Statistical Thermodynamics of Mixtures of Rodlike Particles. 1. Theory for Polydisperse Systems

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ABSTRACT: The combinatory partition function for a system of rodlike particles of diverse axis ratios mixed with a quasispherical solvent has been derived by use of the model and elaboration of the procedure previously employed for a binary system in which the solute is monodisperse. A single disorder parameter $y = x \sin \psi_x$, where x is the axis ratio for solute particles of a given component and $\sin \psi_x$ measures their average inclination with respect to the axis of the domain, or phase, characterizes all solute components for which $x > y$. Components with $x < y$ are unoriented. Chemical potentials are given for the various components, and the basic relations required for treatment of the equilibria between an isotropic and an anisotropic, or liquid crystalline, phase are derived.

The thermodynamic properties of binary mixtures consisting of a low molecular solvent and a monodisperse rodlike solute can be treated according to the theory presented a number of years ago.[1] Experiments on equilibria between nematic liquid-crystalline phases and a dilute isotropic phase in mixtures of α-helical polypeptides[2-5] or of p-phenylene polyamides[6-8] with suitable solvents have confirmed the main predictions of that theory, including the occurrence of triphasic equilibria involving an isotropic and two anisotropic phases in "endothermic" systems.[4,5] Agreement between theory and experiment appears to be semiquantitative. It seemed appropriate therefore to adapt the theory to polydisperse mixtures, such as are normally encountered in real systems. The required extension of the theory is straightforward, as we show in this paper.

Derivation of the Partition Function

The systems considered consist of mixtures of rodlike particles differing in axis ratio x dispersed in a solvent. We assume the rods to have identical diameters, their lengths being variable. For simplicity, we take the solvent to be isodiametric with its diameter equal to the (mean) thickness of the rods. Hence, $x_{\text{solvent}} = 1$. A solute segment is defined as the portion thereof having the same volume as a molecule of solvent, and hence geometrically equivalent to the latter. Thus, x is both the axis ratio and the number of segments comprising the solute molecule.

We consider a liquid-crystalline domain, or phase, in which the solute particles are preferentially oriented with respect to the cylindrical axis of the domain. As we show, the particles thus oriented may include only the larger species for which x exceeds some lower bound, smaller members of the distribution of species being randomly distributed over solid angle.

Let solute molecule j with axis ratio x_j be oriented at an angle ψ_j with respect to the axis of the domain as shown in Figure 1a. In order to implement the combinatory analysis using a lattice scheme, we subdivide the molecule[1] into $y_j = x_j \sin \psi_j$ submolecules, as shown in Figure 1b, each submolecule being aligned parallel to the domain axis. If one of the axes of the cubic lattice is taken parallel to the domain axis, then each submolecule occupies a sequence of lattice sites parallel to this axis. The system as a whole consists of submolecules confined to such rows, and the problem simplifies to one of mixing submolecules and vacancies (i.e., solvent molecules) in one dimension.[1]

The foregoing device, employed previously, is justified by the consideration that the expectation of interferences between segments of different molecules cannot be materially affected by this maneuver. It will be observed that y_j specifies simultaneously the departure of molecule j from perfect alignment and the number of submolecules into which it must be subdivided to conform with the model.

Let the solute molecules, n_2 in number, be inserted sequentially into the space subdivided into n_0 lattice sites. Their locations are chosen at random, apart from the requirement that occupation of a site by a segment is exclusive. The orientation of each molecule j relative to the domain axis is specified, however, by its "disorientation index" y_j.

After $j - 1$ molecules have been introduced in this manner, the expected number of situations available to the jth solute molecule is

$$\nu_j = \left(n_0 - \sum_1^{j-1} x_i\right) \left[\frac{n_0 - \sum_1^{j-1} x_i}{n_0} \right]^{y_j - 1} \left[\frac{n_0 - \sum_1^{j-1} x_i}{n_0 - \sum_1^{j-1} x_i + \sum_1^{j-1} y_i} \right]^{x_j - y_j} \tag{1}$$

where x_j and y_j denote the axis ratio and disorientation, respectively, of this molecule. The first factor, being the number of vacancies, is the number of sites accessible to the first segment of the first submolecule of molecule j. On the assumption that the distribution of occupied sites in a given row parallel to the domain axis is independent of circumstances in neighboring rows, the expectation of vacancy of a site required for the first segment of a succeeding submolecule is just the volume fraction of vacancies. This is the basis for the second factor in eq 1. If, however, a given site is known to be vacant (and hence established to be eligible for occupation by a segment) then the site following it in the same row can only be occupied by the initial segment of a submolecule; otherwise it must be vacant. Hence, the conditional expectation of vacancy is in this case the ratio of vacancies to the sum of vacancies and submolecules. The last factor in eq 1 expresses this "mole fraction", and it is raised to the power expressing the total number of segments in molecule j other than those that are the initial ones of submolecules.

