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Entropy-driven phase separation and configurational correlations on a lattice: Some rigorous results

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We prove that if there is a phase separation in a fully packed (FP) athermal system, it must be between pure components only. We then rigorously demonstrate that no phase separation in an athermal FP state of hard particle mixtures on a *lattice* is possible merely due to size disparity or nonadditivity, if the configurations are weakly correlated, i.e., are quasirandom. We consider a mixture of linear polymers at *all* packing fractions and argue that no phase separation is possible in an athermal state. The last result also applies to a mixture of flexible particles and hard dimers. Our results contradict many recent numerical results.

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I. INTRODUCTION

It is commonly believed that energetic effects govern the phenomenon of phase separation in a simple fluid mixture of two species of particles A and B, where B cannot be larger than A in size. The belief is based on an implicit assumption that at infinite temperatures, where energy consideration is irrelevant, there are no *correlations* in the placement of particles. Excluded volume effects, so that particles do not overlap, do not change the conclusion [1]. Let Γ_A and Γ_B denote the number of *distinct* configurations for the pure states of A and B, respectively. The number of distinct configurations Γ for the mixture, which appears in the partition function, contains not only the combined original configurations of the pure states, but also other states in which the particles are mixed. The difference, $\Delta\Gamma_{\text{mix}}=\Gamma-\Gamma_A\Gamma_B$ represents all distinct *mixed* states[2]. In the absence of correlations, mixing is random and $\Delta\Gamma_{\text{mix}}\sim\Gamma$; the entropy of mixing is *positive* and the mixed state is entropically favorable. However, recent work [3–5] has made the situation obscure mainly because of a rigorous and elegant mapping, first introduced by Widom [6], of a special *lattice* mixture onto an Ising model in a magnetic field. The model mixture has no energetics in terms of particles; the particles are not allowed to overlap. Yet the model exhibits [6,4] an entropically driven phase separation. (It should be stressed that there is energetics between spins in the corresponding Ising model.) Widom noted a ''clustering tendency'': *when particles of one species cluster together, a greater volume is accessible to particles of the other species*. He explicitly demonstrated phase separation by invoking the Ising mapping, thereby giving credence to the clustering tendency as a driving force for separation.

Let z_α denote the activity for $\alpha=A,B$ particles. The phase separation occurs when z_B exceeds some critical value, i.e., when the packing fractions exceed some critical value and persists even in the *fully packed* (FP), i.e., maximally packed, *state* [6], which occurs when $z_B\cong\sqrt{z_A}\to\infty$. Frenkel and co-workers [5] associate the phase separation with nonadditivity in the mixture. However, numerical evidence is also provided for separation in additive hard-core mixtures on a *lattice* with enough size disparity. The separation is again expected to persist in the FP state. They further argue that the separation must exist not only in rigid particle mixtures but also in *flexible particle* mixtures such as a blend of linear polymers.

However, there are conflicting results in the literature [1,3,5–8] on the possibility of phase separation in additive mixtures, and the conflict is far from being settled [9], despite a renewed flurry of current activities. Both numerical simulations and analytical approximations have certain disadvantages and the experiments suffer from slow dynamics [9]. Some resolution is needed as the problem is central in many diverse fields such as binary fluid mixtures, colloids, polymers, mixtures of colloids and polymers, granular materials, etc.

Some investigations [1,8] conclude against a phase separation in hard particle mixtures, while others [3,5] argue for it. It is important to note and is intuitively obvious that if the size disparity for *hard-sphere particles* is sufficiently large for the small particles to enter into the voids left by larger particles, there *cannot* be a phase separation. The latter scenario [3,5], therefore, cannot be generally valid. The investigation of a blend of flexible particles, each of a fixed architecture, on a Bethe lattice [7] also shows no phase separation in the athermal limit, despite the fact that the two species can have any size disparity. This conflicts with numerical conclusion [5]. Recently, we have also investigated phase separation induced by size disparity in a compressible polymer solution in its own monomeric solvent [10], but the mixture is not athermal.

