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Effective χ in a lattice theory of mixtures

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Using general thermodynamic arguments for an incompressible lattice system, we demonstrate that the effective χ must be a complicated function of temperature, composition, polymerization indices, and the coordination number of the lattice, even though the bare χ is merely a parameter. We go beyond the random mixing approximation and present a lattice theory of mixtures which yields an effective χ consistent with experiments. [S1063-651X(96)04409-1]

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I. INTRODUCTION

Conventional mean-field or regular solution theories are primarily based on the random mixing (also known as Bragg-Williams) approximation (RMA) [1,2]. The basic assumption is that there is *no* correlation between neighboring interacting species, an assumption that should be good at infinite temperatures. However, because of the nature of the approximation, theories based on it have a limited applicability from a quantitative point of view. It is in connection with polymers where such a theory known as the Flory-Huggins theory (FHT) [3,4] has been used almost exclusively everywhere. The use of the theory even beyond its range of applicability [5] has made the field very murky (see below). Our aim here is to *clarify* the situation.

In particular, we explicitly demonstrate that even a simple lattice model is capable of explaining many of the observed features in experiments. We accomplish this by going beyond the RMA and present a theory of incompressible mixtures. The theory is an approximation but applicable everywhere, even near phase transitions. In the following, we specifically consider the FHT, but the discussion is equally applicable to any regular solution theory or any conventional mean-field theory.

The simplest model of a polymer mixture (solution, blend, etc.) is to treat a linear chain as a self-avoiding walk on a regular lattice of coordination number q and to treat monomers (including solvent molecules) as having identical sizes. The model is defined in the next section. The interaction between monomers is restricted to neighboring units and is described by a dimensionless parameter $\chi=\beta q\varepsilon$, $\beta=1/T$, having a *trivial* dependence on q and the temperature T. (We set the Boltzmann constant to be unity.) Here, one may take the parameter ε to denote the energy of interaction between unlike units. The interaction energy in reduced units is $\beta E=\chi\phi_c/q$, where ϕ_c is the density of contacts between unlike monomers and must be treated as a new and independent density in addition to the composition. Thus, the entropy S must also be a function of these two independent densities. Such an ensemble or any equivalent ensemble with *two* variables is needed to provide a complete thermodynamic description, the free energies of various ensembles being related by proper Legendre transforms. In the RMA, the following holds.

(a) The contact density ϕ_c is given by $\phi_c=\hat{\phi}_c^0=q\phi_m\phi'_m$ regardless of ε and β. Here, ϕ_m and ϕ'_m are the monomer densities of the two interacting species.

(b) The entropy of mixing S_{mix} is the same as for the athermal state $(\chi=0)$ and is independent of ε and β, even though the interactions are present.

Both these conclusions are incorrect [5] for the original model for both ϕ_c and S_{mix} must change with χ (also see below). In particular, $S_{\mathrm{mix}}(\chi)$ or the entropy $S(\chi)$ must possess a maximum at $\chi=0$ and, therefore, must decrease as interactions are introduced [6]. Similarly, ϕ_c must increase or decrease as the interaction becomes more favorable or unfavorable, respectively. Flory [4] had already realized the seriousness of (b) and had postulated that (c) the change S_{int} in S_{mix} due to interaction must again be of the form $\chi_s\phi_m\phi'_m$ and, therefore, must add an ''entropic'' part χ_s that has *no* temperature dependence.

This conjecture is also incorrect for this additional change S_{int} must vanish at $\chi=0$ whereas the Flory form has the same value for all χ. Note that ϕ_c and χ, both being dimensionless, can be treated as functions of dimensionless quantities ϕ_m and $\beta\varepsilon$, but not functions of ε, which is not dimensionless. This again shows that χ_s *cannot* be temperature independent, since it must vanish at $\varepsilon=0$.

