Physica A 449 (2016) 395–400

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Nonergodic correction to a binary mixture phase diagram

L. Son

Ural Federal University, 19 Mira st., 620002, Ekaterinburg, Russia

HIGHLIGHTS

- Nonergodic correction results in a bifurcation of phase separation line.
- Two critical and one triple points appear due to this bifurcation.
- Microheterogeneous state may exist as a separate nonergodic phase.
- This situation is typical for the eutectic binary systems.

ARTICLE INFO

Article history:
Received 1 September 2015
Received in revised form 28 November 2015
Available online 11 January 2016

Keywords:
Binary phase diagram
Nonergodicity
Microheterogeneity

ABSTRACT

For a binary mixture with limited miscibility of the components, the correction to the equation of state that arises from the finite diffusion velocity is discussed. It is shown that this correction corresponds to a nonergodic microheterogeneity of the mixture. We suggest that the above microheterogeneity may be accounted as corresponding fluctuations of the chemical potential. The mean square of these fluctuations C is an additional thermodynamic variable, and the nonergodic microheterogeneity is an equilibrium property of every binary mixture with limited miscibility. The experimental status of this statement is discussed for eutectic and monotectic systems.

1. Introduction

Binary systems with limited miscibility of the components are being widely investigated. In the crystalline state, microheterogeneity of them (especially of eutectic systems near eutectic composition) is rather common feature (see, for example the experiments on the contact melting [1]). It is natural to suggest that some kind of the microheterogeneity may stay in the liquid state too. This suggestion occurs to be true—for example, in Refs. [2,3], numerous experimental evidences of the microheterogeneity in binary metallic liquids are presented. From the other hand, the microheterogeneity cannot exist as an equilibrium property of ergodic system, since it requires a large spatial density of the interphase boundaries, which have a large excess energy and make the probability of corresponding state negligible due to the Gibbs statistical weight. In the crystalline state, nonergodic microheterogeneity is obvious. In the liquid, it was interpreted as a metastable colloidal state [2,3]. In the present article, we discuss another possibility of its existence.

Statistics of a binary mixture consisting of atoms of A and B type may be understood on the base of the lattice gas model. In the frames of the model, it is supposed that possible atomic positions correspond to the sites of spatial lattice. Possible configurations of the mixture are described in terms of filling numbers $n(r)$, where r is the coordinate of the site, and $n(r) = 1$ if the site is occupied by the atom of A type, and $n(r) = 0$ for the atom of B type. Then, one introduces the effective Hamiltonian for certain spatial configuration of variables $\{n(r)\}$:

$$H\{n\} = -\frac{1}{2}\sum_{r,r'} n(r)J(r-r')n(r') - \sum_{r} \mu(r)n(r). \tag{1}$$

E-mail address: ldson@yandex.ru.

http://dx.doi.org/10.1016/j.physa.2015.12.112
0378-4371/© 2016 Elsevier B.V. All rights reserved.

Hamiltonian (1) determines the Gibbs statistical weight (but, in contrast with "real" Hamiltonian, does not determine the dynamics!), so that thermodynamics is described by partition Z and thermodynamic potential G:

$$Z = \sum_{\{n\}} \exp\left[-\frac{H\{n\}}{T}\right], \qquad G = -T \ln Z. \tag{2}$$

To calculate the partition, one uses the mean field (MF) approximation, which replaces the full statistics (2) with statistics of filling numbers $n(r)$ in single site at point r, embedded into surrounding "field" of neighboring sites. For neighboring sites, one suggests mean value of filling number $\langle n(r')\rangle = x(r')$. For the single site, the partition includes only two terms

$$Z_{MF} = \sum_{n=0,1} \exp\left[n\frac{J}{T}x + n\frac{\mu}{T}\right] = 1 + \exp\left[\frac{J}{T}x + \frac{\mu}{T}\right], \tag{3}$$

where

$$J = \sum_{r'} J(r - r'). \tag{4}$$

Using (3), one easily calculates the mean value $\langle n(r)\rangle$. Obvious self consistency $x = \langle n(r)\rangle$ gives the well known mean-field equation on the mean concentration x:

$$\frac{T}{J}x = \frac{\exp(x+\nu)}{1+\exp(x+\nu)}. \tag{5}$$

The dimensionless chemical potential ν is a Lagrange multiplier which serves to fix the concentration. This equation at $T > J/4$ has only one stable solution for all ν, but at $T \le J/4$ in the vicinity of $x = 0.5$ it splits up into three solutions (two of them are stable, separated by the unstable) and this split results in miscibility gap. Thus, the concentration–temperature phase diagram looks as a cupola dividing two-phase and single-phase domains. This is statistical base of the regular solutions theory.

Note that the lattice gas model is not a unique way to get Eq. (5). One can use any model, which accounts the energy preference of atoms of one and the same kind to get together. Indeed, the right side of this equation is the dependence of the concentration on the chemical potential. This function vanishes at $x+\nu \to -\infty$ and tends to the unity at $x+\nu \to +\infty$, having exponential tails. The left side of (5) is just a linear feedback, which arises due to the MF approximation. Thus, the form of Eq. (5) is fixed by physical arguments and does not depend on the model details.

2. Correction to the equation of state and phase diagram of a regular solution

Hibbs statistics is based on the ergodic hypothesis, which implies that states with equal energies have equal probabilities. At the same time, diffusion of particles has obvious dynamical limitation: atom cannot move from one spatial point to another instantly. Thus, starting from some initial configuration, system cannot reach certain configurations per observation time, in spite of the fact that these configurations have big Hibbs probability. In Refs. [4,5] we accounted these limitations in the frames of the lattice gas model. It was shown that below $T = J/4$ Eq. (5) should be rewritten as

$$\frac{T}{J}x = \frac{e^{\beta}}{1+e^{\beta}} + C\,\frac{e^{\beta}(1-e^{\beta})}{(1+e^{\beta})^3}, \quad \beta = x + \nu. \tag{6}$$

In Refs. [4,5] Eq. (6) was derived by strict account of dynamical limitations. Below, we obtain it by means of mathematically not rigorous but clear considerations. At high temperatures, the system is ergodic and may be described by Eq. (5). According to this equation, below $T = J/4$ (under the dashed curve in Fig. 1) the homogeneous spatial distribution of the components becomes unstable. The tendency to the phase separation appears, and system becomes heterogeneous: some local volumes become enriched with component A, while others—with component B. At the first stage of the process, these volumes are small, and the resulting microheterogeneity may be described by random spatial fluctuations of chemical potential:

$$\nu(r) = \nu + \Delta\nu(r). \tag{7}$$

Thus, one gets a set of Eqs. (5) in different spatial points with different $\nu(r)$. Suggesting smallness of $\Delta\nu$, one can expand (5) with respect to this value up to the second order term. Then, one averages the obtained equation over spatial ensemble. While averaging, the first order term vanishes due to the conservation of the mean concentration. Denoting spatial mean value $\langle \Delta\nu^2(r)\rangle = 2C$, one gets Eq. (6).

Due to the spatial average, this equation corresponds to the spatial scale larger than the mean size of starting microheterogeneity. At this scale, further phase separation in the shadowed area in Fig. 1 is prohibited because Eq. (6) has only one solution. Thus, starting microheterogeneity appears to be frozen. In the frames of mean field approximation, constant C cannot be calculated and should be considered as a phenomenological parameter, which characterizes the microheterogeneity. Its calculation in the frames of constrained dynamics of a regular solution is the topic for future research.