It should be pointed out at this point that there do exist genuine phase separations in the athermal limit [11,12]. A phase separation between a polymer-rich phase and a polymer-poor phase occurs in an equilibrium polymerization process of *branched* polymers in the athermal limit [11]. The phenomenon has not attracted much interest, presumably because of its complexity. In the polymerization model, the density of a functional (end point, trifunctional, tetrafunctional, etc.) group is controlled by its respective activity (H, w_3,w_4, etc.), and the bond density is controlled by a bond activity K. It is found that if odd functionalities *disappear* in the limit $H\to0$, the athermal phase separation also disappears. In particular, there is *no* phase separation in an athermal linear polymer solution. The placement of branched polymers on the lattice is *random*, only if all functional activities are equal to one [11]. In this case, the model reduces to random bond percolation where the physics is trivial: there is no phase separation; only gelation occurs. For functional activities different from one, *correlations* emerge in the system and induce phase separation. A similar situation occurs in some surface models [11]. Since the problem has been thoroughly investigated, we would not pursue it further.

The existence of phase separation in the FP state implies that $\Delta\Gamma_{\mathrm{mix}}$ is thermodynamically insignificant [2]. This can happen only if the *configurational correlations* in the placement of particles in each configuration are strong enough to forbid mixing. These correlations are responsible for the clustering tendency and are usually induced by interactions. However, in athermal cases they can be induced by geometrical constraints like branching [11,12] or size disparity [5], or by *constraining* the way [4,6] some particles are placed on the lattice by decorating [6] the lattice. We will establish in the next section that if there is a phase separation in the FP state, it must be between the two pure components. In the rest of the paper (Secs. III–V), we consider only lattice models, as is the case with the Widom model. We make *no* comments on continuum analogs. We demonstrate rigorously in Sec. III, that a phase separation in two pure components is impossible in the FP state on a *lattice*, if the correlations are *weak*, i.e., if the configurations are quasirandom. We follow a line of approach that has proven very useful in a different context [13]. We obtain a rigorous lower bound on the entropy of mixing for this state. Deciding whether a system is additive or not is not unique for asymmetric particles. Here, we consider closest distances between the centers of mass of particles to decide whether the system is additive or not. By considering many models in the FP state, we demonstrate that the issue of additivity does not play an important role in determining phase separation. Instead, the configurational correlation plays an important role in governing phase separation. The investigation for a blend of flexible polymer chains is carried out at *all* packing densities in Sec. IV. The results in this section are based on the general symmetry properties of magnetic systems. In all model systems besides the Widom model that we study here, we find *no* phase separation. The final section contains a brief summary of our results.

II. FULLY PACKED (FP) STATE

In all known cases with a single critical point, which include ordinary ferromagnets, the spherical model, the Bose-Einstein condensation, order-disorder transitions in alloys, the athermal equilibrium polymerization, etc., the discontinuity in the order parameter η (the tie line) continues to grow, as we increase some parameter γ that takes us away from the critical point along the line of first-order transitions. The discontinuity in η reaches its maximum possible value as γ takes its maximum allowed value. The Bose-Einstein condensation and the equilibrium polymerization are genuine athermal phenomena. Moreover, in all these cases we cannot ‘‘penetrate’’ the coexistence region, no matter how we approach the coexistence. (We overlook spinodals, which do not exist in rigorous statistical mechanics.) The spontaneous magnetization reaches its saturation value at the absolute temperature $T=0$. Similarly, the density of particles in the zero momentum state or the absolute difference in the density of the two components reaches its maximum value at $T=0$. This is also what we expect to happen in the (FP) state, in which the two coexisting phases must correspond to the two *pure* components, having either only particles of A kind, or of B kind, provided there exists a phase separation. The density discontinuity must be a maximum. The above scenario is certainly true in Widom's model, which is nothing but the two-dimensional Ising model in a field. This model and the equilibrium polymerization model [11,12,14] also show that an *athermal particle model can also be viewed in some cases as a magnetic model with energetics and vice versa*. Moreover, numerical simulations reported so far also strongly indicate that the phase separation must be between the two *pure components* in the FP state. This is evident from the numerical results [5(a),5(b)]. The tie line continues to increase in width with the activity of the large particle.