In spite of the drastic approximations, the FHT theory is widely used in fitting experimental data. This results in an effective χ_{eff} that is found to have a nontrivial dependence on temperature, composition, polymerization indices, etc. [7–10]. The complicated behavior of χ_{eff} has mystified workers in the field for a long time and various attempts [7–15] have been made to explain the unusual behavior. More recently, Hammouda and Bauer [10] have concluded that the composition dependence in χ_{eff} cannot be attributed to the compressibility of the mixture. Therefore, we consider an incompressible system here. In the following, we take $\chi_{\mathrm{eff}}=\overline{\chi_{\mathrm{eff}}}\equiv\chi\phi_c/q\phi_m\phi'_m$ as our main emphasis is to study phase separation.

Thermodynamics requires S to be a function of two independent densities ϕ_m and ϕ_c when $\varepsilon\neq 0$, in addition to other parameters. Consequently, $\overline{\chi_{\mathrm{eff}}}$ must depend, in general, on q, molecular weights M and M', χ, and ϕ_m in any complete theory, notwithstanding the fact that the bare χ is a parameter in the lattice model; one does not need to invoke com-

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pressibility for such a dependence. We present a lattice theory of the model of polymer blends and solutions that not only satisfies thermodynamics, but also predicts phase separation and yields $\chi_{\rm eff}$ that is consistent with experiments. The theory provides closed form expressions for the entropy and the free energy and is applicable everywhere.

II. THERMODYNAMICS

Let the two species be denoted by A and A', both of which may be polymers containing $M=L+1$ and $M'=L'+1$ monomers, or a polymer $(M>1)$ and solvent $(M'=1)$. Let ϕ_m and ϕ'_m be their monomer densities, and ϕ and ϕ' be their bond densities: $M\phi=L\phi_m$, $M'\phi'=L\phi'_m$. Further, let ϕ_a, ϕ'_a, and ϕ_c denote the densities of unbonded AA pairs, unbonded $A'A'$ pairs, and AA' pairs, respectively. On the lattice, we have the following identities: $q\phi_m=2\phi+2\phi_a+\phi_c$, $q\phi'_m=2\phi'+2\phi_b+\phi_c$, with $\phi_m+\phi'_m=1$. The latter is the incompressibility condition. Thus, we have only two *independent* densities that we take to be ϕ or ϕ_m and ϕ_c in the following. Corresponding to the densities ϕ and ϕ_c, we have two independent activities that we denote by K and w, respectively, with $w=\exp(-\beta\varepsilon)$. The total partition function Z of the lattice model is [6] $Z=\sum\Omega(q,M,M',B,N_c)K^B w^{N_c}$, where Ω is the number of ways of putting the polymer mixture on the lattice of N sites and the sum is over all possible values of B and N_c, consistent with N, q, M, and M'. Here, B is the total number of bonds of all A polymers and N_c is the number of nearest-neighbor AA' monomer pairs. We have shown explicitly the entire set of quantities (excluding N) Ω depends on, even though we will usually only exhibit the dependence on B and N_c (or, equivalently, ϕ and ϕ_c) in the following for convenience.

For a system in which polymers are of a fixed length, as we consider here, an entire polymer must be added or removed from the system. Therefore, K^L acts as the activity per A molecule. With this understanding, there is no harm in thinking of K as the activity per bond. The constraint of fixed-length polymers is taken care of by Ω: it contains only those *configurations* that are consistent with having polymers of fixed lengths. In case A denotes a monomeric species, B must be replaced by the number of monomers. Now, K denotes the activity for a monomer.

Let us introduce the entropy $S(\phi,\phi_c)=\ln\Omega/N$, where $\phi=B/N$ and $\phi_c=N_c/N$ in the thermodynamic limit $N\rightarrow\infty$ that is always implied below. Notice that S is a function of two densities ϕ and ϕ_c corresponding to two activities K and w. To be precise, $\beta\mu=\ln K$ is the reduced chemical potential for the bond density ϕ. In equilibrium, the reduced free energy $\omega=\ln Z/N=-F/T$ is a function of K and w, and is related to the entropy by the Legendre transform $\omega(K,w)=-\beta F(K,w)=S(\phi,\phi_c)+\phi\ln K+\phi_c\ln w$, with

$$\partial S/\partial\phi=-\ln K=-\beta\mu,\quad \partial S/\partial\phi_c=-\ln w=\beta\varepsilon. \tag{1}$$

