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Freezing of binary hard-disc alloys: II. The fluid-disordered crystal transition

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Abstract. The density-functional theory of freezing is extended to the case of binary mixtures of hard discs viewed as a simple model for monolayers adsorbed on a smooth substrate. The theory is applied to the fluid-disordered crystal transition. The results are similar to those already obtained for the three-dimensional case: when the ratio of diameters is lowered, the phase diagram changes rapidly from a spindle, over a lower azeotrope to an eutectic diagram. Evidence is also found for the existence of a two-dimensional analogue of the empirical Hume-Rothery rule.

1. Introduction

The density-functional (DF) theory of inhomogeneous fluids (see Evans 1979) has paved the way for the formulation of a first-principles theory of freezing which, although still in elaboration (see Lutsko and Baus 1989, Baus 1989), has already been successfully applied, during the last ten years, to the freezing of various simple potential systems (for a review, see Haymet 1987, Baus 1987, 1990). Very few authors, however, have considered the important case of the freezing of mixtures. While Barrat *et al* (1987), Smithline and Haymet (1987) and Rick and Haymet (1989) have already investigated the freezing of bulk mixtures, we will consider here the case of mixtures adsorbed on a smooth substrate. In this first attempt to extend the DF theory of freezing to mixtures with a reduced dimensionality, we will consider only a fairly rough model for such mixtures, namely, a binary mixture of hard discs (HD) of different diameters moving on a structureless surface. The equation of state and the pair structure of the fluid phase of this model have already been studied in a previous publication (Barrat *et al* 1988). Here, we will study the fluid–solid transition of the HD mixture. We will restrict considerations hereby to the freezing into one particular solid, namely, a substitutionally disordered crystal with a triangular lattice structure. In other words, the solid alloys to be considered here have no compositional long-range order although they may have a short-range compositional order similar to that of the fluid phase. Besides this, the underlying crystal structure will be assumed to have a perfect positional long-range order with each site of the triangular lattice occupied either by a small or a large HD. This transition is thus the exact analogue of the three-dimensional case considered previously by Barrat *et al*

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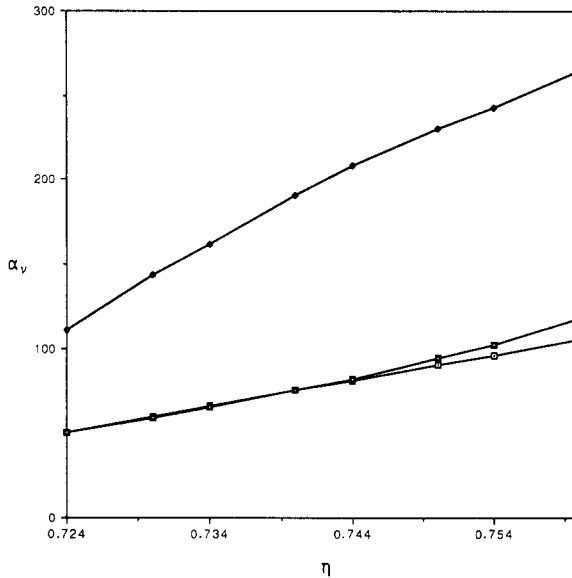


Figure 1. The Gaussian width parameters α_ν of (2.3) versus the total packing fraction η for $x_1 = 0.8$ and $\gamma = 0.88$. The curves are guides to the eye: $\alpha_1 \sigma_1^2$ (open squares), $\alpha_2 \sigma_2^2$ (dots). Also shown for comparison is the pure case $x_1 = 1$, $\gamma = 1$ (filled squares).

(1987). In the equal-diameter limit, it also reduces to the single-component HD system studied by Colot and Baus (1986). One further point worth noting is that the positional long-range order that is assumed here implies that the results are suitable for comparison with computer simulations of large but finite HD systems, but not necessarily with real systems where, in two dimensions, the thermally excited defects are strong enough to destroy this positional long-range order (Landau and Lifshitz 1984). Finally, the DF theory that will be used here to study the freezing of this model system is the same as that used in the three-dimensional case by Barrat *et al* (1987). We hence refer the reader to the latter publication for more details. One item not readily available in the two-dimensional case, however, concerns the direct-correlation functions, used as ingredients in the present DF theory of freezing, for which we have used the results of Baus and Colot (1987) as extended to binary mixtures by Barrat *et al* (1988).