The following discussion justifies the above scenario. A compressible and athermal binary mixture of A and B species is described by the partition function $(N\to\infty)$

$$Z_N=\sum\ \Gamma(N_1,N_2)K_1^{N_1}K_2^{N_2}, \tag{1}$$

where Γ is the number of distinct configurations of N_A and N_B particles, each of size a^d and b^d, respectively, on a d-dimensional hypercubic lattice of *fixed* total sites $N=N_0+N_1+N_2$. Here, a and b are the sides (in the units of the lattice spacing, which we take to be 1 in the following) of each hypercubic particle A and B, respectively, and $N_1=N_Aa^d$ and $N_2=N_Bb^d$. The number of voids is represented by N_0. The sum is over distinct values of N_1 and N_2. The activities for the two species are K_1 and K_2, respectively, defined in a manner that will make the presentation below simpler. The corresponding chemical potentials are μ_1 and μ_2: $\beta\mu_j=\ln K_j$, $\beta=1/T$, where the absolute temperature T is in the units of the Boltzmann constant.

From Eq. (1) the following will be established.

(i) As $K_1\to\infty$ for any *finite and fixed* K_2, $N_1\to N$ and we have an *incompressible* pure A component. We continue to have the pure *incompressible* A component as $K_2\to\infty$ (after $K_1\to\infty$).

(ii) As $K_2\to\infty$ for any *finite and fixed* K_1, $N_2\to N$ and we have an *incompressible* pure B component. We continue to have the pure *incompressible* B component as $K_1\to\infty$ (after $K_2\to\infty$).

If we introduce two new variables $u_i=1/(1+K_i)$, we observe that we have pure *incompressible* components A and B along the u_2 and u_1 axes, respectively, except possibly at the origin O; see Fig. 1, where OC schematically represents the coexistence curve terminating at the critical point C. The state of the system at the origin O requires careful consideration; this will be done below.

The incompressible limit is most easily obtained by taking the ‘‘zero-temperature’’ limit $\beta=1/T\to\infty$, which makes the

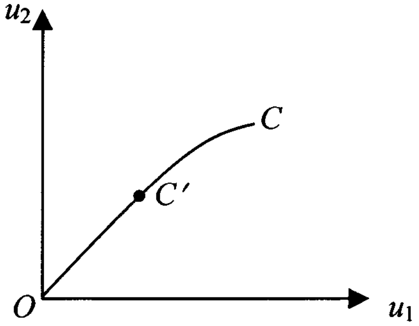

FIG. 1. Schematic coexistence curve *OC* in the u_1-u_2 plane, when there is phase separation at *O*. The possibility of an immiscibility loop between *C* and C', when there is no phase separation at *O* is highly unlikely.

activities K_i diverge, provided the corresponding chemical potentials are *positive*. It is the only case we will consider below.

The corresponding free energy $(1/N)\ln Z_N\,(N\to\infty)$ is nothing but the adimensional pressure βP, where we have set the elemental cell volume $\nu_0=1$:

$$\beta P = S + \beta\mu_1\phi_1 + \beta\mu_2\phi_2, \tag{2}$$

or

$$P = TS + \mu_1\phi_1 + \mu_2\phi_2, \tag{3}$$

where ϕ_i are the number densities N_i/N and $S(\phi_1,\phi_2) \equiv (1/N)\ln\Gamma(N_1,N_2)$, $N\to\infty$, is the entropy per site, which satisfies

$$(\partial S/\partial\phi_i) = -\beta\mu_i, \quad i=1,2. \tag{4}$$

In equilibrium, the right-hand side in Eqs. (2) and (3) must be positive and at its maximum because of Eq. (4). This yields the above two results (i) and (ii), as $T\to 0$. The adimensional pressure βP along the u_1,u_2 axes is infinitely large. Alternatively, $P=\mu_j=\max\{\mu_1,\mu_2\}$, with the corresponding density $\phi_j=1$. At the coexistence, *P* must be the same in both phases. This requires $\mu_1=\mu_2$ at coexistence.

It is also convenient to introduce a related partition function

$$\tilde{Z}_N \equiv Z_N/K_2^N = \sum \Gamma(N_1,N_2)K^{N_1}\eta_0^{N_0}, \tag{5}$$

where $K=K_1/K_2$ and $\eta_0=1/K_2$, and $N_2=N-N_1-N_0$. The sum is over N_0 and N_1. The entropy *S* is now a function of the void density $\phi_0=N_0/N$ and ϕ_1, such that

$$(\partial S/\partial\phi_0) = \beta\mu_2, \quad (\partial S/\partial\phi_1) = -\beta\Delta\mu. \tag{6}$$