From the convexity of the free energy ω, we observe that

$$(\partial\phi/\partial K)_w>0,\quad (\partial\phi_c/\partial w)_K>0, \tag{2}$$

the inequalities turning into equalities as $K\rightarrow\infty$ or $w\rightarrow\infty$, respectively. From the free energy $\widetilde{\omega}(\phi,w)=-\beta\widetilde{F}(\phi,w)=S(\phi,\phi_c)+\phi_c\ln w$, customarily used in literature [4] because the ensemble with fixed ϕ and T are easily prepared in experiments, we have

$$\partial\widetilde{\omega}/\partial\phi=-\beta\mu,\quad (\partial\phi_c/\partial w)_\phi>0, \tag{3}$$

the inequality again turning into an equality as $w\rightarrow\infty$. Thus, ϕ_c must be a monotonic increasing function of w.

For $w=1$, we have an athermal mixture. In this case, we can introduce $\Omega_{\rm ath}(q,M,M',B)$ by summing $\Omega(q,M,M',B,N_c)$ over all possible values of N_c consistent with a fixed N, q, M, M', and B. The partition function now becomes $Z_{\rm ath}=\sum\Omega_{\rm ath}(q,M,M',B)K^B$. Hence, $\Omega_{\rm ath}>\Omega$, i.e., $S_{\rm ath}>S(\chi\equiv0)$: the entropy S achieves its maximum value in the athermal state [6] and decreases from its maximum value $S_{\rm ath}=\ln\Omega_{\rm ath}/N$ as interactions are introduced. Thus, the athermal entropy is the maximum possible entropy and occurs when $\beta\varepsilon=0$, i.e., $w=1$.

For $w=1$, and simple fluids $(M=M'=1)$, ϕ_c is given exactly by $\hat{\phi}_c^0=q\phi_m\phi'_m$ For polymers, we expect the value of ϕ_c to be smaller: The proximity of monomers of a given species required for bonding is equivalent to reducing unbonded bond densities $\phi_{mu}=\phi_a+\phi_c/2$ and $\phi'_{mu}=\phi'_a+\phi_c/2$ and, therefore, ϕ_c must decrease. This argument must be valid even when interactions are present. Therefore,

$$\phi_c(\chi)<\hat{\phi}_c(\chi), \tag{4}$$

the caret indicating simple fluids. For fixed w, we can treat ϕ_c to depend on q, M, M', ϕ_m, and w. Hence, $\overline{\chi}_{\rm eff}$ is also a function of these variables. We do not need compressibility to account for such dependence.

We can summarize the thermodynamics of the model by the following fundamental thermodynamic relations:

$$dS=-\beta\mu d\phi+\beta\varepsilon d\phi_c=-\beta\mu d\phi+\beta dE,$$

$$d\widetilde{\omega}=-\beta\mu d\phi-\varepsilon\phi_c d\beta=-\beta d\widetilde{F},$$

$$d\omega=\phi d(\beta\mu)-\varepsilon\phi_c d\beta=-\beta dF. \tag{5}$$

III. NEW THEORY

We now present a theory which is an extension of a theory of polymer solutions $(M'=1)$ developed recently [16] to the present case $(M'>1)$. We approximate the lattice by an infinite tree (Bethe lattice) of the same coordination number, on which the model is solved exactly. This ensures that thermodynamics is *always* satisfied. Moreover, it has been argued recently that the Bethe lattice calculations are also superior to mean-field theories [17]. The method of solution on the tree is standard and well known [18]. Therefore, we only quote results for a binary system. Extensions to multicomponent systems is straight forward and will be reported elsewhere.

