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Fluctuation effects on the coexistence curve for binary polymer-solvent systems

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Recent experimental studies [1-4] showed that the Flory-Huggins theory fails in describing the coexistence curves for binary polymer-solvent systems. Sanchez [1] found the following scaling law for the coexistence curve

$$|\Phi - \Phi_c|/\Phi_c \sim (-r)^\beta N^{0.102\pm0.002}$$ (1)

where \(N\) is the degree of polymerization of polymer chains, \(\Phi\) is the polymer volume fraction along the coexistence curve, \(\Phi_c\) is the critical polymer volume fraction, \(r = (T - T_c)/T_c\), where \(T\) is the temperature and \(T_c\) is the critical temperature. The critical exponent \(\beta\) has been measured to be 0.327. In contrast to (1), the mean field Flory-Huggins theory predicts the following equation for the coexistence curve

$$|\Phi - \Phi_c| \sim (-r)^{1/2} N^{-1/4} ; \Phi_c \sim N^{-1/2}$$ (2)

The experimental value of \(\beta\) for polymer segregation is the same as that for the segregation in binary liquids or for the Ising model. On that account one can expect that the critical exponent \(\beta = 0.327\) in (1) has to be attributed to the fluctuations of the order parameter. It is well-known that the fluctuation effects in the vicinity of the critical point are described by using the Landau-Ginzburg-Wilson (LGW) model. In combination with the renormalization group method the latter is the basis of the modern theory of critical phenomena.

One may assume that the \(N\) exponent of (1) is also affected by the fluctuations of the order parameter. Recently, Muthukumar [5] made an attempt to attribute the \(N\) exponent of (1) to the three-body interactions between the polymer segments.

In the present article we propose the theory of segregation taking into account the fluctuations of the order parameter. The main idea of our approach consists in the following. Starting with the Flory-Huggins theory we reformulate the latter in the vicinity of the critical point in terms of the Landau theory of phase transitions. After that, in usual manner, we go from the Landau theory to the Landau-Ginzburg-Wilson model.
The Flory-Huggins theory gives the following expression for the free energy of mixing of the polymer solution in units of kT.

\[ F = \frac{\Phi}{N} \ln \Phi + (1 - \Phi) \ln (1 - \Phi) + \chi \Phi (1 - \Phi). \] (3)

The spinodal curve and the critical point are defined, respectively, as follows

\[ \frac{\partial^2 F}{\partial \Phi^2} = 0, \quad \frac{\partial^3 F}{\partial \Phi^3} = 0. \] (4) (5)

The critical polymer volume fraction \( \Phi_c \) and the critical value \( \chi_c \) are obtained from (4-5) as follows

\[ \Phi_c = (1 + \sqrt{N})^{-1}, \quad 2\chi_c = N^{-1}(1 + \sqrt{N})^2. \]

In the vicinity of the critical point the spinodal curve is obtained as

\[ \frac{\partial^2 F}{\partial \Phi^2} = 2(\chi_c - \chi) + \frac{1}{2} N^{1/2} \Phi^2 + \ldots = 0 \] (6)

where the notation \( \Phi = \Phi - \Phi_c \) is introduced. We define the Landau Hamiltonian \( F_L \) by the first part of equation (6). The coexistence curve in the Landau theory of phase transitions is defined by the condition

\[ \partial F_L / \partial \Phi = 0. \] (7)

Both the spinodal curve and the coexistence curve are predicted in the Landau theory to be symmetrical. Integrating the first part of (6) and taking into account (7) we obtain the Landau Hamiltonian as follows

\[ F_L = (\chi_c - \chi) \Phi^2 + \frac{1}{12} N^{1/2} \Phi^4 + \ldots \] (8)

The Hamiltonian of the Landau-Ginzburg-Wilson model is obtained by adding the gradient term \( c(\nabla \Phi)^2 \) to (8). Joanny [6] and de Gennes [7] found that the local concentration inhomogeneities lead to the following contribution to the free energy

\[ \frac{R^2}{36N\Phi(1-\Phi)}(\nabla \Phi)^2 \] (9)

where \( R^2 = Na^2 \) is the mean square end-to-end distance of the polymer chain. In (9), in the vicinity of the critical point, we replace \( \Phi \) by the critical value \( \Phi_c \) and \( 1 - \Phi_c \) by 1. Then, the LGW Hamiltonian is obtained as

\[ H = \frac{a^2}{36\Phi_c}(\nabla \Phi)^2 + (\chi_c - \chi) \Phi^2 + \frac{1}{4!} 2N^{1/2} \Phi^4. \] (10)

The gradient term in (10) depends on the degree of polymerization through \( \Phi_c \). The Flory-Huggins theory predicts \( \Phi_c \sim N^{-1/2} \). From the literature [3-4], it is found that \( \Phi_c \sim N^{-0.38 \pm 0.01} \). In the present article we adopt the power law \( \Phi_c \sim N^{-a} \), where for \( a \) one can use either the mean field value or the experimental value. We note that the present theory cannot predict the critical value \( \Phi_c \).