This form of the partition function is useful in considering the incompressible, i.e., the FP limit of the mixture. For this, we take $\eta_0\to 0$, which requires taking $K_2\to\infty$, i.e., $\mu_2>0$ and $\beta\to\infty$. We also note that $K\to 0$ (pure *B* component) or ∞ (pure *A* component) depending on whether $\Delta\mu=\mu_1-\mu_2$ <0 or >0 in the same limit. The corresponding ''free energy'' is $\beta\tilde{P}=(1/N)\ln\tilde{Z}_N$, $N\to\infty$, with $\tilde{P}=P-\mu_2$:

$$\tilde{P} = P - \mu_2 = TS - \phi_0\mu_2 + \phi_1\Delta\mu. \tag{7}$$

We must maximize $\tilde{P}$ for the equilibrium. We again consider the limit $T\to 0$. The equilibrium state corresponds to no voids $(\phi_0=0)$ for $\mu_2>0$. In this case, the entropy becomes a function of ϕ_1 only, so that

$$(dS_{\text{FP}}/d\phi_1) = -\beta\Delta\mu, \tag{8}$$

where the subscript FP denotes quantities in the incompressible limit $(\phi_0=0)$. For $\Delta\mu\to 0^+$, we have only *A* particles. For $\Delta\mu\to 0^-$, we have only *B* particles. The important point to note is that we have either $\phi_1=1\,(\Delta\mu>0)$ or $\phi_2=1\,(\Delta\mu<0)$, as $T\to 0$ followed by $\Delta\mu\to 0^\pm$. Thus, we again conclude that in the FP state, the coexistence occurs at $\Delta\mu=0$ between $\phi_1=1$ and $\phi_2=1$.

For $\eta_0\to 0$, the sum in Eq. (5) reduces to only over N_1, as $N_0=0$. Moreover, $K=1$ at the coexistence. Thus, at the coexistence in the incompressible limit, we have

$$\tilde{Z}_N = \overline{\Gamma} \equiv \sum_{N_1} \Gamma(N_1,N-N_1), \tag{9}$$

where the overbar indicates quantities at the coexistence in the incompressible limit. It is evident from Eq. (9) that the entropy $\overline{S}=(1/N)\ln\overline{\Gamma}$ in this case must be the maximum possible entropy:

$$\overline{S} \geqslant S_{\text{FP}}(\phi_1), \quad \phi_1\in(0,1). \tag{10}$$

From Eqs. (10) and (8), when applied to the coexistence $(\Delta\mu=0)$, we conclude that the convexity of the entropy requires that it must be a *constant* over the range (0,1) of ϕ_1:

$$S_{\text{FP}}(\phi_1) = \text{const}, \quad \phi_1\in(0,1). \tag{11}$$

It is evident from the above that if there is a transition in the FP state, then $\Delta\mu\to 0^\pm$ allows us to discover the coexisting phases. The coexisting phases are pure components (one of the two densities is zero), and *not* mixed states (neither of the densities is zero). It is also obvious that $\Delta\mu$ plays the role of the *symmetry-breaking field* in the problem. As is a customary practice in statistical mechanics, a *nonzero* symmetry-breaking field must be applied and then allowed to go to zero in order to determine the nature of the coexisting phases. In addition to $\Delta\mu=0$, μ_2 must also be the same in the coexisting phases; thus, $\tilde{P}=0$, i.e., $P=\mu_2$ in the coexisting phases. This is precisely what happens in the FP limit in Widom's model, where the role of $\Delta\mu=0$ is played by the magnetic field *H*.

Thus, it is not possible to have a phase separation between two mixed states at intermediate densities in the incompressible state. The phase separation must occur only between two pure components here. Therefore, in the following we will restrict ourselves to considering the possibility of phase separation into pure components only. For this reason, we will no longer use the subscript FP to represent quantities in the FP states.

Before leaving this section, we wish to make the following important observation. The above discussion treats the particles as hard particles of a shape so that FP states exist ($\phi_0 = 0$). However, it is easy to extend the discussion to flexible particles, as long as FP states exist. Thus, the above conclusions will also apply to a blend of linear chains or flexible polymers of fixed architectures like stars, brushes, combs, dendrimers, etc.