We break the total chemical potential $\mu=\mu_{\rm ath}+\mu_{\rm int}$ and the total entropy $S=S_{\rm ath}+S_{\rm int}$ into athermal and interaction parts, the latter vanishing in the athermal limit. We find $(r=q-1)$

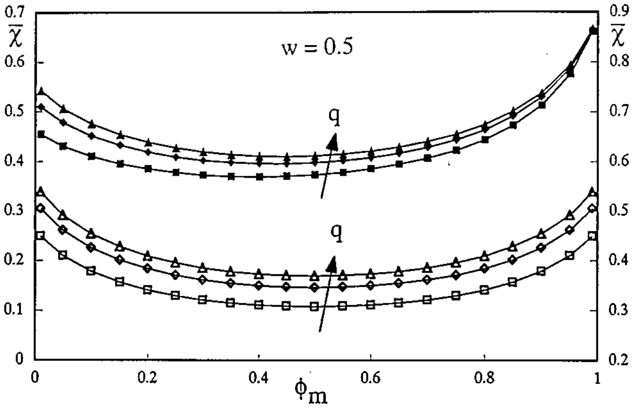

FIG. 1. $\overline{\chi}=\overline{\chi_{\text{eff}}}/q$ for $w=0.5$ and $q=6$, 8, and 10 (see arrows) for a solution (filled symbols and left axis) and for a symmetric blend (empty symbols and right axis).

$$\beta\mu_{\text{ath}}=(1/L)\ln(\phi_n/g)-(m/m'L')\ln(\phi_n'/g')+(1-m/m')\ln(2\phi_u/qr), \tag{6}$$

$$\beta\mu_{\text{int}}=(qm/2)[(n/m)\ln(\phi_a/\phi_a^0)-(n'/m')\ln(\phi_a'/\phi_a'^0)], \tag{7}$$

$$S_{\text{ath}}=(q/2)\ln r-\phi_n\ln(\phi_n/g)-\phi_n'\ln(\phi_n'/g')+\phi_u\ln(2\phi_u/qr), \tag{8}$$

$$S_{\text{int}}=\phi_a\ln(\phi_a^0/\phi_a')+\phi_a'\ln(\phi_a'^0/\phi_a)+\phi_c\ln(\phi_c^0/\phi_c), \tag{9}$$

where $\phi_n=\phi_m/M$ and $\phi_n'=\phi_m'/M'$ are number densities of the two species, $\phi_u=\phi_{mu}+\phi_{mu}'=q/2-(\phi+\phi')$ is the density of all chemically unbonded bonds, $m=M/L$, $m'=M'/L'$, $n=m-2/q$, $n'=m'-2/q$, and g (or g') is 1 or $q/2r$ if M (or M') is 1 or larger, respectively. For $w=1$, $\phi_a=\phi_a^0=\phi_{mu}^2/\phi_u$, $\phi_b=\phi_b^0=\phi_{mu}'^2/\phi_u$, and $\phi_c=\phi_c^0=2\phi_{mu}\phi_{mu}'/\phi_u$. This ensures that $\mu_{\text{int}}=0$ and $S_{\text{int}}=0$ when $w=1$. For $w=1$, $\phi_c=\phi_c^0=2\sqrt{\phi_a^0\phi_a^0}$. If now $q\to\infty$, $\phi_c\to q\phi_m\phi_m'$. Thus, the FHT corresponds to $w\to1$, $q\to\infty$, as claimed earlier [16].

In order to derive Eqs. (6)–(9), we first obtain w and K in terms of densities so that we can use them in Eq. (1). We integrate Eq. (1) to obtain S. The constant of integration is fixed by matching the present entropy for $\phi'=0$ (this represents a melt of A polymers) with that obtained in Ref. [16]. Thus, S is obtained uniquely (on the Bethe lattice). For w, we obtain

$$w=\phi_c/2\sqrt{\phi_a\phi_a'}, \tag{10}$$

as was also the case for polymer solutions [16]. Incidentally, Eq. (10) was earlier derived by Rushbrooke [19] in one dimension and by Guggenheim [20] for the general case using a very different method.

