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TWO PARTICLE CLUSTER CALCULATION OF THE CHEMICAL SPINODAL

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The spinodal curve for demixing in a binary mixture is calculated in the two-particle cluster approximation. It is found that the difference between the equilibrium composition x_e and the spinodal composition x_s is smaller than in the mean-field approximation. The results agree remarkably well with the semi-empirical formula for the metastable region proposed by Cook and Hilliard (Trans. Met. Soc. AIME **233** (1965) 142).

1. Introduction

From a thermodynamic point of view, the spinodal line separates an unstable region from a metastable region in the phase diagram. For a binary mixture, it is the locus of points for which

$$\left(\frac{\partial^2 g}{\partial x^2}\right)_{T,p} = 0,$$

where g is the Gibbs free energy per particle and x is the mole fraction of one of the components.

A convenient way to describe a binary mixture is to use the analogy between such a system and the simple Ising model[1,2]). The advantage of this description is that it allows one to use the statistical mechanical treatments which have been developed to deal with Ising models. The simplest treatment that still gives a good qualitative picture of the demixing phenomenon is the mean-field approximation[1,2]), also known as the regular solution model[3,4]). However, in this treatment, the width of the metastable region is overestimated. Simple ways to improve upon the mean-field treatment are provided by cluster methods[5,6]). The first attempt in doing so was made by Bethe[7]). The Bethe method is equivalent to the quasi-chemical approximation of Guggenheim[4]). However, both theories contain thermodynamic inconsistencies.

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A consistent way of taking into account two-particle correlations is provided by the constant-coupling approximation of Kasteleyn and Van Kranendonk[8]), which was extended to larger clusters by Strieb et al.[9]). Another very successful cluster method is the Kikucki-procedure[10]). In the appendix, we show that the pair-approximation of the Kikuchi-method[11]) leads to the same expression for the free energy as the constant coupling approximation. The application of the two-particle cluster method to the isotropic–nematic phase transition gives a considerable improvement over the mean-field approximation in the calculation of the width of the metastable region[12]).

In this paper, we apply the two-particle cluster method to the discription of demixing in binary mixtures.

In section 2, we briefly discuss the model we use for the binary mixture and present the essential features of the cluster variation method. In section 3, we apply this method to the calculation of the binodal line (equilibrium composition as a function of temperature) and of the spinodal line. The results are compared with the semi-empirical relation for the metastable region proposed by Cook and Hilliard[9]). It is found that the two-particle cluster variation results are in close agreement with those, obtained from this expression.

2. Cluster variation theory for binary mixtures

In the Ising model for a binary mixture AB, a coordinate σ_i is introduced for every lattice site with $\sigma_i = +1$ if the site is occupied by an A-atom, and $\sigma_i = -1$ if the site is occupied by a B-atom. Taking only nearest neighbour interactions into account and omitting all terms that are independant of the configuration of the atoms on the lattice, the energy can be written as

$$\mathcal{H} = -\varphi \sum_{\langle i,j \rangle} \sigma_i \sigma_j. \tag{1}$$

In (1), the summation $\langle i, j \rangle$ runs over all distinct pairs of nearest neighbours and

$$\varphi = \tfrac{1}{2}[\varphi_{AB} - \tfrac{1}{2}(\varphi_{AA} + \varphi_{BB})], \tag{2}$$

where φ_{AA}, φ_{BB} and φ_{AB} are the interacting energies of AA, BB and AB pairs, respectively. It is clear that demixing will only occur if φ is positive. To complete the analogy with the magnetic Ising model, it is convenient to introduce the order parameter

$$\eta = 1 - 2x, \tag{3}$$

which takes on values between -1 and $+1$ and is the analogue of the spontaneous magnetization in the magnetic Ising model.

In the cluster variation method[5]), the free energy per particle is expanded in a series,

$$f = f_0 + f'_{(2)} + f'_{(3)} + \cdots .$$

Applying the cluster variation method to Hamiltonian (1) one obtains for the zeroth-order term[4])

$$-\beta f_0 = -\tfrac{1}{2} z\varphi\beta\bar{S}^2 + \ln Z_1, \tag{4}$$

with

$$Z_1 = \operatorname{Tr} \exp(z\varphi\beta\bar{S}\sigma_1) = 2\cosh(z\varphi\beta\bar{S}).$$

Further, z is the number of nearest neighbours and $\bar{S}$ is a variation parameter, which best value is determined by minimizing the free energy. This yields the following equation for $\bar{S}$:

$$\bar{S} = \langle\sigma_1\rangle_{(1)}. \tag{5}$$

Here, $\langle\cdots\rangle_{(1)}$ denotes an average with respect to the one-particle distribution function

$$\sigma_{(1)} = \frac{\exp(z\varphi\beta\bar{S}\sigma_1)}{Z_1}. \tag{6}$$

The term f_0, given by (4), is just the usual mean-field free energy.