III. SOME NEW MODELS

Let us first briefly review the results for the Widom model, which is defined on a square lattice. The model contains two different kinds of particles: the ''large'' (A) particles and the ''small'' (B) particles. The most important aspect of the model, in our opinion, is the *geometrical lattice constraint* that the A particles must reside inside the lattice cell, but B particles on the lattice bonds. This gives rise to an unusual configurational correlation, which makes the mixing *nonrandom*. This can be easily seen as follows. Consider the two FP pure states, containing N_A A particles and $2N_B$ B particles on two square lattices of N_A and N_B sites, respectively. For the mixture state, we consider a lattice with $N = N_A + N_B$ sites. The only possible state on this lattice is the one that is phase separated [2]. For example, if we try to remove an A particle, we leave behind an empty cell in which we cannot put any B particle. Thus, a mixed state is *impossible*. Indeed, the number of B particles that can be successfully placed on the lattice for any configuration of N_A particles depends not only on the number of empty cells, but also on their *configuration*. It is always less than $2N_B$, except in the phase separated state in which all the empty cells cluster together. We call this type of correlation *strong*, in which configurations of empty cells or of A particles become *decisive* in determining the number of successful B particle insertions. The correlations are generated in the model due to the geometrical constraint and force $\Delta\Gamma_{\text{mix}} \sim 0$. They would be absent in the presence of sufficient free volume. They would also be absent, had we allowed B's to reside inside the cells of a lattice of $N = N_A + 2N_B$ sites. The reason for phase separation is the presence of geometrically generated correlations; size disparity or nonadditivity alone is not sufficient by itself, as we will demonstrate below in many examples.

A. A model with triangles

Let us consider a variant of the Widom model, in which each B particle is cut into two equal triangles along the diagonal that coincides with the lattice bond; see Fig. 2. The triangles are restricted to live on lattice bonds without overlap with other triangles or large squares. There is still a size disparity, but the system is now additive. However, the model has *no* phase separation, as the following intuitive argument suggests. Whenever a large particle is removed, four triangles can be put in its place. Thus, the strong configurational correlation of the Widom model has disappeared. We call this type of correlation *weak* in which the number of small particles that can be put depends only on the number of empty cells and not on their configurations. The configurations are *quasirandom* in that four triangles must be put in each empty cell. To make the argument more precise, we follow Frenkel and Louis [4]. Using z_t to denote the activity for a triangle, we find that the contribution from a lattice bond with a single cross is $\zeta = (1 + z_t)$, and with no cross is ζ^2. The numbers of bonds with two crosses, with one cross and with no cross are

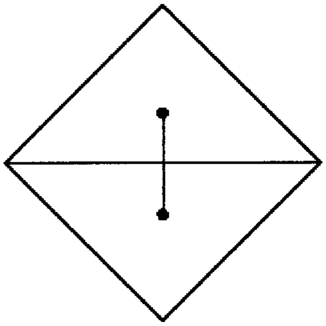

FIG. 2. The small diamond particle in the Widom model is replaced by two triangles obtained by cutting it along its diagonal occupying a lattice bond. The filled spot (●) denotes the center of mass of the particle.

$$N_2 = \sum n_i n_j, \quad N_1 = 4N_A - 2N_2, \quad N_0 = 2N - 4N_A + N_2, \tag{12}$$

respectively, where $N_A = \Sigma n_i$. The contribution to the partition function from the triangles is ζ^T, where $T = N_1 + 2N_0 = 4(N - N_A) = 4(N - \Sigma n_i)$. Thus, the problem is reduced to *decoupled* Ising spins in an external magnetic field, which have *no* phase separation. It is easy to see that there is no clustering tendency in the model.

B. Square particles of disparate sizes

Consider a square lattice of unit bond length. We consider a mixture containing square particles A and B of sizes $a \times a$ and $b \times b$, with $b < a$, and an aspect ratio $a = a/b$. The system is additive if the centers of mass of the two particles can line up; otherwise, it is nonadditive; see Fig. 3. It is easily seen that the clustering tendency exists, provided both a and b are different from 1. Let l denote the least common multiple of a and b. Consider FP pure states. It is easy to see that the number of distinct configurations Γ_A and $\Gamma_B \sim 1$;

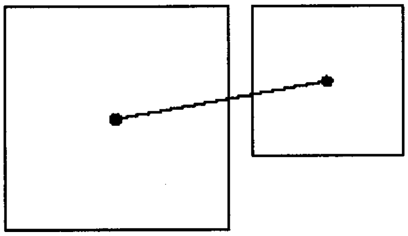

FIG. 3. The center of mass of the small square does not line up with that of the large square. See legend in Fig. 1 for (●).

