

Lattice model of living polymerization. III. Evidence for particle clustering from phase separation properties and “rounding” of the dynamical clustering transition

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Equilibrium polymerization is studied here as a prototype for clustering transitions that commonly occur in systems of interacting particles at equilibrium. These transitions are often difficult to locate because of transition “rounding” associated with a limited extent of cluster growth, competing association or dissociation processes that initiate or inhibit clustering, and other constraints on the particle clustering dynamics. Instead of singularities in thermodynamic and transport properties, more subtle property changes signal the onset of particle clustering, explaining why clustering transitions are often overlooked or misinterpreted. We utilize a Flory–Huggins model for the equilibrium (“living”) polymerization of linear polymer chains to identify experimental signatures (features in the osmotic pressure, osmotic compressibility, and specific heat) that can be used to locate and quantify the transition “rounding” in general clustering transitions. The computation of a flattening in the concentration dependence of the osmotic pressure in the one-phase region motivates our consideration of the temperature dependence of the second virial coefficient and the variation of the theta temperature T_θ with “sticking energy” Δh as possible important indicators of particle clustering. The ratio of the critical temperature T_c for phase separation to T_θ , along with other “critical constant” ratios, such as the osmotic compressibility factor Z_c , are also calculated and discussed in connection with establishing criteria for identifying particle clustering transitions and for quantifying the relative “strength” of these transitions. © 2000 American Institute of Physics. [S0021-9606(00)50825-3]

I. INTRODUCTION

It is well known that strong interparticle interactions tend to induce the “condensation” of particle systems into liquid or crystalline states of matter or to cause phase separation if the particles are suspended in another fluid. Although many questions remain about the microscopic origin of these processes,^{1–15} these condensation transitions are generally viewed as, at least, qualitatively understood. Ideas and mathematical techniques arising from the accumulated experience in modeling fluid condensation, fluid phase separation, and crystal formation are routinely applied to interpreting almost any “ordering” process encountered. Particle clustering processes that depart from this scheme are usually attributed to “nonequilibrium effects.” For example, the formation of colloid particle clusters in solution and in polymeric matrices is normally discussed in terms of irreversible aggregation processes, such as diffusion-limited aggregation or cluster-cluster aggregation, and collectively this phenomenon is often referred to as “floculation” or “aggregation.”^{16–19} Previous advances in theories of liquid condensation, phase separation, and crystal formation also influence the common nonequilibrium interpretation of glass formation where high potential barriers are often presumed to prevent a strongly interacting particle system from access-

ing its “true” equilibrium ordered state (e.g., crystal) within reasonable time scales.^{20–22} However, the presumption of irreversibility in theoretical discussions of particle clustering often conflicts with observations indicating that the clustering is reversible.^{23–34}

Reversible particle clustering at equilibrium represents a distinct mode of “condensation” which has features quite different from crystallization, fluid formation, or nonequilibrium aggregation processes. In this state of matter, particles form stable cluster ensembles that are *intrinsically polydisperse*^{35–37}—the condition of equilibrium dictating the size distribution and the mode of clustering (string, network fractal structures, or compact globular aggregates). These dynamical clustering states can occur in the gas phase,^{11,12,38–44} complex fluids (such as synthetic colloidal suspensions,³ microemulsions,⁴⁵ foods like milk,⁴⁶ red blood cells,^{47–51} protein solutions,^{52–55} etc.) and in disordered solids (e.g., thermally reversible gels^{56–61}). As in the condensation of particles into the liquid state, the average size of the clusters can change rapidly with temperature upon approaching the “clustering transition,”^{35,62} and thereby produce solution turbidity,⁶³ but the dynamical clusters persist over a broad temperature range rather than the narrow one appropriate to the vicinity of a critical point for fluid condensation or phase separation.⁶⁴ Particle concentration and other variables influ-

encing the interparticle interaction represent additional important factors governing the average cluster size and geometrical form (stringlike, clumps, branched polymer membranes, etc.). Moreover, these clustering transitions occur either upon heating or cooling, depending on the sign of the entropy change accompanying the clustering process.³⁵ At least some of the observed particle clustering processes that have been written-off as being “nonequilibrium” or “metastable” processes are expected to belong to this class of *equilibrium* clustering transitions.

The existence of equilibrium “dynamical clustering states” with universal thermodynamic properties has many ramifications. These clustering processes can yield both highly organized compact aggregates of specialized structure⁶⁵ or geometrical form, such as spherical micelles⁶⁶ or fractal structures that appear similar in form over a hierarchy of observational scales.^{67–72} Since mobility fluctuations naturally accompany the formation of fractal aggregates at equilibrium, their occurrence also has significant implications for noise and transport processes observed near equilibrium.^{73–76} Equilibrium clustering processes should be relevant over a wide range of scales—clustering of molecules in gases,^{11,12} clustering of filler particles in solution and polymer matrices,³ clustering of charged^{30–34,77–80} and uncharged polymers in solution,^{81,82} and the self-assembly of a wide variety of specialized structures of biological significance.^{65,83,84}

Since we anticipate that many of the equilibrium properties of associating systems should be insensitive to the geometrical form of association,³⁵ we have systematically developed the mean-field theory of self-associating linear polymers at equilibrium (“living polymers”) in some detail as, perhaps, the simplest example of an equilibrium system of associating particles that form fractal clusters.⁸⁵ Paper I describes³⁵ some essential thermodynamic properties of living polymers (average chain length, average fraction of associated monomers, specific heat, entropy, polymerization temperature, and chain length distribution), while Paper II focuses³⁵ on how interparticle association modifies the tendency of polymer solutions towards phase separation. The two prior papers note that a wide range of associating particle systems (living polymers, thermoreversible gels, micelles) exhibit similar generic thermodynamic properties (e.g., cluster mass variations with monomer concentration and temperature, specific heat variations with temperature, etc.). The present paper continues our study of the clustering transition in living polymer solutions by placing special emphasis on the “rounding” of the phase transition due to the presence of initiator molecules. This rounding is expected to be a general property of dynamical particle clustering transitions (although other effects than initiation can be the source of rounding in general; see discussion), and the general conclusions drawn from our calculations should apply much more broadly. For example, our treatment of the transition rounding appears relevant to recent disagreements over whether thermally reversible gelation should be considered as a “phase transition” and if so, what kind.^{60,61,86–88} Questions have also been raised about the nature of the micelle formation transition.⁷⁰ To pursue the question of “transition

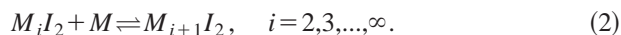
type” in living polymerization, we calculate and analyze physical properties that are usually investigated in connection with more traditional phase transitions (liquidification, phase separation), that provide thermodynamic signatures of the dynamic clustering transition and that can be used to classify and quantify these transitions.

The osmotic pressure Π , osmotic compressibility κ , and the specific heat C_p exhibit characteristic changes at phase transitions that reflect changes in the phase stability of fluid mixtures. The magnitude and scale of concentration fluctuations as well as the relaxation time of these fluctuations are largely determined by κ . The osmotic compressibility κ is also a significant quantity for interpreting light and neutron scattering from living polymer solutions and for understanding the transport properties (collective mass diffusion, Soret coefficient) of these solutions. However, our main reason for focusing on κ and Π in the present paper is to establish what they indicate about the location and nature of the polymerization transition as a function of the initiator concentration r . The specific heat C_p of living polymer solutions provides another useful indicator of the character of the clustering transition, and some previously derived results³⁵ for C_p (Paper I) are recalled as part of our quantification of transition “rounding” phenomenon in equilibrium associating particle systems.

Section II briefly reviews the model and mean-field approximation, along with calculations of Π , κ , and the second virial coefficient. Illustrative numerical calculations and comparison with neutron scattering data are given in Sec. III.

II. MODEL AND GENERAL THEORY

As in Papers I and II,³⁵ the unreacted system is taken as composed of n_s solvent molecules, n_m^0 monomers of species M , and n_I molecules of the initiator that activates the monomers and thereby enables them to propagate into polymers. Polymerization is assumed to proceed under conditions of chemical equilibrium as described by the hierarchy of chemical reactions,^{35–37}



Because reaction (1) is assumed to be irreversible, an equilibrium system contains no free initiator, but only unreacted monomers M , polymers M_iI_2 ($i = 2, 3, \dots, \infty$), and solvent, with n_m , $\{n_i\}$, and n_s molecules of each species, respectively. This equilibrium system is described using a minimal incompressible Flory–Huggins lattice model with N_l total lattice sites and with a single site occupancy constraint for the individual monomers and for solvent and initiator molecules.³⁵ As shown in Paper I, the Helmholtz free energy F for the polydisperse system then reduces to the form,

$$\begin{aligned} \frac{F}{N_I k_B T} = & (1 - \phi_m^0 - \phi_I) \ln(1 - \phi_m^0 - \phi_I) + \phi_m \ln \phi_m \\ & + \phi_m (1 - \phi_m^0 - \phi_I) \chi + \frac{\phi_I}{2(1-A)} \\ & \times \left[(1-A) \ln \frac{\phi_I(1-A)}{z} + A \ln A \right. \\ & \left. + \chi(1 - \phi_m^0 - \phi_I)(4-3A) + \frac{\Delta f}{k_B T} + 3 - 2A \right], \end{aligned} \quad (3)$$

where the concentration $\phi_m = n_m/N_I$ of unreacted monomers is evaluated from the equilibrium condition as

$$\phi_m = \frac{B - \sqrt{B^2 - 4(\phi_m^0 - \phi_I)K_p}}{2K_p}, \quad (4)$$

with $K_p = \exp(-\Delta f/k_B T)$ the equilibrium constant for the polymerization reaction in Eq. (2) and the parameter $B \equiv 1 + (\phi_m^0 - \phi_I/2)K_p$ is a function of the temperature, initial monomer concentration $\phi_m^0 = n_m^0/N_I$, initiator concentration $\phi_I = n_I/N_I \equiv r\phi_m^0$, and the dimensionless specific free energy $\Delta f/k_B T$. The parameter $r = \phi_I/\phi_m^0$ plays the role of the dimensionless initiator composition, k_B designates Boltzmann's constant, and χ denotes the dimensionless effective monomer-solvent interaction parameter. The semiflexibility factor J is omitted from in Eq. (3) since, as explained in Papers I and II, the contributions from stiffness may be subsumed into Δf . The quantity $A(T, \phi_m^0, \phi_I, \Delta f)$ of Eq. (3) is then given by