2. Theoretical method

We consider a binary mixture of HD of diameters σ_1, σ_2 , with $\gamma = \sigma_1/\sigma_2 \leq 1$, enclosed in a volume V at constant temperature T ($\beta = 1/k_B T$). The local density of each component, $\rho_\nu(\mathbf{r})$ with $\nu = 1, 2$, is a periodic function of \mathbf{r} in the solid phase (s) and an \mathbf{r} -independent (uniform) function in the fluid phase (f). The difference in Helmholtz free energy per unit volume between the two phases, $\Delta f = f_s - f_f$, can be written, at constant average density, as

$$\beta \Delta f = \sum_{\nu=1,2} \int \frac{d\mathbf{r}}{V} \rho_\nu(\mathbf{r}) \ln(\rho_\nu(\mathbf{r})/\rho_\nu) - \sum_{\nu,\mu=1,2} \frac{1}{2} \int \frac{d\mathbf{r}}{V} \int d\mathbf{r}' \Delta \rho_\nu(\mathbf{r}) \Delta \rho_\mu(\mathbf{r}') C_{\mu\nu}(|\mathbf{r} - \mathbf{r}'|; x, \beta) \quad (2.1)$$

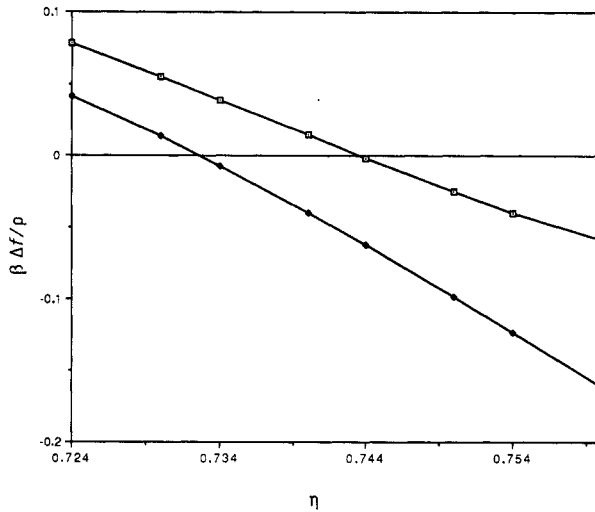


Figure 2. The difference in free energy per particle, $\beta \Delta f / \rho$, as obtained from the minimisation of (2.1), versus η for $x_1 = 0.8$, $\gamma = 0.88$ (open squares) and $x_1 = 1$, $\gamma = 1$ (dots).

where the $C_{\mu\nu}(|\mathbf{r}|; x, \rho)$ are the direct-correlation functions of the fluid phase of HD of total density $\rho = \rho_1 + \rho_2$ and concentration $x = \rho_1 / \rho$, as given by (14) of Barrat *et al* (1988). In (2.1), we have put $\Delta\rho_\nu(\mathbf{r}) = \rho_\nu(\mathbf{r}) - \rho_\nu$, with ρ_ν the spatially averaged density:

$$\rho_\nu = (1/V) \int d\mathbf{r} \rho_\nu(\mathbf{r}) \quad (2.2)$$

where $\rho_\nu(\mathbf{r})$ will be further approximated in terms of Gaussian profiles as

$$\rho_\nu(\mathbf{r}) = x_\nu \sum_{\mathbf{R}} \left(\frac{\alpha_\nu}{\pi} \right) \exp(-\alpha_\nu |\mathbf{r} - \mathbf{R}|^2) \quad (2.3)$$

where $\{\mathbf{R}\}$ is the set of Bravais lattice vectors of the triangular lattice, and $x_\nu = \rho_\nu / \rho$ the concentration of the ν th component. Equation (2.3) implies that, on average, HD of species ν have a probability x_ν to occupy any given lattice site \mathbf{R} . The inverse widths of the Gaussians in (2.3), α_ν , play the role of the order parameters of the fluid–solid transition. For $\alpha_\nu > 0$, the particles of species ν are localised around the lattice sites, whereas for $\alpha_\nu = 0$, they are uniformly distributed in space. The values of α_ν will be determined by minimising (2.1), with respect to α_1 and α_2 . The basic approximation underlying (2.1), besides the Gaussian approximation of (2.3), concerns the use of an effective fluid of density $\hat{\rho}$ to describe the solid. This density will be determined by requiring that the smallest reciprocal lattice vector of the triangular lattice coincides with the position of the main peak of the total static structure factor:

$$S(k; x, \hat{\rho}) = \sum_{\mu\nu} x_\mu x_\nu S_{\mu\nu}(k; x, \hat{\rho})$$

of the effective fluid of total density $\hat{\rho}$ and concentration x (see Barrat *et al* 1987). This density $\hat{\rho}$ depends on the total average density of the solid, $\rho = \rho_1 + \rho_2$, and on its concentration x . Once $\hat{\rho} = \hat{\rho}(\rho, x)$ is known, equation (2.1) can be minimised with

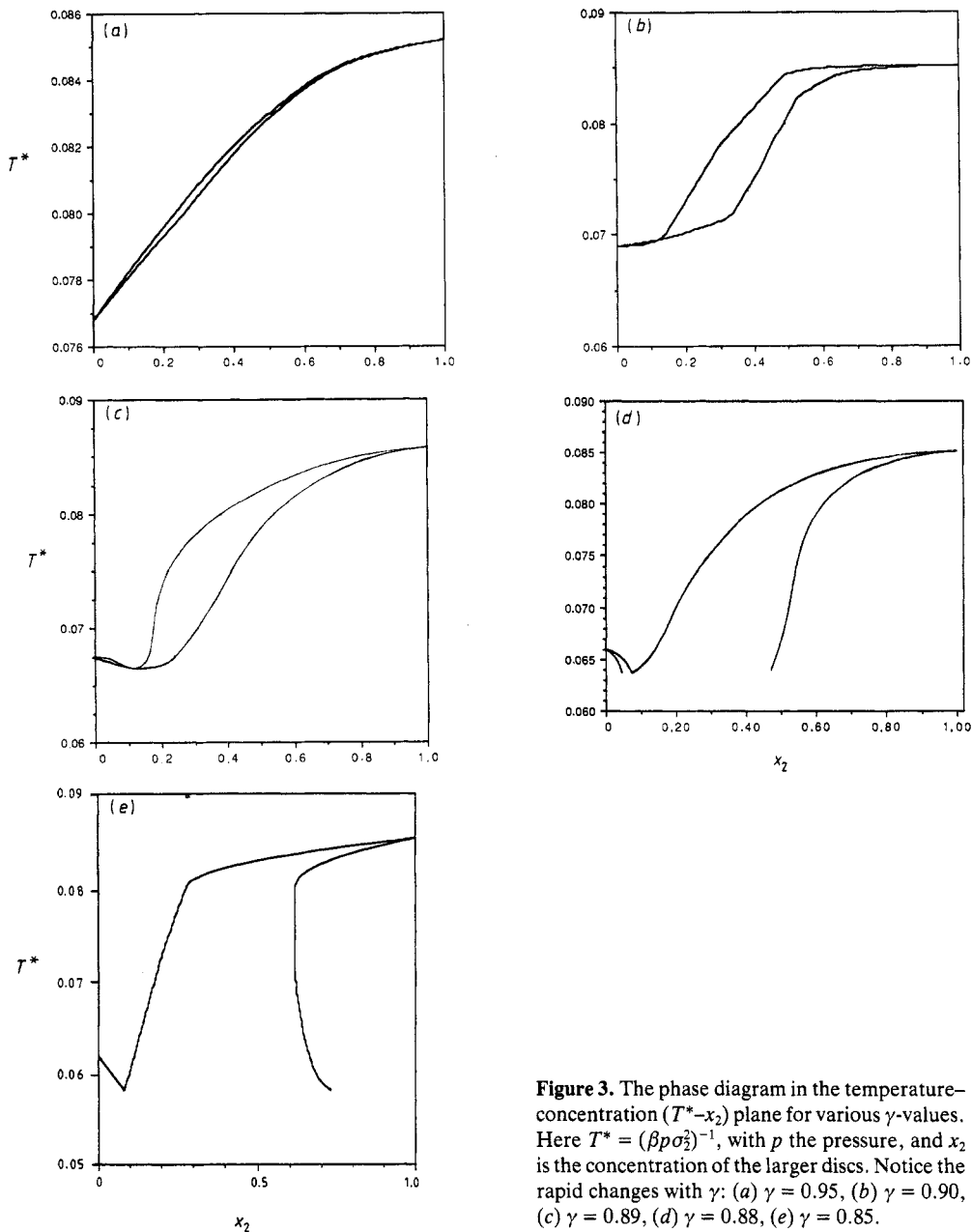


Figure 3. The phase diagram in the temperature–concentration (T^* – x_2) plane for various γ -values. Here $T^* = (\beta p \sigma_2^2)^{-1}$, with p the pressure, and x_2 is the concentration of the larger discs. Notice the rapid changes with γ : (a) $\gamma = 0.95$, (b) $\gamma = 0.90$, (c) $\gamma = 0.89$, (d) $\gamma = 0.88$, (e) $\gamma = 0.85$.

respect to α_ν ($\nu = 1, 2$) and the stable solids can be located. In the limit of large α_ν -values, the first term in the RHS of (2.1) can also be simplified, using (2.3), to give

$$\sum_{\nu=1,2} \int \frac{dr}{V} \rho_\nu(r) \ln\left(\frac{\rho_\nu(r)}{\rho}\right) = \sum_{\nu=1,2} \rho_\nu (\ln(\alpha_\nu \sigma_2^2) - \ln(4\eta_1 \gamma^{-2} + 4\eta_2) - 1) \quad (2.4)$$

where $\eta_\nu = (\pi/4)\sigma_\nu^2 \rho_\nu$ are the HD packing fractions and $\gamma = \sigma_1/\sigma_2 \leq 1$. This approximation, (2.4), can only be used provided $\alpha_\nu \sigma_2^2 \geq 30$. For smaller values of α_ν , the LHS

of (2.4) has to be evaluated numerically (Xu 1989). Once the free energy (2.1) has been minimised, the fluid–solid coexistence can be determined via a double-tangent construction on the free enthalpies of the solid and the fluid as explained by Barrat *et al* (1987). The equation of state used for the fluid is given by (7) of Barrat *et al* (1988).

3. Results