We use Eq. (10) to obtain ϕ_c and $\overline{\chi_{\text{eff}}}$. We show $\overline{\chi}=\overline{\chi_{\text{eff}}}/q$ for $q=6$, 8, and 10, $w=0.5$, in Fig. 1 and for $w=0.7$, 0.8, and 0.9, $q=6$, in Fig. 2 for a solution ($L=1000$, $L'=0$, full symbols) and a symmetric blend ($L=L'=1000$, empty symbols). Note $\overline{\chi_{\text{blend}}}<\overline{\chi_{\text{solution}}}$, the difference decreasing as $w\to1$. The minimum in $\overline{\chi_{\text{solution}}}$ moves toward $\phi_m=0$ as $w\to1$, thus making $\overline{\chi_{\text{solution}}}$ almost monotonic. For the symmetric blend, the minimum stays at $\phi_m=\frac{1}{2}$.

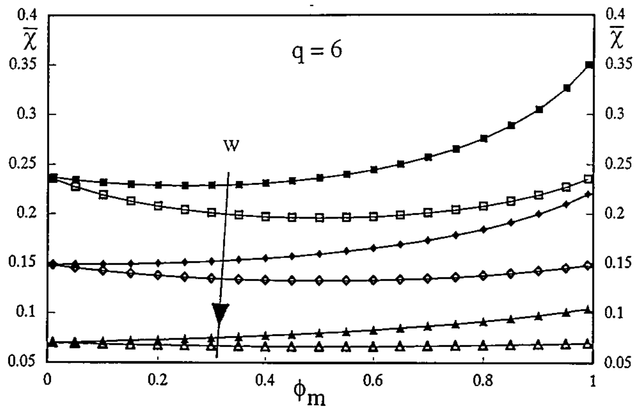

FIG. 2. $\overline{\chi}$ for $w=0.7$, 0.8, and 0.9, top, middle, and lower pair, respectively, as arrow indicates. See legend for Fig. 1.

The free energy ω is also easily calculated and broken into ω_{ath} and ω_{int}, the latter vanishing when $w=1$:

$$\omega_{\text{int}}=\frac{1}{2}\left(q-2+\frac{2}{M'}\right)\ln(\phi'^2{}_{mu}/\phi_u\phi_a'),$$

$$\omega_{\text{ath}}=\frac{L'}{M'}\ln r-\frac{1}{M'}\ln(\phi_n'/g')+\frac{1}{2}\left(q-2+\frac{2}{M'}\right)\ln(2\phi_u/q). \tag{11}$$

The free energy ω depends on quantities pertaining to the primed species for which no activity (similar to K) is allowed in the partition function (and the density ϕ_u of chemically unbonded bonds for which, again, no activity is allowed). Thus, ω denotes the adimensional osmotic pressure through a membrane across which the primed species is allowed to migrate and is always non-negative.

For $w>w_\theta$, see below, there is a line of critical points as $M\to\infty$ at $K=K_c(w)=(\lambda'/r)^{1/M'}w^{1-r}$, where $\lambda'=g'(M'-2L'/q)$. For $w<w_\theta$, the theory predicts phase separation between A- and A'-rich phases. Both results can be checked easily. The critical point for phase separation is given by

$$w_c=\sqrt{a}(\sqrt{\rho\rho'}-1)/(a+\rho), \tag{12}$$

with $\rho=Mr'+1$, $\rho'=M'r'+1$, $r'=q-2$, and $a=M/M'$. For $q\to\infty$, we find that $w_c\to1-(\sqrt{M}+\sqrt{M'})^2/2qMM'$. Hence, $\chi_c=-q\ln w_c\to(\sqrt{M}+\sqrt{M'})^2/2MM'$, obtained in the FH approximation. As $M\to\infty$, $w_c\to w_\theta=\sqrt{1-1/\rho'}$ at the θ-point $K=K_\theta=K_c(w_\theta)$, $w=w_\theta$, $M\to\infty$ which is a tricritical point in our theory (see Ref. [16]). For $q\to\infty$, or $\rho'\to\infty$, $w_\theta\to1$ as suggested earlier. For simple fluids, one must set $M=M'=1$ in the above theory. Thus, our theory also provides a consistent theory of a simple fluid.