$$A \equiv \phi_m \exp(-\Delta f/k_B T). \quad (5)$$

The osmotic pressure Π can be evaluated from the standard derivative of the free energy F with respect of the number n_s of solvent molecules,

$$\begin{aligned} \frac{\Pi a^3}{k_B T} = & -a^3 \frac{\partial [F/k_B T]}{\partial V} \Big|_{T, n_m^0, n_I} \\ = & - \frac{\partial [F/k_B T]}{\partial n_s} \Big|_{T, n_m^0, n_I} \\ = & -\ln(1 - \phi) - (1/2)\phi_I \frac{4-3A}{1-A} + (1/2)\phi_I - \chi\phi^2 \end{aligned} \quad (6)$$

with $\phi \equiv \phi_m + \sum_{i=2} \phi_i$ denoting the total polymer concentration which is related to the solvent concentration ϕ_s as $\phi = 1 - \phi_s = \phi_I + \phi_m^0$, a^3 being the volume associated with a single lattice site, and ϕ_m and A are determined by Eqs. (4) and (5). Equation (6) recovers the well-known expression⁸⁹ for the excess chemical potential of the solvent in a living polymerization system without initiator after noticing that the terms $(1/2)\phi_I$ and $(1/2)\phi_I(4-3A)/(1-A)$ equal the sums $\sum_{i=2} \phi_i/(i+2)$ and $\sum_{i=2} \phi_i$, respectively.

The dynamical clustering transition temperature of associating particle systems characteristically varies monotonically with the concentration of associating species ("mono-

mer," surfactant, particle). For small concentrations, the "polymerization line" $T_p = T_p(\phi_m^0)$ is often observed to have an Arrhenius temperature dependence, and at high concentrations the polymerization transition temperature T_p tends to approach a constant $T_p(\phi_m^0 \rightarrow 1)$ which we term the *absolute polymerization temperature*,

$$T_p(\phi_m^0 \rightarrow 1) = T_p^*. \quad (7)$$

As described in Paper I, we define the polymerization temperature as the temperature at which the specific heat C_p ,

$$C_p \approx C_v = -k_B T^2 \frac{\partial^2 [F/k_B T]}{\partial T^2} \Big|_{N_I, \phi_m^0, \phi_I},$$

has a maximum. When $r=0$, the above definition coincides with the usual Dainton and Ivin expression,⁹⁰

$$T_p^{(o)} = \frac{\Delta h}{\Delta s + k_B \ln \phi_m^0},$$

where Δh and Δs denote, respectively, the enthalpy and the entropy of the polymerization reaction in Eq. (2) and where the superscript (o) emphasizes that this result refers to the idealized limit of $r \rightarrow 0^+$. In loose terms, Δh is called the "sticking energy." The absolute polymerization temperature $T_{p,o}^* = T_p^*(r \rightarrow 0^+)$ in the limit of vanishing initiator concentration $r \rightarrow 0^+$ is much easier to calculate and often represents a good approximation for T_p^* , and we term $T_{p,o}^*$ as the "ideal absolute polymerization temperature." Section III explains how the absolute polymerization temperature plays an important role in understanding the coupling between particle association and the phase stability of associating particle systems at equilibrium.

The osmotic second virial coefficient A_2 provides a measure of interparticle interactions that can become substantially modified by many-body particle associations.^{89,91,92} The magnitude of A_2 also determines the degree of chain swelling and other solvent quantity dependent effects in living polymer solutions. In the absence of particle association (vanishing sticking energy $\Delta h \rightarrow 0$ and initiator concentration $r \rightarrow 0^+$), the dimensionless second virial coefficient A_2 equals,⁸⁹

$$A_2 = (1/2)(1 - 2\chi), \quad \Delta h \rightarrow 0, r \rightarrow 0^+ \quad (8)$$

which is a well known result⁸⁹ of Flory-Huggins theory for polymer solutions. When equilibrium clustering is present, A_2 may be defined either in terms of the total polymer concentration ϕ or the experimentally more accessible initial monomer concentration ϕ_m^0 . In the former case, the second virial coefficient $A_2^{(\phi)}$ is obtained by keeping ϕ_I constant and expanding Eq. (6) about the $\phi \rightarrow 0$ limit to yield,

$$A_2^{(\phi)} = (1/2)(1 - 2\chi) + \Delta A_2^{(\phi)}, \quad \phi_I \text{ const}, \quad (9)$$

$$\begin{aligned} \Delta A_2^{(\phi)} = & -(1/4)\phi_I K_p^2 [1 + \gamma^{-1/2} - 2K_p \phi_I \gamma^{-3/2} \\ & + (3/2)K_p \phi_I \gamma^{-1/2} + (3/2)K_p^2 \phi_I^2 \gamma^{-3/2}], \end{aligned} \quad (10)$$

where $\gamma \equiv 1 + 5K_p \phi_I + (9/4)K_p^2 \phi_I^2$. Alternatively, the dimensionless second virial coefficient $A_2^{(\phi_m^0)}$ is determined by

taking $\phi_I = r\phi_m^0$, keeping r constant, and expanding the first two terms of Eq. (6) around $\phi_m^0 \rightarrow 0$ to produce,

$$A_2^{(\phi_m^0)} = -\chi(1+r)^2 + (1/2)(1+r)^2 - (1/2)r(1-r)K_p, \quad r \text{ const.} \quad (11)$$

The two definitions of A_2 in Eqs. (9) and (11) are not equivalent and are useful in different circumstances. While $A_2^{(\phi)}$ is appropriate for comparisons with experiments performed at a constant initiator concentration ϕ_I , but variable initial monomer concentration ϕ_m^0 , $A_2^{(\phi_m^0)}$ is designed for interpreting measurements of A_2 performed with a constant ratio r and variable initial monomer concentration ϕ_m^0 . The theta temperature T_θ is defined as the temperature at which A_2 vanishes identically and may be obtained numerically from either Eq. (9) or Eq. (11).

The effective intermonomer interaction in living polymer solutions is greatly modified by many-body particle association interactions that are greatly influenced by the initiator concentration. Thus, direct measurements of the interaction potential between two associating particles (monomers) does not yield complete information about the propensity of the particles to cluster at higher particle concentrations. This observation is potentially interesting in connection with recent measurements on colloidal particle solutions where the direct interaction between two-reference particles has been found as predominantly repulsive,⁹³ but where clustering occurs at higher colloidal or polymer concentrations.^{94,95}

The isothermal osmotic compressibility coefficient κ is another basic property of living polymer solutions and is evaluated from Eq. (6) as

$$\kappa = \frac{1}{\phi} \left. \frac{\partial \phi}{\partial \Pi} \right|_{T, \phi_I} = \frac{a^3}{k_B T} \left\{ \frac{1}{\phi} \left[\frac{1}{1-\phi} - \frac{\phi_I K_p}{2(1-A)^2} \frac{\partial \phi_m}{\partial \phi} \right]_{T, \phi_I} - 2\chi\phi \right\}^{-1}, \quad (12)$$

where the derivative $\partial \phi_m / \partial \phi$ simply follows from Eq. (4),

$$\left. \frac{\partial \phi_m}{\partial \phi} \right|_{T, \phi_I} = \left. \frac{\partial \phi_m}{\partial \phi_m^0} \right|_{T, \phi_I} = \frac{1}{2} \left[1 - \frac{B-2}{\sqrt{B^2 - 4(\phi_m^0 - \phi_I)K_p}} \right]. \quad (13)$$

Apart from our theoretical interest in κ in connection with the rounding of the polymerization transition (see next section), the osmotic compressibility κ is related to the intensity of low angle coherent light and neutron scattering from living polymer solutions, and many transport properties in semidilute solutions strongly depend on κ . In particular, the extrapolated zero-angle neutron scattering intensity is proportional to κ ,

$$I(0) = k_N \phi^2 \left(\frac{\kappa k_B T}{a^3} \right), \quad (14)$$

with the proportionality factor being a product of the scattering contrast k_N and the square of the total polymer composition ϕ . Substituting the expression for κ from Eq. (12) into Eq. (14) leads to a generalization of the standard RPA formula to the polydisperse, initiator-induced-living polymerization,

$$\frac{k_N}{I(0)} = \frac{1}{\phi_s} + \frac{1}{\phi \mathcal{M}} - 2\chi. \quad (15)$$

The ‘‘mass parameter’’ \mathcal{M} is defined as

$$\mathcal{M} = \frac{rL^2 - L(L-1)[1 - K_p \phi_m^0(1-r/2)]}{rL^2 - L(L-1)[1 - K_p \phi_m^0(1-r/2)] - \phi_m^0 K_p (L-1)^2}, \quad (16)$$

and depends on the average degree of polymerization L ,

$$L = \frac{\phi_m + \sum_{i=2}^{\infty} \phi_i \frac{i}{i+2}}{\phi_m + \sum_{i=2}^{\infty} \frac{\phi_i}{i+2}} = \frac{\phi_m^0(1-A)}{(1-A)\phi_m^0 - (1/2)\phi_I}, \quad (17)$$

the dimensionless initiator concentration $r = \phi_I / \phi_m^0$, the initial monomer concentration ϕ_m^0 , and the free energy of polymerization $\Delta f / k_B T = -\ln K_p$. Equations (15) and (16) differ from the mean-field formula [Eq. (3) of Ref. 96, an RPA approximation within the polymer-magnet analogy] used by Greer and co-workers⁹⁶ to analyze their neutron scattering data for poly(α -methylstyrene) in deuterated tetrahydrofuran, although they yield the same limits as Eq. (3) of Ref. 96 at both high temperatures, where polymers are absent, and, at low temperatures, where the polymer contribution from the $1/\phi \mathcal{M}$ term is negligible compared to the $1/\phi_s$ contribution in Eq. (15). A rather simple interpretation of \mathcal{M} emerges for a system without initiator. As shown by Stockmayer,⁹⁷ \mathcal{M} coincides for these systems with the distinct measure \mathcal{L} for the average degree of polymerization,

$$\mathcal{L} = \frac{\sum_{k \geq 1} k \phi_k}{\sum_{k \geq 1} \phi_k}. \quad (18)$$

Employing the correspondence $\mathcal{M} = L$ for $r > 0$ yields the same high temperature limit as Eq. (16), but significant discrepancies occur at low temperatures where the presence of initiator greatly alters the molecular weight distribution (see Paper I).

