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New Approaches to Statistical Thermodynamics of Blends Containing Copolymers

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SUMMARY: Key ideas of the mean-field theory of copolymer blends are formulated and some basic equations derived in the framework of this theory for the calculation of phase diagram of polymer blends are presented.

Introduction

For thermodynamic description of homopolymer blends several theories exist nowadays whose conclusions are in reasonable agreement with experimental data available. Sophisticated approaches employed in such theories normally are not so efficient when considering blends of copolymers. The reason is that a specimen of a synthetic copolymer involves enormous (practically infinite) set of molecules differing in number of monomeric units, composition andsequence distribution. Just this circumstance is likely to be responsible for the absence of a universal thermodynamic theory of blends comprising copolymers with an arbitrary chemical structure.

We managed to solve within the framework of the simplest model the fundamental problem of this theory which consists in deriving equations for the calculation of cloud-point curve, spinodal and critical points for any blend of linear copolymers with known characteristics of their primary molecular structure [1]. In terms of this unified approach it is possible to examine phase behavior of either statistic copolymers or block copolymers showing microphase separation. Covering wide range of polymer blends our theory is convenient for the construction of theoretical phase diagrams of particular blends since the equations derived comprise minimal number of thermodynamic parameters (like the Flory χ-parameters) experimentally found for a number of polymers.

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General Treatment

Thermodynamic mean-field consideration of a polymer blend can be performed in terms of two auxiliary subsystems. In the first of them all chemical bonds joining monomeric units are believed to be retained whereas physical interactions between such units are completely ignored. This subsystem of "chemical bonds" is nothing but ideal gas of polymer molecules. Conversely, in the second auxiliary subsystem physical interactions of units to one another are taken into account whereas chemical bonds connecting adjacent units are regarded to be broken. This subsystem of "separate units" represents, evidently, ordinary low-molecular liquid of monomeric units. In the framework of the approach advanced the dependence of the free energy of this liquid on densities of units and temperature is taken to be known. Since particular appearance of this dependence does not play key role for the theory advanced in order to carry out calculations of phase diagram of particular blends it is expedient to choose the simplest model of low-molecular liquid, namely, "lattice fluid" model. Free energy of a polymer blend, F, in the framework of the mean-field approximation represents a sum of two items $F = F_{CB} + F^*$. The first of them is the free energy of subsystem of chemical bonds while the second one equals the difference of free energy of subsystem of separate units and that of ideal gas of these units. Since the dependence F^* on densities ρ_α of monomeric units M_α and temperature is taken to be known then the problem of thermodynamic description of blends reduces to finding dependence of F_{CB} on external fields η_α acting on units M_α.

There are two variants of the mean-field theory for the description of thermodynamics of copolymer blends. In the first of them scales of spatial change of densities $\rho_\alpha(\vec{r})$ and fields $\eta_\alpha(\vec{r})$ are presumed to be large enough as compared to geometrical size of macromolecules. These latter can be viewed in this case as zero-dimensional points in the Euclidean space. Here the detailed chemical structure of polymer chains turns out to be unessential, so that it would suffice to distinguish them only in size and composition by vector $\mathbf{l}$ whose α-th component l_α equals the number of units M_α in a polymer molecule. Then, in the framework of this Large-Scale Mean-Field Theory (LSMFT) it is possible to introduce macroscopic concentrations of such molecules, $C(\mathbf{l}, \vec{r})$, and considering them as individual components to resort to the methods of traditional thermodynamics. Under such an approach a blend along with temperature and volume (pressure) is also characterized either by numbers of molecules $n(\mathbf{l})$ with fixed value of composition vector $\mathbf{l}$ or by distribution $F(\mathbf{l})$ of these molecules for chemical size and composition (SCD)

$$F(\mathbf{l}) = \frac{n(\mathbf{l})}{M} \quad where\ M = \sum_{\mathbf{l}} \sum_{\alpha=1}^{m} l_\alpha n(\mathbf{l}) \tag{1}$$