IV. CONCLUSIONS

We conclude with the following two observations: In a continuum theory, we do not have any geometrical constraints between ϕ_a, ϕ'_a, and ϕ_c as on a lattice, see the beginning of Sec. II. Therefore, one cannot reduce the problem to two independent densities. In general, all three pair densities must be treated as independent. Hence, we need to introduce three independent χ parameters. It is only on a lattice that a suitable combination of the three χ parameters uniquely describes the statistical mechanics of the binary system. Thus, no justification can be offered for a lattice theory containing two combinations, as is the case in the theory by Lipson [21]. Such a theory necessarily disregards the geometrical constraints imposed by the lattice.

The theories presented by Bates *et al.* [8] and by Dudowicz, Freed, and Madden [14(a)] do provide a complicated behavior of the effective χ parameter. (The effective χ there is defined in a different way than we have.) However, the theory by Bates *et al.* [8] violates the fundamental thermodynamic relation $(\partial\phi_c/\partial w)_\phi > 0$ [see Eq. (3)] which states that the specific heat must be non-negative. It is easy to calculate the specific heat C_ϕ at constant ϕ using the result given in Ref. [8]. We find $C_\phi = C(\phi_m\phi'_m)^{3/2}/\sqrt{|\chi_s - \chi|} < 0$, where C is an uninteresting negative quantity and χ_s is quoted in Ref. [8].

A similar problem occurs in the lattice cluster theory of Fred and co-workers [14] because of the error introduced by truncation. The free energy is given as a finite-order polynomial in ε^* (which in our notation is $2\varepsilon\beta$) and $1/q$. The expansion is carried out about the point $\varepsilon^* = 1/q = 0$. Hence, the truncation is valid near the expansion point, the expansion being a high-temperature expansion. From a comparison with Monte Carlo simulations, it has been suggested that the theory due to Dudowicz, Freed, and Madden [14(a)] is highly reliable for $|\varepsilon^*| < 0.3$ for $q = 6$. However, problems appear at low temperatures. Consider the specific heat C_ϕ for large q in this theory for a solution: $C_\phi \cong C_0[1 + (\phi_m - \phi'_m)\varepsilon^* + (1 - 12\phi_m\phi'_m + 18\phi_m^2\phi'^2_m)\varepsilon^{*2}/2]$, where ϕ'_m is the solvent density and $C_0 = 2(\chi\phi_m\phi'_m)^2/q > 0$. It is evident that C_ϕ is not necessarily non-negative. For example, for $\phi_m = \phi' = \frac{1}{2}$, C_ϕ is negative for $|\varepsilon^*| \geqslant 1.5$. Thus, the theory is valid only at high temperatures. The problem is worse for the Pesci-Freed theory [14(b)] which, according to Dudowicz, Freed, and Madden [14(a)], should be valid in the $M \to \infty$ limit. In this theory $C_\phi = C_0 - 2[A_6 + A_7 + 3(A_8 + A'_8)]\phi_m\phi'_m$ where A_6, A_7, A_8, (polymer), and A'_8 (solvent) are given in Ref. [14(b)]. Again, C_ϕ need not be non-negative. For example, take $\phi_m = 0.9$, then C_ϕ is negative for all $\varepsilon^* \geqslant -0.3$. Since the expansion terms have no definite signs, the problem will persist even if one goes to higher orders. In any case, the truncation becomes invalid as phase transitions are approached because of associated singularities in thermodynamic quantities.

V. SUMMARY

In summary, we have shown that $T\overline{\chi_{\text{eff}}}$ or χ_S must depend on ϕ_m and w. We have presented a theory of blends (and solutions) that seems to exhibit qualitatively correct behavior. This is a closed form lattice theory of an incompressible system valid everywhere, including low temperatures. In contrast, some of the more recent theories are not.

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