III. CALCULATIONS

Illustrative calculations are first performed for the living polymerization of poly(α -methylstyrene) in methyl cyclohexane with sodium naphthalide as the initiator. The values of the enthalpy and entropy of polymerizations and the initiator concentration have previously been determined for this living polymer system (see Refs. 36 and 37) as $\Delta h = -35$ kJ/mol, $\Delta s = -105$ J/(mol K), and $r = 0.0044$. The interaction parameter (Flory χ -parameter) is taken as $\chi = 177/T$ as in the model calculations presented³⁵ in Fig. 4 of Paper II.

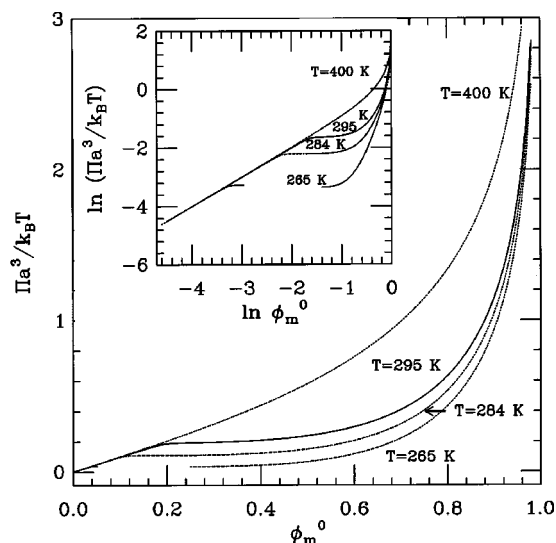


FIG. 1. The dimensionless osmotic pressure $\Pi a^3/k_B T$ of a living polymer solution as a function of initial monomer concentration ϕ_m^0 for several temperatures. The values of the enthalpy and entropy of polymerization are taken from experiments for poly(α -methylstyrene) in methyl cyclohexane [$\Delta h = -35$ kJ/mol, $\Delta s = -105$ J/(mol K)], the dimensionless initiator (sodium naphthalide) concentration r is assumed to be $r = 0.0044$ as in the experiments of Greer *et al.* (Ref. 36, 37), while the effective monomer-solvent interaction parameter χ is fixed as $\chi = 177/T$. This χ is chosen as different from that for the systems in Ref. 96 in order to illustrate richer aspects of the phase behavior. The same values of Δh , Δs , χ , and r are used in Figs. 1–8, unless otherwise specified. The osmotic pressure is fairly insensitive to temperature in the low monomer concentration (ideal solution range) and varies very slowly with ϕ_m^0 over the range of ϕ_m^0 during which polymerization becomes substantial. The flattening effect persists in the one-phase region of the living polymer solutions and becomes more accentuated as the two-phase region is approached. The critical temperature of the system in Fig. 1 is $T_c = 283$ K. The inset provides the same data in a log–log representation.

A. Osmotic pressure Π , the second virial coefficient A_2 , and the critical osmotic compressibility factor Z_c

Figure 1 displays the dimensionless osmotic pressure $\Pi a^3/k_B T$ for this model system as a function of the initial monomer concentration ϕ_m^0 over the wide temperature range 265–400 K. At low monomer concentrations ϕ_m^0 , ideal solution behavior $\Pi \sim \phi_m^0$ is recovered, but a “plateau” in Π develops when ϕ_m^0 exceeds the “critical polymer concentration” ϕ_m^{*} at which the polymers begin to form (see Paper I). Notably, this leveling of the osmotic pressure curve vs ϕ_m^0 in Fig. 1 occurs over a range of temperatures *above* T_c , and this effect is more evident in the inset of Fig. 1 which presents $\ln(\Pi a^3/k_B T)$ vs $\ln \phi_m^0$. A further increase of ϕ_m^0 leads to a sharp elevation in Π due to an increase of excluded volume interactions among the growing polymer chains. The open interval in the 265 K isotherm of Fig. 1 demarks a two-phase region between $\phi_m^0 = 0.05$ and $\phi_m^0 = 0.25$, showing that the plateau effect in Π extends below the critical temperature for phase separation. No plateau is observed at $T = 400$ K, which is well above the ideal absolute polymerization temperature³⁵ $T_{p,o}^* \equiv T_p^{(o)}(\phi_m^0 = 1) = 333$ K, consistent with the absence of polymers in the high temperature system. The observation of a flattening in the concentration dependence of the osmotic pressure (e.g., in micelle formation,⁷⁰ simulations of associ-

ating polymers with “stickers,”⁸⁸ or living polymer type aggregation in simulations⁹⁸ and in experiments for clay dispersions⁹⁹) has been compared or attributed to a first order phase transition. Our calculations demonstrate, however, that this “singular” behavior of Π is also representative of an equilibrium particle clustering transition. Care should evidently be taken in assigning the “transition type” based solely on osmotic pressure data.

The leading order interparticle interaction effects responsible for the appearance of the plateau in Π are quantified by the second virial coefficient A_2 [see Eqs. (9) and (11)]. Figure 2(a) depicts the temperature variation of the second virial coefficient $A_2^{(\phi_m^0)}$ for the same system as in Fig. 1 ($r = 0.0044$) and for three other model systems having different initiator concentrations r . The dashed line corresponds to the $r \rightarrow 0^+$ limit and illustrates the linear dependence of $A_2^{(\phi_m^0)}$ on $1/T$, characteristic of the Flory theory of polymer solutions⁸⁹ [see Eq. (8)]. Solid lines refer to nonzero r and indicate that the Flory type linear behavior becomes *strongly modified* by the presence of initiator that promotes particle association.

The nonlinearity of the $A_2^{(\phi_m^0)}(T)$ curves is appreciable even for the rather low initiator concentration $r = 0.0044$ employed in the measurements of Greer *et al.*^{36,37} Another conspicuous feature illustrating the influence of particle association on $A_2^{(\phi_m^0)}$ is the increase in the theta temperature T_θ with the initiator concentration r , where T_θ is defined by the condition $A_2^{(\phi_m^0)} = 0$. This increase is rather slow [see the upper inset to Fig. 2(a)], but contrasts with the opposite trend found for the critical temperature T_c for phase separation which *decreases* with r [see the lower inset to Fig. 2(a)]. Evidently, the influence of particle clustering on “solvent quality” (the propensity towards phase separation or polymer swelling) is not a simple matter in living polymer solutions. A strong temperature dependence of $A_2^{(\phi_m^0)}$, like that in Fig. 2(a), has been predicted for gases of polar molecules,^{100,101} and “living polymerization” has recently been observed in computer simulations of model gases of polar molecules.^{7–10}

B. Critical sticking energies Δh_θ and Δh_c and the absolute polymerization temperature T_p^*

For ordinary polymer solutions, the theta temperature T_θ and the critical temperature T_c for phase separation coincide in the high molecular weight limit since the conditions for the vanishing of the second virial coefficient and for phase stability become identical in this limit.⁸⁹ An appreciable gap between T_θ and T_c normally occurs in solutions of low molecular weight polymers because of the larger entropy changes that accompany phase separation in small molecule fluids. (The analogous ratio of the Boyle temperature to the critical temperature is widely documented for fluid condensation.^{102,103}) Figure 2(b) illustrates the influence of the interparticle sticking energy $|\Delta h|$ on T_θ and T_c when the other polymerization and interaction parameters (Δs , r , χ) are the same as in Fig. 1. The temperatures T_θ and T_c are independent of $|\Delta h|$ until $|\Delta h|$ exceeds two distinct critical values $|\Delta h_\theta|$ and $|\Delta h_c|$, respectively. The “critical sticking

