

Figure 2. Relative difference in the packing fraction at phase coexistence for a hard-sphere mixture with diameter ratio $\alpha = 0.95$. η_s: packing fraction of the solid; η_f: packing fraction of the liquid. X_f is the molar fraction of large particles in the liquid. The full curve is the theoretical prediction of [4]. The computer simulation data are represented by triangles. The broken curve is drawn as a guide to the eye.

Next consider the simulations for the diameter ratio $\alpha = 0.90$. For $\alpha < 0.92$ density-functional theory predicts that the phase diagram should exhibit a eutectic. No such behaviour is observed in our simulations (see figure 3). Rather than a two-phase region with a eutectic point at $X \simeq 0.13$, we observe a phase diagram with an azeotropic point at $X \simeq 0.22$.

Hence we see that for $\alpha = 0.90$ the discrepancies between density-functional theory and computer simulation are even more serious than for $\alpha = 0.95$. Tests for hard-sphere mixtures with $\alpha < 0.90$ and for crystal structures other than FCC are currently under way.

The present findings cast doubt on the applicability of second-order density-functional theory for the prediction of melting lines in binary mixtures. It would be very interesting to see whether a third-order density-functional theory such as the one recently proposed by Barrat *et al* [11] is in better agreement with the simulation results. It seems a sad but inescapable conclusion that the simpler (and therefore more popular) second-order density-functional theories are distinctly better in predicting melting behaviour *a posteriori* than *a priori*.

The investigations reported in this paper were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands

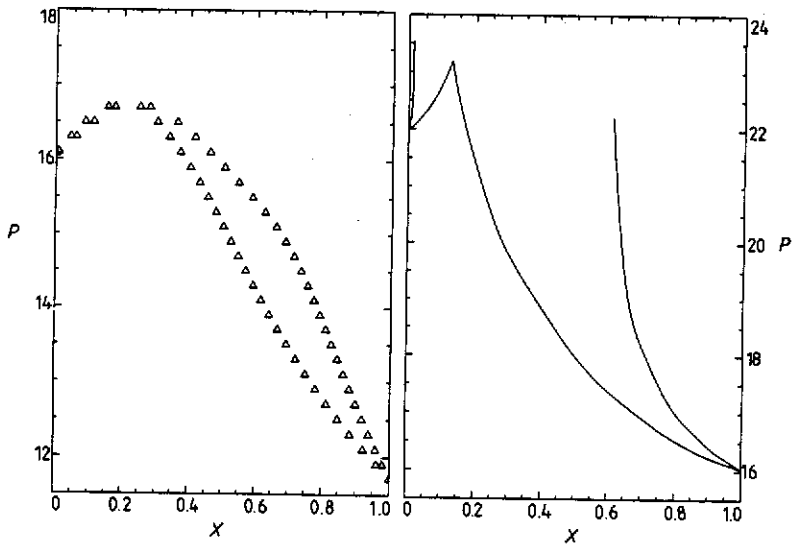

Figure 3. Phase diagram of a binary hard-sphere mixture for diameter ratio $\alpha = 0.90$. For the sake of clarity the predictions of density-functional theory and the simulation results have been drawn separately. The left-hand diagram shows the results obtained from computer experiments (triangles). The diagram on the right shows the theoretical prediction of Barrat *et al* [4]. Note that the simulations indicate the presence of an azeotropic point, whereas the theory predicts eutectic behaviour.

Organisation for Scientific Research (NWO). The work of the FOM Institute is part of the scientific program of FOM and is supported by the Netherlands Organisation for Scientific Research (NWO).

References

[1] Baus M 1987 *J. Stat. Phys.* **48** 1129
[2] Baus M and Colot J L 1985 *Mol. Phys.* **55** 653
[3] Hoover W G and Ree F M 1968 *J. Chem. Phys.* **49** 3609
[4] Barrat J L, Baus M and Hansen J P 1986 *Phys. Rev. Lett.* **56** 1063
1987 *J. Phys. C: Solid State Phys.* **20** 1413
[5] Smithline S J and Haymet A D J 1987 *J. Chem. Phys.* **86** 6486
Rick S W and Haymet A D J 1989 *J. Chem. Phys.* **90** 1188
[6] Jackson G, Rowlinson J S and van Swol F 1987 *J. Chem. Phys.* **91** 4907
[7] to be published
[8] Frenkel D 1986 *Molecular Dynamics Simulations of Statistical-Mechanical Systems* ed. G Ciccotti and W G Hoover (Amsterdam: North-Holland)
[9] Frenkel D and Ladd A J C 1984 *J. Chem. Phys.* **81** 3188
[10] Widom B 1963 *J. Chem. Phys.* **39** 2808
[11] Barrat J L, Hansen J P and Pastore G 1988 *Mol. Phys.* **63** 747