Consolidation of eq 1 gives

$$\nu_j = \frac{\left(n_0 - \sum_1^{j-1} x_i\right)^{x_j}}{\left[n_0 - \sum_1^{j-1} (x_i - y_i)\right]^{(x_j - y_j)} n_0^{\,y_j - 1}} \tag{2}$$

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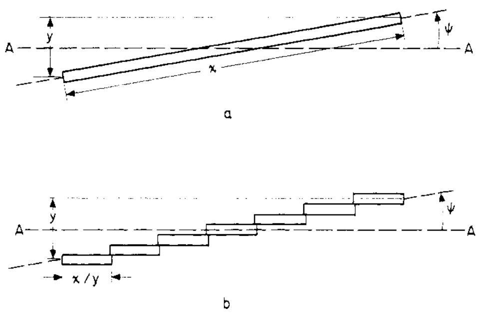

Figure 1. (a) A rodlike particle of axis ratio x oriented at angle ψ to the domain axis AA. (b) The model comprising $y = x \sin \psi$ submolecules, each submolecule being parallel to the domain axis AA.

Expressed for convenience in terms of factorials, this becomes

$$\nu_j = \frac{(n_0 - \sum_1^{j-1} x_i)![n_0 - \sum_1^{j} (x_i - y_i)]!}{(n_0 - \sum_1^{j} x_i)![n_0 - \sum_1^{j-1} (x_i - y_i)]! {n_0}^{y_j - 1}} \qquad (3)$$

with negligible error.

The combinatory part of the configuration partition function for the mixture is given by[1]

$$Z_{\mathrm{M}} = \prod_1^{n_2} \nu_j \prod_{x,y} \omega_{x,y}^{n_{x,y}} / n_{x,y}! \qquad (4)$$

where $n_{x,y}$ is the number of molecules of axis ratio x and disorientation index y, and $\omega_{x,y}$ is the solid angle occupied by species of this designation relative to the solid angle for $y = 1$, this being the state of reference. Substitution of eq 3 in 4 yields

$$Z_{\mathrm{M}} = \frac{[n_0 - \sum_1^{n_2} (x_i - y_i)]! \prod_{x,y} \omega_{x,y}^{n_{x,y}} / n_{x,y}!}{(n_0 - \sum_1^{n_2} x_i)! {n_0}^{(\sum_1^{n_2} y_i) - n_2}} \qquad (5)$$

Replacement of n_0 with $n_1 + \sum_x x n_x$, where n_1 and n_x are the numbers of molecules of solvent and of solute with axis ratio x, yields

$$Z_{\mathrm{M}} = \left[\frac{(n_1 + \sum_x y_x n_x)!}{n_1! (\prod_x n_x!)(n_1 + \sum_x x n_x)^{\sum_x n_x (y_x - 1)}} \right] \prod_x [n_x! \prod_y \omega_{x,y}^{n_{x,y}} / n_{x,y}!] \qquad (6)$$

where y_x is the mean value of y for "x-mers".

The last factor in eq 6 takes account of the dispersions of orientations y_x of the various species. As was shown previously,[1] the approximation

$$n_x! \prod_y \omega_{x,y}^{n_{x,y}} / n_{x,y}! \approx {y_x}^{2n_x} \qquad (7)$$

is satisfactory for $y < x/2$, which is the range of dominant importance. Adoption of this approximation yields

$$Z_{\mathrm{M}} \approx \frac{(n_1 + \sum y_x n_x)! \prod {y_x}^{2n_x}}{n_1! (\prod n_x!)(n_1 + \sum x n_x)^{\sum n_x (y_x - 1)}} \qquad (8)$$

where the products and sums are over all values of x.