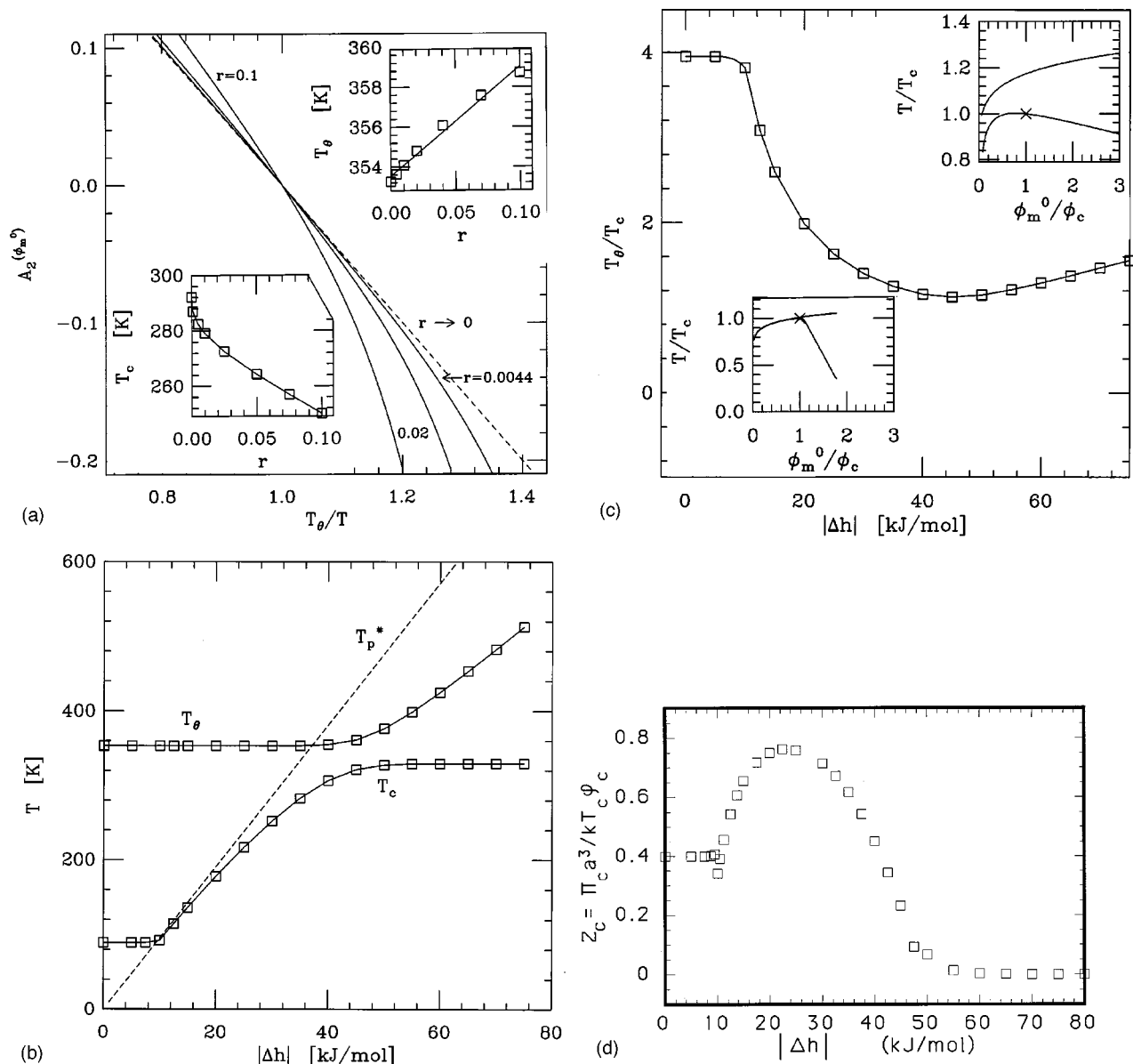


FIG. 2. (a) The dimensionless second virial coefficient $A_2^{(\phi_m^0)}$ of a living polymer solution, computed from Eq. (11) as a function of the reciprocal of the reduced temperature T_θ/T (where T_θ is the theta temperature) for several fixed dimensionless initiator concentrations $r = \phi_I/\phi_m^0$. The dashed line illustrates $A_2^{(\phi_m^0)}$ for the limiting case of $r \rightarrow 0^+$ where $A_2^{(\phi_m^0)}$ varies linearly with $1/T$. Insets depict the variations of the theta temperature T_θ and the critical temperature T_c with r . (b) The absolute polymerization temperature $T_p^* \approx T_p^{(o)}(\phi_m^0 = 1)$, theta temperature T_θ , and critical temperature T_c for the phase separation of a living polymer solution as functions of the sticking energy $|\Delta h|$. The initiator concentration r is fixed as $r = 0.0044$. Both T_c and T_θ are unchanged below the critical values of the sticking energy Δh_c and Δh_θ , respectively, at which the absolute polymerization line intersects the curves for $T_c(\Delta h)$ and $T_\theta(\Delta h)$. T_c saturates for large $|\Delta h|$, but T_θ apparently does not, leading to the nonmonotonic variation of T_θ/T_c exhibited in (c). When the sticking energy becomes large, the critical composition ϕ_c approaches the constant value $\phi_c = 0.0448$. The solid lines are guides for the eye. (c) The ratio of theta temperature T_θ and critical temperature T_c for the phase separation of a living polymer solution as a function of the sticking energy $|\Delta h|$. The solid line in the main figure is a guide for the eye. The upper inset depicts the ideal polymerization line and the spinodal curve for a representative sticking energy ($|\Delta h| = 50$ kJ/mol) which falls to the right of the minimum in T_θ/T_c in the central figure. The bottom inset corresponds to $|\Delta h| = 20$ kJ/mol which lies to the left of the minimum. The critical points of the spinodal curves are denoted by 'x's in both insets, and the upper curves in the insets denote the polymerization lines $T_p(\phi_m^0)$. Note the qualitative change in the shape of the phase diagram between the "weak" and "strong" coupling regimes of the lower and upper insets, respectively. (d) Critical osmotic compressibility factor $Z_c = \Pi_c a^3 / (k_B T_c \phi_c)$ of a living polymer solution. The interaction parameters are the same as those specified in Fig. 1 and correspond to poly(α -methylstyrene) in methyl cyclohexane. The sensitivity of Z_c to the "sticking energy" makes this property potentially useful for detecting particle clustering.

energy" Δh_θ corresponds to the values of Δh at which the absolute polymerization temperature $T_p^* \approx T_p^{(o)}(\phi_m^0 = 1)$ equals the theta temperature in the absence of polymerization. We have previously found that the critical enthalpy Δh_c corresponds to the sticking energy at which T_p^* equals the

critical temperature of the nonassociating system (see Paper II). Further physical interpretation of Δh_θ emerges in the $r \rightarrow 0^+$ limit, where $T_{p,o}^* = \Delta h/\Delta s$ and $T_\theta(r \rightarrow 0^+) \equiv T_{\theta,o} = 2c$ with c denoting the coefficient in the temperature dependence of $\chi = c/T$. These two temperatures should ap-

proach equality for $r \rightarrow 0^+$ because of the prevalence of very high molecular weights in that limit. Thus, equating $T_{p,o}^*$ and $T_{\theta,o}$ leads to relation,

$$\Delta h_{\theta} = 2c\Delta s, \quad r \rightarrow 0^+, \quad (19)$$

which demonstrates that the critical enthalpy of polymerization for the theta temperature T_{θ} is completely determined by two quantities: the entropy of polymerization and the interaction parameter $\chi = c/T$. Comparison of Eq. (19) above and Eq. (17) of Paper II shows that Δh_{θ} and Δh_c are simply proportional to each other when r is small,

$$\Delta h_{\theta} = 4\Delta h_c, \quad r \rightarrow 0^+. \quad (20)$$

Taking the values $\Delta s = -105$ J/(K mol) and $c = 176.63$ employed in Fig. 2(b) produces $\Delta h_c(r \rightarrow 0) = -9.3$ kJ/mol and $\Delta h_{\theta}(r \rightarrow 0) = -37.1$ kJ/mol which agree quite well with graphical estimations of $\Delta h_c \approx -10.0$ kJ/mol and $\Delta h_{\theta} \approx -37.5$ kJ/mol for $r = 0.0044$, as deduced from Fig. 2(b). In the next subsection, we show how the phase diagram and critical properties of living polymer solutions change qualitatively in the sticking interaction ranges defined by Δh_{θ} and Δh_c .

C. Dimensionless property ratios providing evidence of dynamical clustering

Measurements of the temperature ratio T_{θ}/T_c and other dimensionless solution properties influenced by particle clustering, e.g., the ‘‘critical osmotic compressibility factor’’ $Z_c = \Pi_c a^3 / (k_B T_c \phi_c)$, where the subscript c denotes the critical condition for the property or the ‘‘rectilinear diameter’’¹⁰³ (which defines the averaged composition of the two branches of the coexistence curves), provide essential information about the existence and the extent of clustering in fluids.

Figure 2(c) describes how the ratio T_{θ}/T_c varies with $|\Delta h|$. For small sticking energies $|\Delta h|$, the ratio $T_{\theta}/T_c \approx 3.95$ is close to the mean-field value of $T_{\theta,o}/T_{c,o} = 4$ in the absence of polymerization,¹⁰⁴ but greatly diminishes with increased $|\Delta h|$, achieves a minimum ($T_{\theta}/T_c = 1.12$), and begins to increase again because the critical temperature saturates with $|\Delta h|$ while T_{θ} continues to grow [see Fig. 2(b)]. The critical sticking energy Δh_{θ} separates a strong coupling regime, where $|\Delta h| > |\Delta h_{\theta}|$ and where the polymerization transition line lies above the cloud point curve, from a weak coupling regime determined by $|\Delta h| < |\Delta h_{\theta}|$ and characterized by the overlapping of these two curves over a wide range. Examples of these two types of behavior are generated by taking $\Delta h = -50$ kJ/mol and $\Delta h = -20$ kJ/mol ($\Delta h_{\theta} = -37.1$ kJ/mol), and these representative examples are presented in the upper and lower insets to Fig. 2(c), respectively. The shape of the phase diagram changes *qualitatively* between these two regimes.

Not only can clustering alter these dimensionless property ratios, but it is also possible that clustering can change the universality class^{11,12} for the phase separation (i.e., critical exponents and amplitude ratios). There have been many reports of apparent mean-field critical behavior for micelles

in solution and ionic fluids^{11,12,105} which suggest the potential importance of particle clustering in the classification of phase transitions.

The critical osmotic compressibility factor $Z_c = \Pi_c a^3 / (k_B T_c \phi_c)$ is another important quantity that strongly depends on the sticking energy Δh [see Fig. 2(d)]. The variation of the Z_c with $|\Delta h|$ in Fig. 2(d) resembles the curve $Z_c = Z_c(|\Delta h|)$ obtained⁴² from the Wertheim theory¹⁰⁶ for single component associating fluids. (The qualitative similarity extends also to the dependence of the critical temperature and critical composition on Δh , a dependence that is analyzed in detail in Paper II.) The compressibility factor Z_c calculated by Jackson *et al.*⁴² with the Wertheim theory first increases gradually with $|\Delta h|$, passes through a maximum, and then decreases monotonically, a behavior characteristic of particle clustering. The maximum in Z_c in Fig. 2(d) is, however, much greater than the maximum of Z_c in Ref. 42, and the limiting ($\Delta h \rightarrow \infty$) values of Z_c vary between these two approaches (zero vs a small constant⁴²). The large magnitude of the maximum in Z_c in Fig. 2(d) is apparently related to the nonzero initiator concentration ($r = 0.0044$) employed in our computations. A large Z_c has also been observed in the ionic salt ammonium chloride along with mean-field type critical behavior¹⁰⁷ associated with particle clustering.¹⁰⁸ The change in Z_c from its $\Delta h \rightarrow 0$ value in Fig. 2(d) likewise reflects the existence of clustering and may be used in conjunction with other critical property ratios for providing quantitative information about the clustering process. Additional experiments determining Z_c in associating systems would be helpful in further developing this criterion for identifying particle clustering.