The results obtained in terms of molecules can be reformulated in terms of quasicomponents which are monomeric units M_α. However, the price for such rough consideration of a blend of polydisperse polymers is the loss of free energy additivity with respect to individual phases which is inherent to ordinary thermodynamics. Hence, unlike the latter thermodynamics of monomeric units is nonlocal. Another its fundamental distinction consists in the incorrectness of the concept of chemical potential as applied to a quasicomponent. In fact, in thermodynamics of low-molecular compounds chemical potential μ_α of the α-th kind molecules in some phase is equal, by definition, to the change of the Gibbs free energy due to the transportation of one such a molecule from the infinity to this phase at constant pressure and temperature. As for blends comprising copolymer molecules of distinct composition and chemical structure here a procedure of this sort has evidently no sense because it is impossible to transfer an individual unit M_α escaping simultaneous transference of the entire macromolecule containing this unit. The third special feature of thermodynamics of monomeric units is concerned with the inapplicability of the Gibbs phase rule. Actually, maximal possible number of coexisting phases in a polymer blend is controlled by the number of parameters of SCD describing this blend rather than by the number m of its quasicomponents.

The above approach, when macromolecules are thought of as pointwise particles, fails to calculate the unit concentration profiles in the vicinity of interphase boundaries. This approach is also unsuitable for the description of mesophases which form as a result of microphase separation of blends containing block copolymers. When solving similar problems the necessity arises to allow for the change of units' concentrations and that of external field at spatial scales comparable with size of macromolecules. Such an account can be realized within the framework of the Small-Scale Mean-Field Theory (SSMFT) in terms of which polymer molecules differ not only in chemical size and composition but also in detailed chemical structure, i.e. in pattern of arrangement of monomeric units. To set such a structure of a linear molecule of a copolymer one is supposed to specify the sequence σ in which units are situated along a copolymer chain. The number of sequences of this sort grows exponentially with the length l of a molecule and for actual statistical copolymers essentially exceeds the Avogadro number. This is why it is impossible in principle to characterize a specimen of such a copolymer by specifying the concentrations of individual chemical compounds bearing in mind that the vast majority of them will be represented by no more than a single macromolecule. Clearly, in this case the notion of chemical potential for molecules with given structure σ is physically senseless. There is a fundamental difference between a blend of polydisperse homopolymers and that of copolymers consisting in the fact that the latter unlike the former can not be described by traditional thermodynamics. So, when developing SSMFT of copolymer blends recourse should be made to one of nontraditional approaches normally employed in statistical physics of disordered systems. In conformity with this approach in order to find the free energy in a subsystem of chemical bonds, F_{CB}, it is necessary to determine the free energy of a polymer molecule with an arbitrary chemical structure σ and then to average it over probability distribution of such structures $\mathcal{P}(\sigma)$. The probability measure $\mathcal{P}(\sigma)$ of macromolecules of particular polymer blend depends, firstly, on the conditions of the synthesis of polymers mixed and, secondly, on the proportions of these latter in a blend.

Phase Diagram

The easiest for calculation are the diagrams of polymer blends which do not show microphase separation since their thermodynamic behavior is described by LSMFT. To the equilibrium state of a blend, characterized by n external parameters (thermodynamic and structural), a point corresponds within their n-th dimensional hyperspace. This point drifting under the change of these parameters can intersect some specific n-dimensional hypersurfaces. The most important among them is that where nuclei of the incipient phase appear in homogeneous system. Equations defining such a hypersurface of cloud points read

$$\Phi_\alpha = \Phi^0 G_\alpha(\mathbf{s}) \qquad s_\alpha = \exp\left\{\left[\mu_\alpha^*\left(\Phi^0\right) - \mu_\alpha^*(\Phi)\right] / T\right\} \qquad (2)$$

$$T\Phi^0 G(\mathbf{s}) + vP^*(\Phi) = T\Phi^0 G(\mathbf{1}) + vP^*\left(\Phi^0\right) = vP \tag{3}$$

where P and T represent pressure and temperature, v is a monomeric unit volume, Φ_α^0 and Φ_α are volume fractions of α-th type units in principal and incipient phase, respectively. Here $\left(\Phi^0 = \Phi_1^0 + \ldots + \Phi_m^0\right)$, while μ_α^* and P^* stand for the chemical potential of α-th type units and pressure in the subsystem of separate units reckoned from the values of these quantities in the ideal gas. As it follows from equations (2), (3) the calculation of cloud-point hypersurface (and thus its two-dimensional sections which are cloud-point curves) suggests the knowledge of generating function $G(\mathbf{s})$ of SCD (1) of molecules of the system in hand

$$G(\mathbf{s}) = \sum_{\mathbf{l}} F(\mathbf{l}) \prod_{\alpha=1}^{m} s_\alpha^{l_\alpha} \qquad G_\alpha(\mathbf{s}) = \frac{\partial G(\mathbf{s})}{\partial \ln s_\alpha} \qquad G_{\alpha\beta}(\mathbf{s}) = \frac{\partial^2 G(\mathbf{s})}{\partial \ln s_\alpha \partial \ln s_\beta} \tag{4}$$