Introducing Stirling's formula for the factorials, and dismissing the attendant small error, we obtain

$$-\ln Z_{\mathrm{M}} = n_1 \ln v_1 + \sum n_x \ln v_x - (n_1 + \sum y_x n_x) \times \ln \left(\frac{n_1 + \sum y_x n_x}{n_1 + \sum x n_x} \right) - \sum n_x [\ln (x {y_x}^2) - (y_x - 1)] \qquad (9)$$

where $v_1 = n_1/(n_1 + \sum x n_x)$ and $v_x = x n_x / (n_1 + \sum x n_x)$ are the volume fractions of solvent and of x-mer, respectively. Equation 9 may be written alternatively as follows

$$-\ln Z_{\mathrm{M}} = n_1 \ln v_1 + \sum n_x \ln v_x - (n_1 + \sum x n_x)[1 - v_2(1 - \bar{y}_n/\bar{x}_n)] \ln [1 - v_2(1 - \bar{y}_n/\bar{x}_n)] - \sum n_x [\ln (x {y_x}^2) - (y_x - 1)] \qquad (9')$$

where $v_2 = \sum v_x$ is the volume fraction of all solute species, and $\bar{x}_n = \sum x n_x / \sum n_x$ and $\bar{y}_n = \sum y_x n_x / \sum n_x$ are the number averages of x and y.

If $y_x = 1$ for all x, corresponding to perfect alignment with respect to the domain axis, eq 9, and likewise eq 9′, reduce to the ideal mixing law as required for mixing in one dimension. In the opposite extreme of random orientations of solute molecules, it is appropriate[1] to take $y_x = x$ for all x. Equations 9 and 9′ then reduce to

$$-\ln Z_{\mathrm{M}} = n_1 \ln v_1 + \sum n_x \ln v_x - \sum n_x [\ln x - (x - 1)] - \sum n_x \ln x^2 \qquad (10)$$

which is identical to the familiar expression for polymer mixtures, apart from the disorientation entropy term. This term, the last one in eq 10, replaces the usual lattice term $\sum n_x \ln (z - 1)$ where z is the coordination number of the lattice. It follows directly from eq 7, which comprehends a greater subdivision of solid angle than strict adherence to the lattice admits. This difference compared to the usual formulation is of no consequence in regard to results deduced from the partition function, provided that the same rendition is used consistently.

In the foregoing derivation of Z_{M} we have deliberately disregarded noncombinatory contributions. These could be acknowledged, if desired, by adding the usual term in χ which formally represents exchange interactions but may include other contributions as well.[9,10] As we shall not call upon such terms in this series of papers, they are omitted.

Equilibrium Disorder

Differentiating eq 9 or 9′ with respect to y_x and equating the result to zero, one obtains

$$\exp(-2/y_x) = 1 - v_2(1 - \bar{y}_n/\bar{x}_n) \qquad (11)$$

This equation possesses two real solutions y provided that the concentration v_2 and mean axis ratio $\bar{x}_n$ are sufficiently large. The lower of these solutions locates the maximum in Z_{M}.

According to eq 11 the value of y_x that maximizes Z_{M}, i.e., the equilibrium value of y, *is independent of* x. Hence, the subscript on y_x may be dropped and eq 11 may be replaced by

$$\exp(-2/y) = 1 - v_2(1 - \bar{y}_n/\bar{x}_n) \qquad (12)$$

where y is the *disorder parameter* that characterizes *average orientations of all species for which* $x > y$. For smaller species, if any for which $x \leq y$ are present, Z_{M} increases monotonically with y_x up to its physical limit $y_x = x$. It follows that $y_x = x$ for such species. In eq 12, $\bar{y}_n$ is the average for *all* solute species.

It becomes necessary in general, therefore, to distinguish two categories of solute species in mixtures for which eq 12 yields solutions y and which accordingly are anisotropic at equilibrium. The first category comprises "aligned" species with $x > y$ and whose orientations are positively correlated with the domain axis (denoted by AA in Figure

1). The second includes "random" species with $x \leq y$, if such are present. They are unoriented, their directions being random. The former and latter will be distinguished by subscripts A and R, respectively.