D. Osmotic compressibility κ

The existence of a phase transition should be revealed by derivatives of Π , and we, thus, examine the osmotic compressibility for evidence of a thermodynamic singularity in living polymer solutions. Figure 3 illustrates the dependence of κ on the initial monomer concentration ϕ_m^0 for a range of fixed temperatures approaching the critical temperature $T_c = 283$ K. (Again the parameters of the polymerization model are the same as those in Fig. 1.) The isothermal osmotic compressibility κ develops a minimum near the critical polymerization concentration (cpc) at which the average chain length L extrapolates to unity (i.e., corresponding to the presence of only monomers).³⁵ The arrows in Fig. 3 denote the cpc's obtained from the extrapolations of L depicted in the inset to the figure. Extrapolation of the coherent scattering intensity $I(0)$ to zero angle should then exhibit a minimum near the cpc since $I(0)$ is proportional to κ [see Eq. (14)].

While the presence of extrema in the concentration dependence of κ is suggestive of some type of ‘‘transition phenomenon,’’ it does not provide definitive information about the thermodynamic nature of the transition. To address this issue, Fig. 4 presents κ as a function of *temperature* for fixed ϕ_m^0 and variable r . The initial monomer composition ϕ_m^0 is chosen to equal 0.5, so that the polymerization temperature $T_p = 312$ K is well above the spinodal temperature, $T_{sp}(\phi_m^0 = 0.5) < 200$ K, for phase separation. The osmotic compress-

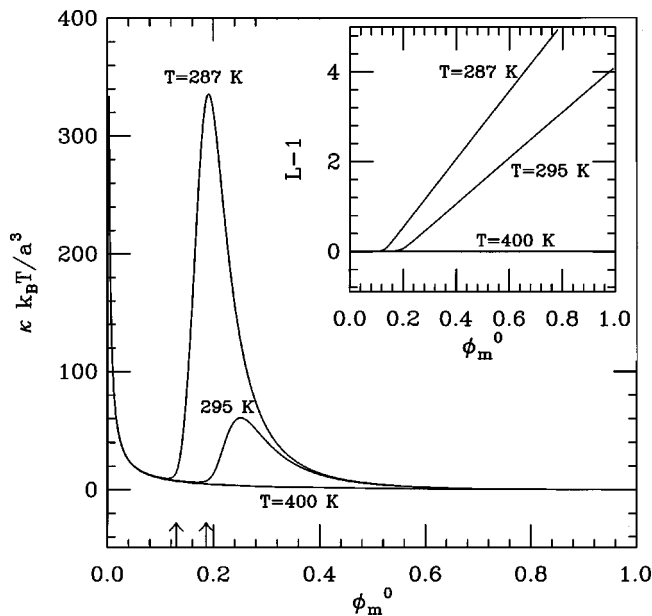


FIG. 3. The dimensionless osmotic compressibility $\kappa k_B T / a^3$ of a living polymer solution as a function of initial monomer concentration ϕ_m^0 for several temperatures. The minima exhibited by κ appear very near the critical polymerization concentrations (cpc) indicated by arrows. The cpc are estimated from plots of the average polymerization index L vs ϕ_m^0 (see inset) by extrapolating $L-1$ to zero (see Paper I).

ibility in Fig. 4 exhibits a relatively strong variation near T_p for the value of $r=0.0044$ used in the experiments of Greer *et al.*^{36,37} The variation of κ with T becomes more pronounced for smaller r , and the $r \rightarrow 0^+$ limit (actually r

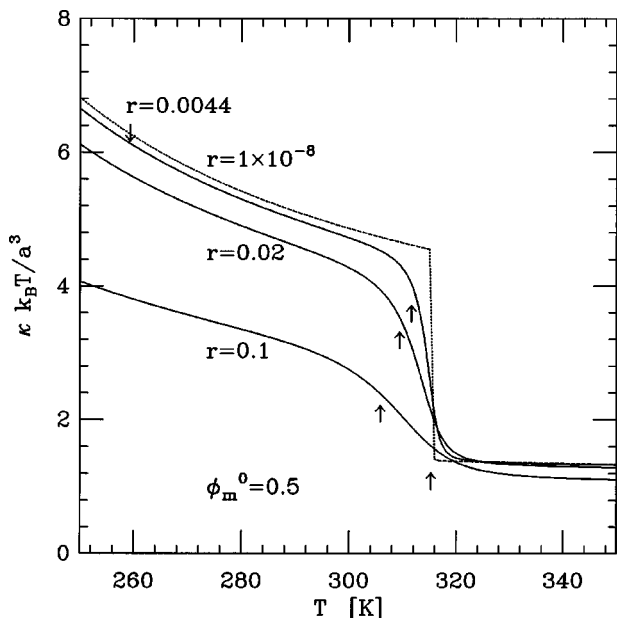


FIG. 4. The osmotic compressibility $\kappa k_B T / a^3$ of a living polymer solution as a function of temperature for fixed $\phi_m^0=0.5$ and several initiator concentrations r . The value for ϕ_m^0 is chosen to ensure that the system is in the one-phase region. A sharp jump in κ occurs in the ideal $r \rightarrow 0^+$ limit where the polymerization transition is a true second order phase transition. The transition becomes rounded with increasing initiator concentration r . Arrows indicate the polymerization transition temperatures T_p for the four systems with the initiator concentrations r indicated on the figure.

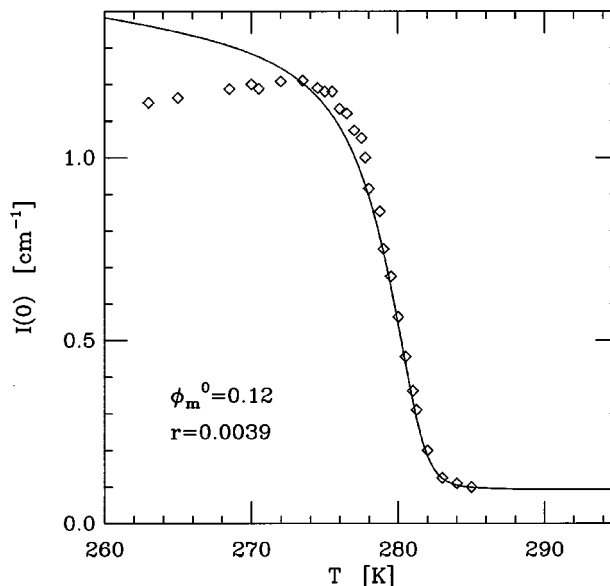


FIG. 5. Comparison of the calculated zero-angle neutron scattering intensity $I(0)$ with experimental data (diamonds) by Greer and co-workers (Ref. 96) for a solution of poly(α -methylstyrene) in deuterated tetrahydrofuran ($\phi_m^0=0.12$ and $r=0.0039$). The enthalpy and entropy of polymerization and the interaction parameter χ are taken as the values used in the fitting procedure of Greer *et al.* (Ref. 96) ($\Delta h = -34.6$ kJ/mol, $\Delta s = 105$ J/(mol K), and $\chi = 70.95/T$).

$=10^{-8}$) is included in Fig. 4 for comparison, along with curves $\kappa(T)$ for $r=0.02$ and 0.1 . In the limit of vanishing initiator concentration $r \rightarrow 0^+$, κ displays a step like jump at T_p , similar to the behavior found for the specific heat (see Paper I and discussion below). These jumps are characteristic of a mean-field second order phase transition.¹⁰⁹ When r increases, κ varies more weakly with temperature in the vicinity of T_p , and the polymerization transition ‘‘broadens’’ (see Fig. 4).

E. Comparison with osmotic compressibility κ measurements

Greer and co-workers⁹⁶ have recently performed neutron scattering measurements for poly(α -methylstyrene) in deuterated tetrahydrofuran ($\phi_m^0=0.12$), thereby providing an opportunity to compare the present theory to experiment. Figure 5 displays the data for the neutron scattering intensity $I(0)$ extrapolated to zero angle. The sample is one of three measured by Greer *et al.*,⁹⁶ and this sample is chosen for comparison because it yields the *largest* discrepancy with theory⁹⁶ and because it contains the largest initial monomer concentration ϕ_m^0 . (A large polymer concentration is important for the applicability of a mean-field theory since long range excluded volume effects are especially relevant in the low concentration region.) The interaction parameter χ is taken as $\chi = 70.95/T$, in accordance with the value $\chi = (74 \pm 10)/T$ used by Greer *et al.*⁹⁶ This value differs from the χ employed in the previous figures that is appropriate to a theta temperature solvent near room temperature. As in the prior comparison of mean-field theory with the scattering data of Greer *et al.*,⁹⁶ our theory predicts the correct qualitative behavior of $I(0)$, but fails to describe a maximum in $I(0)$

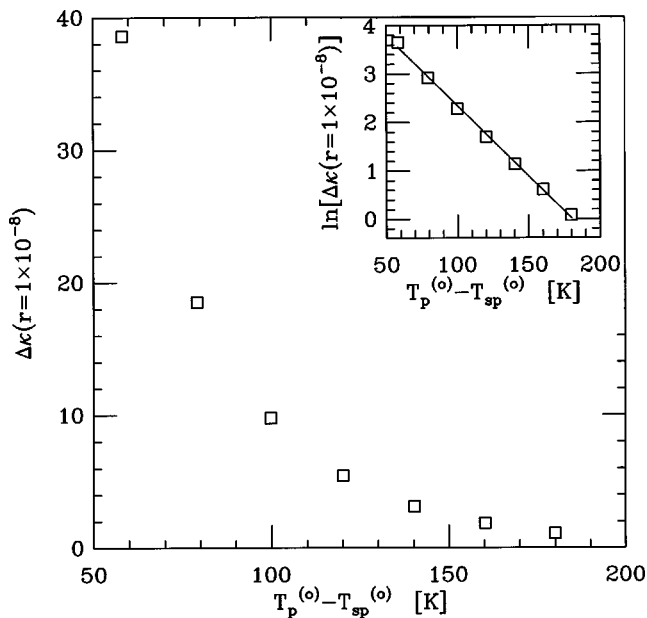


FIG. 6. The jump $\Delta\kappa$ in the osmotic compressibility $\kappa k_B T/a^3$ for a living polymer solution in the $r \rightarrow 0^+$ limit as a function of the temperature difference $\Delta T = T_p^{(o)}(\phi_m^0) - T_{sp}^{(o)}(\phi_m^0)$ between the ideal polymerization temperature $T_p^{(o)}$ and the ideal spinodal temperature $T_{sp}^{(o)} \equiv T_{sp}(r \rightarrow 0^+)$. The inset demonstrates that the step function type discontinuity in κ at $T_p^{(o)}$ is nearly an exponential function of ΔT .