Taking into account the correction term $f'_{(2)}$, due to the contribution of two-particle clusters, one obtains the free energy in the two-particle cluster approximation,

$$-\beta f_{(2)} = -\beta(f_0 + f'_{(2)}) = (1-z)\ln Z_1 + \frac{z}{2}\ln Z_{12}, \tag{7}$$

where

$$Z_{12} = \operatorname{Tr} \exp \beta\varphi\{\sigma_1\sigma_2 + \bar{S}(z-1)(\sigma_1+\sigma_2)\}$$

$$= 2\exp\{(-\beta\varphi)\}\{1 + \exp(2\beta\varphi)\cosh 2\beta\varphi(z-1)\bar{S}\}.$$

Minimizing $f_{(2)}$ with respect to $\bar{S}$, yields the consistency relation

$$\langle\sigma_1\rangle_{(1)} = \tfrac{1}{2}\langle\sigma_1+\sigma_2\rangle_{(2)}, \tag{8}$$

where $\langle\cdots\rangle_{(2)}$ denotes an average over the two-particle distribution function

$$\rho_{(2)} = \frac{\exp \beta\varphi\{\sigma_1\sigma_2 + \bar{S}(z-1)(\sigma_1+\sigma_2)\}}{Z_{12}}. \tag{9}$$

In the next section, the free energy obtained in the two-particle cluster variation approximation will be used to derive analytical expressions for binodal- and spinodal line in the phase diagram of a binary mixture.

3. Calculation of the binodal and spinodal in the two-particle cluster approximation

In view of the model used here, the appropriate thermodynamic potential is the Helmholtz free energy, and the binodal line is defined by the condition

$$\left(\frac{\partial f}{\partial x}\right)_T = 0. \tag{10}$$

In terms of the variable η defined by (3) this condition reads

$$\left(\frac{\partial f}{\partial \eta}\right)_T = 0. \tag{11}$$

The cluster variation method yields an expression for the free energy in terms of the variation parameter $\bar{S}$ which is related to the order-parameter η through

$$\eta = \langle \sigma_1 \rangle_{(1)}. \tag{12}$$

From this it follows that the condition (11) can be written as

$$\left(\frac{\partial f}{\partial \bar{S}}\right)_T = 0. \tag{13}$$

Applied to f_0, this yields the following well-known mean-field expression[1-4]) for the binodal line:

$$\frac{T_e}{T_c} = 2\eta\left[\ln\left(\frac{1+\eta}{1-\eta}\right)\right]^{-1}, \tag{14}$$

where T_c is the critical temperature,

$$T_c = T_e(\eta = 0) = \frac{z\varphi}{k}. \tag{15}$$

From the free energy in the two-particle cluster approximation one obtains for the binodal line

$$\frac{T_e}{T_c} = \ln\left(\frac{z}{z-2}\right)\left[\ln\frac{2\eta}{(1+\eta)[(1-\eta)/(1+\eta)]^{1/z} - (1-\eta)[(1+\eta)/(1-\eta)]^{1/z}}\right]^{-1}. \tag{16}$$

The critical temperature T_c is now given by

$$T_c = \frac{2\varphi}{k \ln[z/(z-2)]}. \tag{17}$$

The above expression for the binodal line was first obtained by Mc Glashan using the quasi-chemical approach[10]).