Let volume fractions and number average axis ratios be defined as follows:

$$v_{2\mathrm{R}} = \sum_{x \leq y} v_x; \qquad v_{2\mathrm{A}} = \sum_{x > y} v_x \tag{13}$$

$$\bar{x}_{n\mathrm{R}} = \sum_{x \leq y} x n_x \Big/ \sum_{x \leq y} n_x \tag{14}$$

$$\bar{x}_{n\mathrm{A}} = \sum_{x > y} x n_x \Big/ \sum_{x > y} n_x \tag{15}$$

Then

$$v_2 = v_{2\mathrm{R}} + v_{2\mathrm{A}} \tag{16}$$

$$v_2/\bar{x}_n = v_{2\mathrm{R}}/\bar{x}_{n\mathrm{R}} + v_{2\mathrm{A}}/\bar{x}_{n\mathrm{A}} \tag{17}$$

and

$$\bar{y}_n = \Big(\sum_{x \leq y} x n_x + y \sum_{x > y} n_x\Big) \Big/ \sum_{x=1}^{\infty} n_x$$

or

$$(\bar{y}_n/\bar{x}_n) v_2 = v_{2\mathrm{R}} + (y/\bar{x}_{n\mathrm{A}}) v_{2\mathrm{A}} \tag{18}$$

Substitution of eq 16 and 18 in eq 12 leads to the alternative relation

$$\exp(-2/y) = 1 - v_{2\mathrm{A}}(1 - y/\bar{x}_{n\mathrm{A}}) \tag{12$'$}$$

Thus, as was to be expected, the disorder parameter y depends only on the concentration and average axis ratio of those components that are mutually oriented. (This equation may be derived directly by differentiation of eq 19 below.)

Constancy of $y_x = y$ for $x > y$ does not denote uniformity of orientation of all species. On the contrary, the mean angular disorientation ψ_x for x-mers with $x > y$ is $\psi_x = \sin^{-1}(y/x)$ which decreases with increase in x. The universality of y for all species $x > y$ greatly facilitates analysis of polydisperse systems, and this fact recommends y (rather than ψ_x) as a succinct measure of disorder, which characterizes the anisotropic phase as a whole.

Strict adherence to the model from which the mixing partition function has been derived would restrict y to positive integral values. In particular, $y < 1$ would be inadmissible inasmuch as $y = 1$ denotes perfect alignment of the rodlike particles. The model is an idealization, however, and its precepts should not necessarily be followed literally. With this in mind, it is noteworthy that the partition function as given by eq 9 and 9′, and all results derived therefrom are continuous functions of y. None exhibits a singularity in the range $0 < y < x$. For these reasons, treatment of y as a continuous (dependent) variable seems justified in applications of the theory.

The validity of sanctioning values of $y < 1$ indicated by eq 12, or eq 12′, under some circumstances[11,12] is more problematical. Values of y in this range cannot be justified within the terms of the lattice model. On the other hand the unnatural constraints implicit in this model are well known. In the papers that follow,[11,12] y usually is allowed to assume any value $y > 0$ required by eq 12 or 12′. However, for those conditions giving $y < 1$ results of alternative calculations are presented, or cited, in which $y = 1$ was taken as a lower bound.

Chemical Potentials

In consequence of the results of the preceding section, it is expedient to recast eq 9′ for the combinatory partition function as follows:

$$\begin{aligned}-\ln Z_\mathrm{M} = {} & n_1 \ln v_1 + \sum n_x \ln (v_x/x) - \Big(n_1 + \sum x n_x\Big) \times \\ & [1 - v_{2\mathrm{A}}(1 - y/\bar{x}_{n\mathrm{A}})] \ln [1 - v_{2\mathrm{A}}(1 - y/\bar{x}_{n\mathrm{A}})] + \\ & \sum_{x \leq y} (x - 1) n_x - \sum_{x \leq y} n_x \ln x^2 - (\ln y^2 - y + 1) \sum_{x > y} n_x\end{aligned} \tag{19}$$