below the polymerization temperature and a declining scattering intensity upon a further cooling. At low temperatures, the polymer contribution to $I(0)$ [i.e., the $1/\phi\mathcal{M}$ term in the RPA formula of Eq. (15)] becomes negligible, and the temperature variation of the mean-field expression for $I(0)$ in Eq. (15) is solely governed by the temperature dependence of the interaction parameter χ . As the temperature is decreased, the interaction parameter $\chi = c/T$ grows, thereby leading to the computed increase of $I(0)$, as expected. Within our model, we would find a flatter $I(0)$ at low temperatures if χ , instead, contains a substantial “entropic” contribution¹¹⁰ of the form $\chi = b + c/T$.

Wheeler and Pfeuty¹¹¹ have recently interpreted the deviation from mean-field predictions as arising entirely from fluctuation effects associated with the polymerization transition, a feature not included in our approach. However, their analysis is based on the assumption of zero mixing energy between solvent and monomers (i.e., $\chi = 0$). Our mean-field description indicates, however, that the presence of the polymer–solvent interactions appreciably affects $I(0)$ below the polymerization transition temperature, so this former interpretation of the neutron scattering data should be extended to include a nonzero monomer–solvent interaction χ . It is notable that the experimental maximum in $I(0)$ (see Fig. 5) occurs at a temperature about 10 K below the polymerization temperature.

F. Measures of the “strength” and “breadth” of dynamical clustering transitions

The singular nature of κ becomes more pronounced as T_p approaches the phase boundary (i.e., the spinodal temperature T_{sp}). To illustrate this experimentally important

phenomenon, Fig. 6 presents the jump $\Delta\kappa$ in the osmotic compressibility κ ($r \rightarrow 0^+$) as a function of the temperature difference $\Delta T \equiv T_p^{(o)} - T_{sp}^{(o)}$. A nearly exponential dependence of κ on ΔT is found,

$$\Delta\kappa(r \rightarrow 0^+) = A_1 \exp[-\alpha(T_p^{(o)} - T_{sp}^{(o)})],$$

$$A_1 \approx 189 \text{ and } \alpha \approx 0.029, \quad (21)$$

where the superscript (o) emphasizes the $r \rightarrow 0$ limit. The compressibility jump $\Delta\kappa$ quantifies the transition “strength” of the polymerization transition. While the interparticle interaction χ does not influence T_p in our simplified Flory–Huggins model,³⁵ it does substantially affect $\Delta\kappa$ and the transition “strength” through T_{sp} . Thus, the presence of critical fluctuations *amplifies* the singular features in the osmotic compressibility near the polymerization transition. This behavior is expected to be general feature of other dynamical particle clustering transitions.

Figure 4 also indicates that the compressibility change $\Delta\kappa$ at T_p diminishes with increasing r , while the polymerization transition centered at T_p becomes smeared over a broader temperature range. An estimate of the “transition breadth” is determined by calculating the temperature derivative $\kappa' \equiv d\kappa/dT$ which has a nearly Gaussian functional form centered at T_p . The width $w_{\kappa'}(r)$ at half-height of this peak is presented in Fig. 7(a) as a function of r . The inset to Fig. 7(a) shows that the transition width $w_{\kappa'}(r)$ approximately follows a power law $w_{\kappa'}(r) \sim r^{0.46}$ over the r range indicated. Restricting r to lie between $10^{-3} < r < 0.1$, we further quantify the “transition strength” by considering the height $h_{\kappa'}$ of the peak in $\kappa'(r)$ as a function of r [see Fig. 7(b)]. The height $h_{\kappa'}$ also decays as a power law, $h_{\kappa'} \sim r^{-0.63}$. The product of $w_{\kappa'}(r)$ and $h_{\kappa'}(r)$ thus scales as $r^{-0.17}$, so that the decrease in the “transition strength” $h_{\kappa'}$ is nearly matched by the growth in the “transition breadth” $w_{\kappa'}$.

It is also instructive to compare $h_{\kappa'}$ and $w_{\kappa'}$ from Figs. 7(a) and 7(b) with the height and width of the specific heat curve $C_p(T)$ at T_p . Figure 8 illustrates how the “rounding” of C_p is influenced by variations in r near the polymerization transition. The insets to Fig. 8 presents the width w_{C_p} [determined as twice the width of the curve defining the decay of C_p for $T > T_p$; the width w_{C_p} is evaluated at a value of C_p that is half the maximum at the polymerization transition] and the height h_{C_p} of C_p at the transition as a function of r . The rounding of C_p due to initiator is similar to that found for κ' . The increase in the transition breadth indicated by C_p is accompanied by a corresponding decrease in transition strength, but the r -dependence of h_{C_p} and w_{C_p} does not follow a simple power-law variation. Thus, the “rounding” of the polymerization transition is manifested somewhat differently for C_p and κ . The concepts of transition breadth and transition strength, generated from the analyses of the isothermal osmotic compressibility κ and the heat capacity C_p , quantify the extent to which the polymerization transition resembles a second order transition. In future work we plan to adapt these estimates to providing useful measures of transition rounding in living polymer solutions and other associating particle systems.

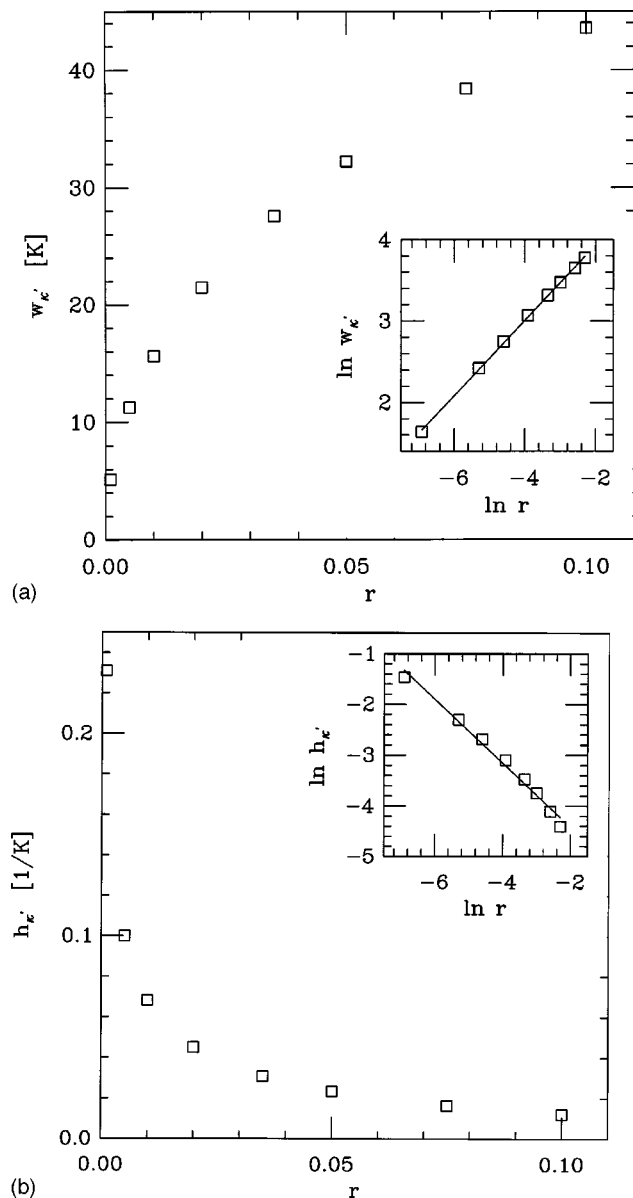


FIG. 7. (a) The width $w_{\kappa'}(r)$ of the polymerization transition in a living polymer solution as a function of initiator concentration r . The derivative of $\kappa(T)$ with respect to temperature has a nearly Gaussian shape near the polymerization temperature. The half-width of this Gaussian function defines the width function $w_{\kappa'}(r)$ for the polymerization transition. The inset demonstrates that $w_{\kappa'}(r)$ has a nearly power-law dependence on r . (b) The strength $h_{\kappa'}$ of the polymerization transition in a living polymer solution as a function of initiator concentration r . We define $h_{\kappa'}$ as the height of the maximum of the derivative $d\kappa/dT$. The inset shows that $h_{\kappa'}$ exhibits a near power-law dependence on r . The product of $h_{\kappa'}$ and the transition width $w_{\kappa'}(r)$ is found to vary slowly with r (see text), so that the broadening of the transition is roughly counterbalanced by a decreased transition strength.