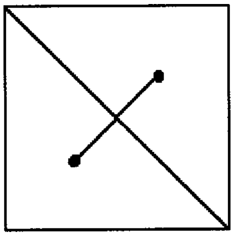

FIG. 4. The small square in Fig. 3 is cut along its diagonal; there are two ways for the cut. See legend in Fig. 1 for (●).

hence, S_A and S_B vanish identically. We now consider a $L \times L$ square lattice with $N = N_A a^2 + N_B b^2 \sim L \times L$ sites. The calculation of the lower bound on the entropy per site for the mixture is trivial due to the following quasirandom packing. We divide the lattice into $n = [N/l^2] l \times l$ l cells, where $[x]$ denotes the integer closest to x. In each l cell, we can either put $(l/a)^2$ A particles or $(l/b)^2$ B particles. We now *randomly* chose $n_A = [N_A(a/l)^2]$ cells. The number of ways of doing this is

$$\Gamma_{LB} = n!/[n_A!(n-n_A)!]. \tag{13}$$

We put $(l/a)^2$ large particles in each of the chosen cells and $(l/b)^2$ small particles in each of the remaining cells. Thus, the placement of A and B particles on the lattice is quasirandom; consequently, the configurational correlations here are weak.

The actual number of distinct states for the mixture must not be less than Γ_{LB}:

$$\Gamma \geqslant \Gamma_{LB}. \tag{14}$$

A rigorous lower bound on the mixing entropy $S_{\text{mix}} \equiv (1/N)\ln(\Gamma/\Gamma_A\Gamma_B), N \to \infty$, is given by

$$S_{LB} = -(1/l^2)\{\phi_A \ln \phi_A + \phi_B \ln \phi_B\} \geqslant 0. \tag{15}$$

Here, $\phi_A = N_A a^2/N$ and $\phi_B = N_B b^2/N$ so that $\phi_A + \phi_B = 1$. The entropy in Eq. (15) violates the requirement in Eq. (11), which is valid in the case of a phase separation. Thus, *there is no basis for phase separation in this case*, no matter what the sizes and their ratios are. It should be remarked that the above lower bound on S_{mix} is not very poor, as it is identical to the *F-H* entropy of mixing [14] for polymers of size l^2. (The bound can be easily improved.) The argument is easily extended to three dimensions without altering the conclusion, which, however, is inconsistent with that derived from Monte Carlo simulations [5].

C. Particles of dissimilar shapes

We divide the smaller square into two right-angle triangles, see Fig. 4, such that each triangle sits in a corner of a $b \times b$ b cell. It is easily seen that the system is always nonadditive. There are two ways in which two triangles can be put in any b cell. Thus, $\Gamma_B \sim 2^{N_B}; \Gamma_A \sim 1$, as before. For the mixture, we follow the construction described in the Sec. II B above, except that each b cell is covered by two triangles in two different ways. The latter contribution cancels exactly the contribution from Γ_B and we obtain the same lower bound in Eq. (15) due to quasirandom packing as before. We conclude that neither dissimilar shapes nor nonadditivity gives rise to phase separation at O in Fig. 1.

So far we have restricted ourselves to FP states, since S_α for the FP pure components can be exactly calculated, and we can identify quasirandom configurations with weak correlations in the mixture. This is not possible for partially packed pure components and we could not argue that the bound obtained using the above method would be a rigorous lower bound. Thus, even though we have rigorously demonstrated the absence of a phase separation at O, the absence of phase separation in the immediate neighborhood of O cannot be demonstrated rigorously by our approach. However, an appeal to continuity demands that there is no phase separation in the immediate neighborhood of O. The most probable scenario is that OC does not exist.

It is very hard to believe that the systems considered in Secs. III B and III C above will remain miscible as the packing fraction is reduced until it reaches some critical packing fraction corresponding to C' when they become immiscible, only to become miscible again at some yet lower critical packing fraction corresponding to C; see Fig. 1, where the portion OC' does not exist any more. This scenario would require the existence of two critical points C and C' with an immiscibility loop in between. We show below that such a scenario is not possible for at least one simple case in which the solvent is a hard dimer (2×1, $2\times1\times1$, etc.). This is a special limit of the blend considered below.