First, we have determined the density range where stable solid alloys can be found. To this end, Δf of (2.1) has been minimised with respect to α_1 and α_2 for given $\eta \equiv \eta_1 + \eta_2$, $x \equiv x_1$ and $\gamma = \sigma_1/\sigma_2$. The resulting α_1 and α_2 depend strongly on η and weakly on x and γ . An example is shown in figure 1. It is seen there that both α_1 and α_2 increase with η , but that the larger discs (α_2) are more strongly localised than the smaller ones (α_1). The value of Δf for mixtures with $\gamma < 0.90$ and $x_2 < 0.5$ is always larger than for the pure case ($\gamma = 1$), as illustrated in figure 2. For such mixtures, the threshold value of η above which the solid alloys appear for the first time increases very rapidly when γ is lowered, and when γ reaches the value 0.85, no stable alloys can be found any more. This is very similar to the three-dimensional findings of Barrat *et al* (1987) and points to the existence of a two-dimensional analogue of the empirical Hume-Rothery rule (see Hume-Rothery *et al* 1969). This rule states that (in three dimensions) the formation of disordered metallic alloys is very improbable when the atomic sizes differ by more than fifteen per cent. The analogy with the three-dimensional case extends also to the phase diagrams since, as shown in figure 3, when lowering γ , the same sequence of rapidly changing phase diagrams is found here as well. Spindle-type phase diagrams are found for $1 > \gamma \geq 0.90$ and these are transformed into a lower azeotrope-type diagram for $\gamma \approx 0.89$ and finally into a eutectic phase diagram for $0.88 \geq \gamma \geq 0.85$ (see figure 3).

4. Conclusions

We have extended the density-functional theory of freezing to the case of a binary mixture of hard discs. The overall behaviour is very similar to that found from the same theory for the hard-sphere mixture. In particular, we find strong evidence for the existence of a two-dimensional analogue of the empirical Hume-Rothery rule.

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