IV. DISCUSSION

An examination of the osmotic pressure Π and the osmotic compressibility κ of living polymer solutions over a range of temperatures reveals several generic features that should be broadly applicable to associating particle systems at equilibrium. The osmotic pressure exhibits little variation with the initial monomer concentration above the "critical polymerization concentration"³⁵ (ϕ_m^*) at which clusters (polymers) first form. Moreover, the scattering intensity $I(0)$

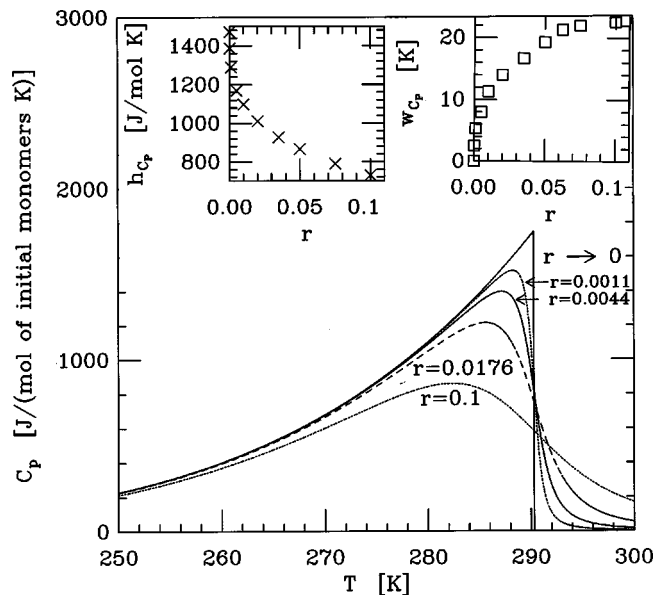


FIG. 8. Rounding of the specific heat C_p of a living polymer solution due to nonzero initiator concentration r . In the formal limit $r \rightarrow 0^+$, the polymerization transition is a second order phase transition, and the mean-field specific heat has a jump discontinuity at $T_p = 290$ K. The transition becomes increasingly rounded as r grows, and this effect is quantified in the insets that display the height of the C_p maximum at the polymerization transition and the transition breadth w_{C_p} . The transition breadth w_{C_p} is determined as twice the width of the curve defining the decay of C_p for $T > T_p$. The width is evaluated at a value of C_p that is half the maximum value at the polymerization transition.

and the collective diffusion coefficient display extrema at ϕ_m^* .^{112,113} The behavior of κ is also examined to provide an improved characterization of the rounding of the clustering transition. The variations in κ approach a step-function in the $r \rightarrow 0^+$ limit, indicative of a second order phase transition in mean-field theory.¹⁰⁹ The step-function substantially broadens even for small r , so that real living polymers with $r > 0$ undergo a "rounded" clustering transition. Even when r is small, the polymerization transition generally does not exhibit the truly singular variations characteristic of a second order transition, but a fairly sharply defined clustering transition nevertheless exists. Since an ideal "phase transition" can only be approximated in real physical systems¹¹⁴ due to geometrical constraints, internal constraints on the particle clustering dynamics, or external fields, we prefer to designate these rounded transitions as varieties of phase transitions. Of course, significant rounding of a second order phase transition can obliterate the nonanalytic property variations normally associated with second order transitions (see Paper I), so new features can arise in "rounded" transitions that have no counterparts in the second order transitions to which they are formally related. To avoid confusion with "singular" phase transitions of first or second order, we suggest that the rounded transitions be termed "analytic" transitions since the free energy is analytic at the transition.

An examination of the underlying physical origins for the flattening of the concentration dependence of the osmotic pressure reveals that the theta temperature T_θ of the living polymer solution becomes substantially modified by the presence of a large sticking energy. This leads to a qualita-

tive change in the polymerization line-spinodal curve phase boundary that has not been appreciated in our previous papers.³⁵ The critical values of the sticking energy Δh_c and Δh_θ , at which the critical and theta temperatures, respectively, begin to change with $|\Delta h|$, correspond to the crossing of plots for the critical and theta temperatures vs $|\Delta h|$ by the (ideal) absolute polymerization line $T_{p,o}^*$, defined as the polymerization transition in the limit of no initiator or solvent. Curiously, an increase of initiator concentration r induces a slight growth of the theta temperature T_θ , whereas the critical temperature T_c for phase separation becomes lowered. These findings imply that the many-body particle association interactions can significantly modify the “bare” polymer-solvent interactions from the χ parameter applying in the absence of initiator, so that the “solvent quality” is quite different than might be expected based on the direct polymer-solvent local interactions. The sensitivity of T_θ/T_c and other dimensionless solution properties of living polymer solutions to clustering can thus be used to identify particle clustering in the fluid mixtures and to quantify the thermodynamic effects of this clustering.

There has recently been much interest and controversy regarding the order of the gelation transition, and some have questioned whether a true phase transition exists at all in this type of multifunctional particle association transition. For example, Tanaka and Stockmayer⁶¹ describe the thermally reversible gelation transition of monodisperse and polydisperse associating polymers as being either a third order or second order phase transition, respectively, based on a Cayley-tree type mean-field theory. Erukhimovitch's field theoretical calculations indicate that gelation is a second order phase transition.⁸⁷ On the other hand, Semenov and Rubinstein⁸⁶ have suggested that gelation corresponds to a percolation process which is purely geometrical phenomenon (i.e., formation of connected clusters spanning the fluid macroscopically). This point of view implies the absence of any phase transition, rounded or otherwise. Similar discussions have appeared in connection with thermally reversible gelation in colloid systems,^{29,115,116} and Bergenholtz and Fuchs¹¹⁷ have recently introduced yet another conception of gelation in colloidal suspensions by offering the suggestion that gelation is a dynamical “caging” transition similar to the mode-coupling model of glass formation in cooled liquids. These disparate views of gelation have their counterparts in recent discussions of glass formation where there is likewise no consensus on what type of transition occurs or even whether a thermodynamic or dynamic transition strictly exists at all.

It is our expectation, based, in part, on the present work for linearly associating polymers (“living polymers”), that thermally reversible gelation is a variety of “rounded” phase transition similar to living polymerization with initiator. Interestingly, the mean-field calculations of Tanaka and Stockmayer⁶¹ show that the existence of multifunctional particle association “broadens” the jump in the osmotic compressibility κ of associating monodisperse polymers into a piecewise continuous “bump” (i.e., a third order phase transition). These mean-field calculations illustrate how multifunctional particle associations can influence the “sharp-

ness” of the gelation transition, leading mathematically to an effect similar to that produced by an increased initiator concentration in living polymerization. The physical origin of the rounding in the gelation clustering transition is different, of course.

Another instructive example of transition rounding is provided by the living polymerization of sulfur where the ring opening probability plays a role analogous to the initiator concentration r in living polymer solutions.^{36,37} Sulfur polymerization illustrates a case where a second rate process (ring opening) initiates the polymerization process and where this secondary process leads to transition “rounding.” Processes that serve to inhibit cluster growth can likewise be expected to lead to transition rounding. Rounding of the clustering transition also occurs generally when the mass of the dynamical cluster is restricted to be finite or has a particular structure dictated by specific interparticle interactions. (Such constraints occur in micelles, protein folding, associating protein clusters, copolymers with particular microstructures, and in some self-assembling biological structures.) Finite-size effects of this kind lead to a saturation of cluster growth as the temperature is varied through the dynamical clustering transition. The constraint of cluster growth to a finite average size should again be similar (see Fig. 1 of Paper I) in its thermodynamic consequences on the clustering transition as in the present living polymer model calculations for $r > 0$. We anticipate that “rounded” clustering transitions are widespread in soft-condensed materials, and we therefore suggest that some of these transitions may have been misinterpreted as nonequilibrium phenomena because of the significant differences between this kind of “condensation” phenomenon and the more traditionally studied variations of fluid ordering (liquidification, phase separation, crystallization).

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¹A. Gavezzotti, *Acc. Chem. Res.* **27**, 309 (1994).

²S. Alexander and J. M. Tague, *Phys. Rev. Lett.* **41**, 702 (1978).

³P. R. ten Wolde, D. W. Oxtoby, and D. Frenkel, *Phys. Rev. Lett.* **81**, 3695 (1998).

⁴P. R. ten Wolde and D. Frenkel, *Science* **277**, 1975 (1997).

⁵A. I. Melker and T. V. Vorobyeva, *Z. Naturforsch. A* **A49**, 1045 (1994).

⁶T. Yamamoto, *J. Chem. Phys.* **107**, 2653 (1997).

⁷M. E. van Leeuwen and B. Smit, *Phys. Rev. Lett.* **71**, 3991 (1993); Y. Levin, *ibid.* **83**, 1159 (1999).

⁸S. C. M. Grother and G. Jackson, *Phys. Rev. Lett.* **76**, 4183 (1996).

⁹J. Z. Siepmann, S. Karaborni, and B. Smit, *Nature (London)* **365**, 330 (1993).

¹⁰E. de Miguel, L. F. Rull, and K. E. Gubbins, *Physica A* **177**, 174 (1991); M. A. Osipov, P. I. C. Teixeira, and M. M. Telo da Gama, *Phys. Rev. E* **54**, 2597 (1996); J. M. Tavares, J. J. Weis, and M. M. Telo da Gama, *ibid.* **59**, 4388 (1999).

¹¹K. S. Pitzer, *J. Chem. Phys.* **99**, 13070 (1995).

¹²K. S. Pitzer, *Acc. Chem. Res.* **23**, 333 (1990).