In the model used here, the condition for the spinodal line reads

$$\left(\frac{\partial^2 f}{\partial \eta^2}\right)_T = 0. \tag{18}$$

Taking into account that the free energy must be minimized with respect to $\bar{S}$, the above condition can be written as

$$\left(\frac{\partial^2 f}{\partial \bar{S}^2}\right)_T = 0. \tag{19}$$

Starting from the mean-field free energy, this equation yields the following expression for the spinodal line:

$$\frac{T_s}{T_c} = 1 - \eta^2. \tag{20}$$

Applying the condition (19) to the free energy in the two-particle cluster approximation, one obtains for the spinodal

$$\frac{T_s}{T_c} = \ln\left(\frac{z}{z-2}\right)\left[\ln \frac{A + (A^2 + 4z(z-2))^{1/2}}{2(z-2)}\right]^{-1}, \tag{21}$$

with

$$A = \left(\frac{1+\eta}{1-\eta}\right)^{(z-1)/z} + \left(\frac{1-\eta}{1+\eta}\right)^{(z-1)/z}.$$

A generally accepted[11]) and widely used[12]) formula for the metastable region in the phase diagram of binary mixtures is the semi-empirical expression of Cook and Hilliard,

$$(x_s - x_c) \approx (x_e - x_c)[1 - 0.422(T/T_c)], \tag{22}$$

where x_s, x_e and x_c are the spinodal-, binodal- and critical composition. This formula is based upon a combination of theoretical arguments and experimental data. In figs. 1 and 2 we compare the width of the metastable region predicted by the Cook and Hilliard formula with the mean-field and two-particle cluster variation results. We see that the agreement in the mean-field treatment is fair but is still considerably improved in the two-particle cluster variation method.

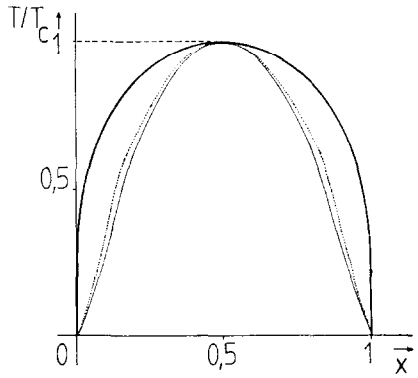

Fig. 1. Binodal-(——) and spinodal line (——) for a binary mixture on a lattice with six nearest neighbours ($z = 6$) in the mean-field approximation. The dotted line represents the chemical spinodal calculated using the semi-empirical expression of Cook and Hilliard.

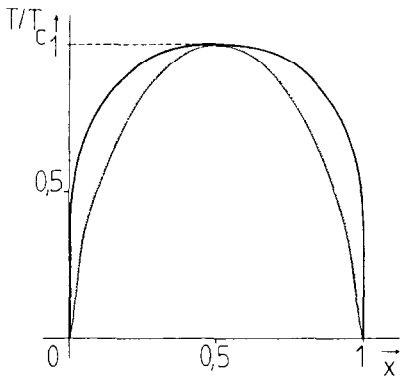

Fig. 2. Binodal-(——) and spinodal line (——) for a binary mixture on a lattice with six nearest neighbours ($z = 6$) in the two-particle cluster approximation. The dotted line represents the chemical spinodal calculated using expression (22) due to Cook and Hilliard.

We conclude that the simple two-particle cluster theory is a valuable improvement over the mean-field description of the phase diagram of a binary mixture.

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Appendix

Application of the constant-coupling approximation to a binary mixture yields expression (7) for the free energy in terms of the variation parameter $\bar{S}$. This parameter is linked with the order-parameter η through relation (12), which can be written as

$$\bar{S} = \frac{1}{2\beta\varphi z} \ln \frac{1+\eta}{1-\eta}. \tag{23}$$

Combination with eqn. (7) gives the free energy in terms of η:

$$-\beta f_{(2)} = \frac{z-1}{2} \ln \frac{1-\eta^2}{4} - \frac{z\beta\varphi}{2} + \frac{z}{2} \ln \left[2 + e^{2\beta\varphi} \left(\frac{1+\eta}{1-\eta} \right)^{(z-1)/z} + \left(\frac{1-\eta}{1+\eta} \right)^{(z-1)/z} \right]. \tag{24}$$

Following Kikuchi's argument[11]), one obtains for the free energy in the pair approximation

$$\exp\left[-\frac{2\beta f}{z} \right] = e^{-\beta\varphi} (x_1 x_2)^{(z-1)/z} \left[2 + e^{2\beta\varphi} \left\{ \left(\frac{x_1}{x_2} \right)^{(z-1)/z} + \left(\frac{x_2}{x_1} \right)^{(z-1)/z} \right\} \right]. \tag{25}$$

Using relation (3), it follows that the two methods lead to the same expression for the free energy.

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