This function is known for many copolymers obtained by free-radical polymerization, polycondensation and polymer-analogous transformations [2]. Equation (3) is the condition of the equality of pressure in coexisting incipient and principal phases whereas equations (2) substitute the ordinary thermodynamic condition of equality of chemical potential in these phases for each of low-molecular compounds.

To find $(n-1)$-dimensional spinodal hypersurface, where a homophase solution becomes absolutely unstable, it is necessary to determine the minimal eigenvalue L_2 of the matrix $\mathbf{M}$

$$\mathbf{M} = \boldsymbol{\kappa}^{-1} - \mathbf{C} \qquad \kappa_{\alpha\beta} = \frac{\Phi^0}{v} X_{\alpha\beta} \qquad \mathrm{C}_{\alpha\beta} = -\frac{1}{T}\frac{\partial^2 f^*(\rho)}{\partial \rho_\alpha \partial \rho_\beta} \tag{5}$$

and to equate L_2 to zero. The elements of matrix $\boldsymbol{\kappa}$ are proportional to the second-order statistical moments $X_{\alpha\beta}$ of SCD (1) and $\mathrm{C}_{\alpha\beta}$ are elements of the matrix of direct correlation functions, $\mathbf{C}$, well known in the theory of low-molecular liquids.

Hypersurface of cloud-points and spinodal hypersurface tangent along hyperline of critical points where the density of any type monomeric units in the incipient phase has the same value as in principal one. Equations of hyperline of critical points are

$$L_2 = 0, \quad L_3 = 0, \quad where\, L_3 = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} \Gamma_{\alpha\beta\gamma}\, \psi_\alpha\, \psi_\beta\, \psi_\gamma \tag{6}$$

Expression for L_3 along with components ψ_α of the eigenvector ψ of matrix $\mathbf{M}$ (5), corresponding to its zeroth eigenvalue, comprises components $\Gamma_{\alpha\beta\gamma}$ of the third-order symmetric tensor Γ as well. These latter in accordance with formula

$$\Gamma_{\alpha\beta\gamma} = -\sum_i \sum_j \sum_k \kappa_{ijk} \left(\kappa^{-1}\right)_{i\alpha} \left(\kappa^{-1}\right)_{j\beta} \left(\kappa^{-1}\right)_{k\gamma} + \frac{f^*_{\alpha\beta\gamma}}{T} \qquad (7)$$

are expressed through the components

$$\kappa_{\alpha\beta\gamma} = \frac{\Phi}{\nu} X_{\alpha\beta\gamma} \qquad f^*_{\alpha\beta\gamma} = \frac{\partial^3 f^*(\rho)}{\partial\rho_\alpha \partial\rho_\beta \partial\rho_\gamma} \qquad (8)$$

of two symmetric tensors. The first of them is characterized by the third-order statistical moments $X_{\alpha\beta\gamma}$ of SCD (1) whereas the second one is defined by the third-order derivatives of the free energy density with respect to densities of monomeric units.

At certain values of the external parameters of a blend some critical points on its phase diagram can become degenerate upon their confluence. Depending on the degree of degeneration they distinguish triple critical, quadruple critical and so on multiple critical points. The problem of their finding has been generally solved for an arbitrary blend containing copolymers [1]. It has been demonstrated that the change of the free energy due to the formation of a small nucleus of incipient phase will be proportional to this nucleus volume. Proportionality coefficient, which can be presented as the expansion into series of some small parameter τ, vanishes on hypersurface of cloud points where $\tau = 0$. Multiplicity of this trivial root predetermines the multiplicity of the critical point. Equation for finding ν-multiple critical point in terms of the coefficients of the above expansion reads

$$L_2 = L_3 = \cdots = L_{2\nu-1} = 0 \qquad L_{2\nu} \neq 0 \qquad (9)$$

General algorithm of the calculation of these coefficients formulated in diagrammatic language [1] is currently realized as a computer program providing a possibility to reveal critical points of any multiplicity for an arbitrary copolymer blend.

References

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