The chemical potential of the solvent in an anisotropic phase is given by

$$\begin{aligned}(\mu_1 - \mu_1^0)/RT = {} & -(\partial \ln Z_\mathrm{M}/\partial n_1)_{T,V,\{n_x\},\mathrm{eq}} = \\ & -(\partial \ln Z_\mathrm{M}/\partial n_1)_{T,V,\{n_x\},y} - \\ & (\partial \ln Z_\mathrm{M}/\partial y)_{T,V,\{n_x\},n_1} (\partial y/\partial n_1)_{T,V,\{n_x\},\mathrm{eq}}\end{aligned}$$

where $\{n_x\}$ denotes the set of mole numbers for all solute components and the subscript eq signifies equilibrium disorder. Since $(\partial \ln Z_\mathrm{M}/\partial y)_{T,V,\{n_x\},n_1} = 0$ for the mixture at its equilibrium degree of disorder y,

$$(\mu_1 - \mu_1^0)/RT = -(\partial \ln Z_\mathrm{M}/\partial n_1)_{T,V,\{n_x\},y} \tag{20}$$

Differentiation of eq 19 followed by substitution from eq 17 and 18 gives

$$\begin{aligned}(\mu_1 - \mu_1^0)RT = {} & \ln (1 - v_2) - \ln [1 - v_{2\mathrm{A}}(1 - y/\bar{x}_{n\mathrm{A}})] + \\ & v_{2\mathrm{R}}(1 - 1/\bar{x}_{n\mathrm{R}}) + v_{2\mathrm{A}}(y - 1)/\bar{x}_{n\mathrm{A}}\end{aligned} \tag{21}$$

In this equation and those to follow y must be identified with the lower (equilibrium) solution of eq 12 or 12′. Substitution of eq 12′ in eq 21 yields the alternative expression

$$\begin{aligned}(\mu_1 - \mu_1^0)/RT = {} & \ln (1 - v_2) + 2/y + v_{2\mathrm{R}}(1 - 1/\bar{x}_{n\mathrm{R}}) + \\ & v_{2\mathrm{A}}(y - 1)/\bar{x}_{n\mathrm{A}}\end{aligned} \tag{22}$$

Expressions for the chemical potentials of solute components derived similarly are, for $x \leq y$

$$\begin{aligned}(\mu_x - \mu_x^0)_\mathrm{R}/RT = {} & \ln (v_x/x) + 2x/y - \ln x^2 + \\ & x v_{2\mathrm{R}}(1 - 1/\bar{x}_{n\mathrm{R}}) + x v_{2\mathrm{A}}(y - 1)/\bar{x} n_\mathrm{A}\end{aligned} \tag{23}$$

and for $x > y$

$$\begin{aligned}(\mu_x - \mu_x^0)_\mathrm{A}/RT = {} & \ln (v_x/x) + 2 - \ln y^2 + \\ & x v_{2\mathrm{R}}(1 - 1/\bar{x}_{n\mathrm{R}}) + x v_{2\mathrm{A}}(y - 1)/\bar{x}_{n\mathrm{A}}\end{aligned} \tag{24}$$

The chemical potentials for an ideal mixture, with concentrations expressed in volume fractions, are given by

$$(\mu_1 - \mu_1^0)/RT = \ln (1 - v_2) - \ln [1 - v_2(1 - 1/\bar{x}_n)] \tag{25}$$

$$(\mu_x - \mu_x^0)/RT = \ln (v_x/x) - \ln [1 - v_2(1 - 1/\bar{x}_n)] \tag{26}$$

Substitution of $y = 1$, $v_{2\mathrm{R}} = 0$, and $v_{2\mathrm{A}} = v_2$ in eq 21 yields eq 25. The same substitutions in the antecedent to eq 23 (not included here) obtained directly through differentiation of eq 19, without substitution from eq 12, yield eq 26.

The chemical potentials that follow from eq 10 for an isotropic phase are

$$(\mu_1 - \mu_1^0)/RT = \ln (1 - v_2) + (1 - 1/\bar{x}_n) v_2 \tag{27}$$

$$(\mu_x - \mu_x^0)/RT = \ln (v_x/x) + x(1 - 1/\bar{x}_n) v_2 - \ln x^2 \tag{28}$$