Now let us turn to the coexistence curve associated with (10). The direct calculation of the coexistence curve can be avoided by introducing the variables

\[ M = \Phi/\Phi_c^{3/2} N^{1/4}, \quad x = r N^{1/2} \Phi_c^{2\sqrt{18}/a} \] (11)

which converts (10) to

\[ y_x = y N^{3/2} \Phi_c^6 = \frac{1}{2} (\nabla_x M)^2 + \frac{1}{2} m_0 M^2 + \frac{u_0}{4!} M^4 \] (12)

with the bare mass

\[ m_0 = 2(\chi_c - \chi)/N\Phi_c^3 \] (13)

and the coupling constant \( u_0 = 2 \). The correlation length \( \xi_x \) associated with (12) scales as [8].

\[ \xi_x \sim (m_0)^{-\nu}. \]

where \( \nu \) is the critical exponent of the LGW model. Using the connection \( x/\xi_x = r/\xi_r \), we obtain the correlation length \( \xi_r \) associated with the Hamiltonian (10) as

\[ \xi_r \sim (\chi_c - \chi)^{-\nu} N^{-1/2} \Phi_c^{3\nu-2}. \] (14)

In the mean field limit (\( \nu = 1/2 \)) with \( \Phi_c \sim N^{-1/2} \) (14) reduces to

\[ \xi_r \sim (\chi_c - \chi)^{-1/2} N^{1/4}. \] (15)

The latter was first obtained by de Gennes [9].

The coexistence curve corresponding to (12) behaves as [8]
\[ M \sim (-m_0)^\beta \] (16)

where \( \beta = 0.327 \). Eliminating \( M \) in (16) in favour of \( \Phi - \Phi_c \) we obtain the coexistence curve as

\[ |\Phi - \Phi_c| \sim (\chi - \chi_c)^{\beta} N^{-\beta+1/4} \Phi_c^{-3\beta+3/2}. \] (17)

We note that in the mean field limit (\( \beta = 1/2 \)) the \( N \) dependence of the gradient term of the LGW Hamiltonian does not influence the coexistence curve. Using the usual approximation for the temperature dependence of \( \chi \)

\[ 2\chi = \theta/T \]

(\( \theta \) is the Flory temperature) we can eliminate \( \chi - \chi_c \) in favour of \( -\tau = (T_c - T)/T_c \). Adopting for \( \Phi_c \) its mean field law \( \Phi_c \sim N^{-1/2} \) we obtain

\[ |\Phi - \Phi_c| \sim (-\tau)^{\beta} N^{\beta/2-1/2}. \] (18)

The \( N \) exponent in (18) coincides with that obtained by de Gennes [10] using the scaling arguments. Adopting the experimental finding \( \Phi_c \sim N^{-0.38} \) we obtain the coexistence curve as

\[ |\Phi - \Phi_c| /\Phi_c \sim (-\tau)^{\beta} N^{0.106} \] (19)

which is in good agreement with the result of Sanchez [1].

The scaling law (19) is valid in the limit \( m_0 \to 0 \). From the definition of \( m_0 \) (Eq.(13)) it follows that for fixed \( \tau \), \( m_0 \) increases with increasing \( N \). Such behaviour of \( m_0 \) means that the scaling region narrows with increasing \( N \). This prediction of the present theory is in agreement with the experimental finding by Dobashi et al. [3]. We note that the narrowing of the critical region originates from the dependence of the gradient term of the LGW Hamiltonian on the degree of polymerization. To ensure the narrowing of the critical region of the coexistence curve with increasing \( N \) the exponent \( a \) in the relationship \( \Phi_c \sim N^{-a} \) must be greater than 1/3. In particular, if we accept the gradient term independent of \( N \) we will obtain a broadening of the scaling region.

In the present article we have considered the effects of the critical fluctuations on the coexistence curve for binary polymer-solvent systems. The crucial meaning on the behaviour of the coexistence curve has the dependence of the gradient term of the LGW Hamiltonian on the molecular weight of the polymer. The present theory does not explain the dependence of \( \Phi_c \) on \( N \). Apparently, the exponent \( a \) is independent of the critical exponents of the LGW model. It is known that the LGW model, in contrast to the Ising model, does not predict the value of the critical temperature. On that account one may expect that the lattice models for polymer-solvent systems may give the correct dependence of \( \Phi_c \) on \( N \). The extension of the Monte Carlo simulations of the lattice model for the polymer-polymer system [11] to the polymer-solvent system can establish \( \Phi_c (N) \) for the lattice model of the polymer-solvent system.

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References