IV. BLENDS

We consider an athermal blend of molecules of two species A and B. We further assume that monomers of either species occupy one unit cell. The molecule A and B represents a solvent, a dimer, a trimer, etc., if it contains one, two, three, etc., monomers. A solvent or a dimer corresponds to a *rigid* particle. The remaining forms represent *flexible* particles or polymers. The polymer problem is related to a ‘‘zero-component’’ magnetic system by extending the analogy first proposed by deGennes [14]. The extension due to Ryu and Gujrati [15] can be applied to a blend of A and B chains in a solvent. These chains are polydisperse, with the average degree of polymerization of each species controlled by activities K_α, H_α, $\alpha = A$ or B. Here, K_α is the ferromagnetic coupling and H_α the magnetic field, and the adimensional Hamiltonian (a minus sign is absorbed in the definition) is

$$H = K_A \sum \boldsymbol{\sigma}_i \cdot \boldsymbol{\sigma}_j + K_B \sum \boldsymbol{\tau}_i \cdot \boldsymbol{\tau}_j + H_A \sum \sigma^{(1)} + H_B \sum \tau^{(1)}; \tag{16}$$

the first two sums are over distinct nearest-neighbor sites and the remaining two sums are over each site of the lattice. The spins $\boldsymbol{\sigma}$ and $\boldsymbol{\tau}$ are the first and the second n components of a $2n$-component spin $\mathbf{S}$ located at each site: $\mathbf{S} = (\boldsymbol{\sigma}, \boldsymbol{\tau})$. The $n = 0$ magnetic partition function, with some trivial normalization, gives the partition function for the blend:

$$Z_p = 1 + \sum \eta_A^{e_A} \eta_B^{e_B} \kappa_A^{B_a} \kappa_B^{B_B}, \tag{17}$$

where $\kappa_\alpha = K_\alpha / z$ is the bond activity, $\eta_\alpha = H_\alpha / \sqrt{z}$ is the end-point activity for $\alpha = A$ or B species, $z = 1 + (H_A^2 + H_B^2)/2$ and the sum is over distinct configurations of polymers. Here, e_α and B_α denote the number of end points and the number of bonds in all of α-species polymer chains. Solvent molecules in the original model will be treated as voids to allow for free volume and, hence, partial packing. A void covers a cell left uncovered by polymers.

Various general conclusions can be drawn immediately from the form of the Hamiltonian in Eq. (16). If there is phase separation, it must be limited to the subspace in which at least one of the two magnetic fields vanishes, due to the up-down symmetry in Eq. (16). In the zero-field limit, both polymers are infinitely long. As one of the magnetic fields increases, polymers corresponding to this field decrease in average size, until they become dimers when the field diverges. In order to keep bond activities fixed and finite, we must also allow the ferromagnetic couplings to diverge simultaneously.

The coexistence between oppositely magnetized phases occurs at *zero* fields in the magnetic model and is obtained as the fields go to zero from either side. Since activities in Eq. (17) must be non-negative, all parameters in Eq. (16) must be non-negative for a valid polymer connection. Hence, *negatively* magnetized phases and, therefore, the magnetic coexistence at zero fields have no physical relevance for the polymer problem. There is no phase separation, no matter what the degree of polymerization of the two kinds of chain, contrary to the numerical conclusion [5] and the theoretical claim [16].

We also do not agree with the original argument of Frenkel and Louis [4] that a polymer solution must phase separate in an athermal state. There is a flaw in their argument. Each configuration of large particles, in general, gives rise to a large number of polymer configurations and not one as assumed [4]. The easiest way to see this is to consider the FP state of the large particles. Such a state can be converted to describe polymer configurations, known as the Hamilton walk problem [13], in which the chain must cover all sites of the lattice. It is well known that their number is exponentially large [13]. Indeed, the above compressible polymer solution can be exactly mapped onto a magnetic model [17], which has no phase separation relevant for polymers.

V. SUMMARY

In summary, by considering various *lattice* models containing hard particles of different shapes and/or sizes, we have rigorously shown that the models cannot phase separate in FP pure components. Consideration is limited to phase separation in pure components, as any phase separation in the FP state must be into these two states. The examples show that the existence of weak configurational correlations due to quasirandomness is sufficient for the absence of phase separation. The strong configurational correlation present in the Widom model is responsible for the observed phase separation. We also show that no phase separation can occur in an athermal blend of polymers at any packing fraction. The last result is also valid for polymers in a solution or a hard dimer solvent. Our results contradict some recent numerical results, thus casting doubts on the usefulness of such methods for studying athermal phase separation.

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