Phase Equilibria

At equilibrium between an isotropic and an anisotropic phase

$$\mu_1 = \mu_1' \tag{29a}$$

$$\mu_x = \mu_x', \quad \text{for all } x \tag{29b}$$

where the anisotropic phase is distinguished by a superscript prime. Substitution from eq 27 for μ_1, from eq 28 for μ_x, from eq 22 for μ_1', and from eq 23 for μ_x' gives for $x \leq y$

$$\ln [(1 - v_2')/(1 - v_2)] = (1 - 1/\bar{x}_n) v_2 - 2/y - B \tag{30}$$

and

$$\ln (v_x'/v_x) = x(1 - 1/\bar{x}_n)v_2 - 2x/y - Bx \qquad (31)$$

where

$$B = v_{2R}'(1 - 1/\bar{x}_{nR}') + v_{2A}'(y - 1)/\bar{x}_{nA}' \qquad (32)$$

Use of eq 24 for μ_x' when $x > y$ gives

$$\ln (v_x'/v_x) = x(1 - 1/\bar{x}_n)v_2 - 2[1 + \ln (x/y)] - Bx \qquad (33)$$

Substitution of eq 30 in 31 yields

$$v_x'/v_x = [(1 - v_2')/(1 - v_2)]^x = (v_1'/v_1)^x, \quad x \leq y \qquad (34)$$

or

$$v_x'/v_x = \exp(-\zeta x), \quad x \leq y \qquad (35)$$

where

$$\zeta \equiv -\ln [(1 - v_2')/(1 - v_2)] = B + 2/y - (1 - 1/\bar{x}_n)v_2 \qquad (36)$$

Similarly, substitution of eq 30 in 33 leads to

$$v_x'/v_x = (y/ex)^2[\exp(2/y)(1 - v_2')/(1 - v_2)]^x, \quad x > y \qquad (37)$$

or

$$v_x'/v_x = (y/ex)^2 \exp(\eta x), \quad x > y \qquad (38)$$

where

$$\eta = 2/y - \zeta \qquad (39)$$

$$\eta = (1 - 1/\bar{x}_n)v_2 - B \qquad (40)$$

Defined in this manner, both ζ and η are positive. For $v_{2R}' << v_2$ and $(y - 1)/\bar{x}_{nA}' << 1$,

$$\eta \approx v_2 \qquad (41)$$

and eq 38 reduces to

$$v_x'/v_x \approx (y/ex)^2 \exp(v_2 x), \quad x > y \qquad (42)$$

If the anisotropic phase is taken to be ideal, as may be appropriate when $y \leq 1$ according to eq 12 or 12′, then substitution from eq 25 and 26 for the chemical potentials μ_1' and μ_x', respectively, in the equilibrium conditions expressed by eq 29 yields

$$\ln[(1 - v_2')/(1 - v_2)] = (1 - 1/\bar{x}_n)v_2 + \ln [1 - v_2'(1 - 1/\bar{x}_n')] \qquad (43)$$

and

$$v_x'/v_x = x^{-2}[1 - v_2'(1 - 1/\bar{x}_n')] \exp(\eta^* x) \qquad (44)$$

where

$$\eta^* = (1 - 1/\bar{x}_n)v_2 \qquad (45)$$

Results of calculations of phase equilibria in polydisperse systems are presented in the three following papers.[11-13]

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Statistical Thermodynamics of Mixtures of Rodlike Particles. 2. Ternary Systems

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ABSTRACT: Phase equilibria have been calculated for athermal, three-component systems comprising a solvent with axis ratio $x_1 = 1$ and two solutes consisting of rodlike particles with axis ratios x_a and x_b, respectively, equal to (40,20), (100,20), and (100,10). The small immiscibility gaps separating the isotropic (dilute) from the anisotropic (more concentrated) phase in the respective two-component systems (1,a) and (1,b) are enlarged by addition of the second solute component. The species a and b, with $x_a > x_b$, occur preferentially in the anisotropic and isotropic phases, respectively. The component with axis ratio $x_a = 100$ is virtually excluded from the isotropic phase when the amount of the smaller component (x_b = 10 or 20) in the system is more than a few percent of *a*. Triphasic equilibria are predicted for the systems x_a,x_b = 100,20 and 100,10.

In this paper we apply the relationships derived in the one preceding[1] (referred to as 1) to systems consisting of two rigid, rodlike solutes having unequal axis ratios, x_a and x_b, and a solvent. As in 1, the breadths of the solute molecules are taken to be the same and equal to the diameter of the isodiametric solvent. The systems are considered to be athermal. The straightforward extensions of the theory that would be required to take account of exchange interactions upon mixing are deliberately disregarded.

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