- ¹³M. H. J. Hagen, E. J. Meijer, G. C. A. M. Mooij, D. Frenkel, and H. N. W. Lekkerkerker, *Nature (London)* **365**, 425 (1993).
- ¹⁴N. W. Ashcroft, *Nature (London)* **365**, 387 (1993).
- ¹⁵R. D. Mountain, *J. Chem. Phys.* **110**, 2109 (1999).
- ¹⁶D. A. Weitz, J. S. Huang, M. Y. Lin, and J. Sung, *Phys. Rev. Lett.* **54**, 1416 (1985).
- ¹⁷D. A. Weitz and M. Oliveria, *Phys. Rev. Lett.* **52**, 1433 (1984).
- ¹⁸M. Y. Lin, H. M. Lindsay, D. A. Weitz, R. C. Ball, R. Klein, and P. Meakin, *Nature (London)* **339**, 360 (1989).
- ¹⁹P. Wiltzius, *Phys. Rev. Lett.* **58**, 710 (1987).
- ²⁰D. Turnbull, *Contemp. Phys.* **10**, 473 (1969).
- ²¹C. A. Angell, *J. Non-Cryst. Solids* **131–133**, 13 (1991).
- ²²C. A. Angell, *Science* **67**, 1924 (1995).
- ²³C. Aubert and D. S. Cannell, *Phys. Rev. Lett.* **56**, 738 (1986).
- ²⁴G. Y. Onoda, *Phys. Rev. Lett.* **55**, 226 (1985).
- ²⁵D. W. Schaefer, J. E. Martin, P. Wiltzius, and D. S. Cannell, *Phys. Rev. Lett.* **52**, 2371 (1984).
- ²⁶M. Kroon, W. L. Vos, and G. H. Wegdam, *Phys. Rev. E* **57**, 1962 (1998).
- ²⁷R. Piazza and G. D. Pietro, *Europhys. Lett.* **28**, 445 (1994).
- ²⁸J. A. Molina-Bolivar, F. Galisteo-Gonzalez, and R. Hidalgo-Álvarez, *J. Colloid Interface Sci.* **208**, 445 (1998).
- ²⁹C. J. Rueb and C. F. Zukowski, *J. Rheol.* **42**, 1451 (1998).
- ³⁰K. Ito, H. Nakamura, H. Yoshida, and N. Ise, *J. Am. Chem. Soc.* **110**, 6955 (1988).
- ³¹N. Ise, H. Matsuoka, and K. Ito, *Macromolecules* **22**, 1 (1989).
- ³²S. Doshio, N. Ise, K. Ito, S. Iwai, H. Kitano, H. Matsuoka, H. Nokamura, H. Okumura, T. Ono, I. S. Sogami, Y. Ueno, H. Yoshida, and T. Yoshiyama, *Langmuir* **9**, 394 (1993).
- ³³A. K. Arora and P. Kesaramoorthy, *Solid State Commun.* **54**, 1047 (1985).
- ³⁴N. Ise, *Angew. Chem. Int. Ed. Engl.* **25**, 323 (1986).
- ³⁵J. Dudowicz, K. F. Freed, and J. F. Douglas, *J. Chem. Phys.* **111**, 7116 (1999); **112**, 1002 (2000) are Papers I and II, respectively, of the present series. These papers give numerous references to prior theoretical and experimental work on associating polymers. References 36 and 37 provide good recent reviews of equilibrium living polymerization from an experimental perspective.
- ³⁶S. C. Greer, *Adv. Chem. Phys.* **94**, 261 (1996).
- ³⁷S. C. Greer, *J. Phys. Chem. B* **102**, 5413 (1998).
- ³⁸R. S. Spangler, *Phys. Rev.* **46**, 698 (1934); G. W. Stewart, *Trans. Faraday Soc.* **29**, 982 (1933).
- ³⁹T. Morita, K. Nishikawa, M. Takematsu, H. Iida, and S. Furutaka, *J. Phys. Chem. B* **101**, 7158 (1997).
- ⁴⁰K. Nishikawa and T. Morita, *J. Phys. Chem. B* **101**, 1413 (1997).
- ⁴¹P. Jedlovsky and R. Vallauri, *Mol. Phys.* **93**, 15 (1998).
- ⁴²G. Jackson, W. G. Chapman, and K. E. Gubbins, *Mol. Phys.* **65**, 1 (1988); see also F. Dolezalek [*Z. Phys. Chem.* **64**, 727 (1908)] for an early treatment of equilibrium particle association.
- ⁴³K. J. Johnson and K. E. Gubbins, *Mol. Phys.* **77**, 1033 (1992).
- ⁴⁴R. D. Mountain, *J. Chem. Phys.* **110**, 2109 (1999).
- ⁴⁵S. H. Chen, J. Rouch, F. Sciortino, and P. Tartaglia, *J. Phys.: Condens. Matter* **6**, 10855 (1994).
- ⁴⁶K. G. de Kruijff, M. A. M. Hoffmann, M. E. van Marle, P. J. J. M. van Mil, S. P. F. M. Roefs, M. Verheul, and N. Zoon, *Faraday Discuss.* **101**, 185 (1995).
- ⁴⁷S. Chien, S. Usami, R. J. Dellenback, and M. I. Gregersen, *Science* **157**, 829 (1967).
- ⁴⁸H. Schmid-Schoenbein, R. Wells, and R. Schildkraut, *J. Appl. Phys.* **26**, 674 (1969).
- ⁴⁹R. W. Samsel and A. S. Perelson, *Biophys. J.* **37**, 494 (1981).
- ⁵⁰R. W. Samsel and A. S. Perelson, *Biophys. J.* **45**, 805 (1984).
- ⁵¹F. W. Wiegel and A. S. Perelson, *J. Stat. Phys.* **29**, 813 (1982).
- ⁵²P. L. San Biagio and M. U. Palma, *Biophys. J.* **60**, 508 (1991).
- ⁵³M. L. Broide, T. M. Tominc, and M. D. Saxowsky, *Phys. Rev. E* **53**, 6325 (1996).
- ⁵⁴M. Muschol and F. Rosenberger, *J. Chem. Phys.* **107**, 1953 (1997).
- ⁵⁵C. R. Berland, G. M. Thurston, M. Kondo, M. L. Broide, J. Pande, O. Ogun, and G. B. Benedek, *Proc. Natl. Acad. Sci. USA* **89**, 1214 (1992).
- ⁵⁶H. Tan, A. Moet, A. Hiltner, and E. Baer, *Macromolecules* **16**, 28 (1983).
- ⁵⁷S. Mal, P. Maiti, and A. K. Nandi, *Macromolecules* **28**, 2371 (1995). Note the Arrhenius temperature dependence for critical gelation concentration found in this paper.
- ⁵⁸B. Jeong, D. S. Lee, J. Shoh, Y. H. Bae, and S. W. Kim, *J. Polym. Sci., Part A: Polym. Chem.* **37**, 751 (1999).
- ⁵⁹C. Coniglio, H. E. Stanley, and W. Klein, *Phys. Rev. B* **25**, 6805 (1982).
- ⁶⁰F. Tanaka and A. Matsuyama, *Phys. Rev. Lett.* **62**, 2759 (1989).
- ⁶¹F. Tanaka and W. H. Stockmayer, *Macromolecules* **27**, 3943 (1994).
- ⁶²S. S. Das, J. Zhuang, A. P. Andrews, S. C. Greer, C. M. Guttman, and W. Blair, *J. Chem. Phys.* **111**, 9406 (1999).
- ⁶³It is common in the experimental literature to identify the locus of temperatures and compositions at which “turbidity” occurs as the “cloud point curve” or “solubility curve.” These phase diagrams do not always correspond to phase separation [G. D. J. Phillies, *Phys. Rev. Lett.* **55**, 1341 (1985)]. The tendency of the “cloud point curve” to become *independent of composition* at high concentrations of the clustering species and the absence of macroscopic phase separation into coexisting phases are symptomatic of a “clustering transition” rather than a phase separation.
- ⁶⁴P. Guenon, F. Perrot, and D. Beysens, *Phys. Rev. Lett.* **63**, 1152 (1989).
- ⁶⁵A. Klug, *Angew. Chem. Int. Ed. Engl.* **22**, 565 (1983).
- ⁶⁶T. Liu, Z. Zhou, C. Wu, B. Chu, K. Scheider, and V. M. Nace, *J. Phys. Chem. B* **101**, 8808 (1997).
- ⁶⁷Q. Ying, J. Marecek, and B. Chu, *J. Chem. Phys.* **101**, 2665 (1994).
- ⁶⁸T. Liu, Z. Zhou, C. Wu, V. M. Nace, and B. Chu, *J. Phys. Chem. B* **102**, 2875 (1998).
- ⁶⁹B. Chu, T. Liu, C. Wu, Z. Zhou, and V. M. Nace, *Macromol. Symp.* **118**, 221 (1997).
- ⁷⁰M. A. Floriano, E. Caponetti, and A. Z. Panagiotopoulos, *Langmuir* **15**, 3143 (1999).
- ⁷¹Note the Arrhenius temperature dependence of the critical micelle concentration in Refs. 66–70.
- ⁷²L. D. Maeyer, C. Trachimow, and U. Koatze, *J. Phys. Chem. B* **102**, 8480 (1998).
- ⁷³M. B. Weissman, *Rev. Mod. Phys.* **60**, 537 (1988).
- ⁷⁴J. C. Dyre, *Phys. Rev. B* **37**, 10143 (1988).
- ⁷⁵E. V. Russell, N. E. Israeloff, L. E. Walther, and H. A. Gomariz, *Phys. Rev. Lett.* **81**, 1461 (1998).
- ⁷⁶N. E. Israeloff and X. Wang, *Rev. Sci. Instrum.* **68**, 1543 (1997).
- ⁷⁷K. N. Bakeev, I. Teraoka, W. J. M. Knight, and F. E. Karasz, *Macromolecules* **26**, 1972 (1993).
- ⁷⁸K. Chakrabarty, R. B. Weiss, A. Sehgal, and T. A. P. Seery, *Macromolecules* **31**, 7390 (1998).
- ⁷⁹K. S. Schmitz and R. J. Ramsay, *Macromolecules* **18**, 933 (1985).
- ⁸⁰B. D. Ermi and E. J. Amis, *Macromolecules* **30**, 6937 (1997).
- ⁸¹J. F. Douglas and J. B. Hubbard, *Macromolecules* **24**, 3163 (1991).
- ⁸²H. Heckmeier, M. Mix, and G. Strobl, *Macromolecules* **30**, 4454 (1997).
- ⁸³P. J. G. Butler, *J. Gen. Virol.* **65**, 253 (1984).
- ⁸⁴L. A. Amos and W. B. Amos, *Molecules of the Cytoskeleton* (MacMillan, London, 1991), Chap. 76.
- ⁸⁵Polymers can be formed into conventional linear string structures, membranellike two dimensional polymers [T. Hwa, E. Kokufuta, and T. Tanaka, *Phys. Rev. A* **44**, R2235 (1991)], or three-dimensional networks (“sponges”), and these structures are characterized by distinct fractal dimensions d_f specifying their swelling in solutions. A Flory-type calculation [J. F. Douglas, *Phys. Rev. E* **54**, 2677 (1996)], based on the Wiener sheet model of random surfaces of variable topological dimension, yields $d_f = 5/3, 2, 15/7$, respectively, for swollen string type, membrane type, and sponge type polymers in three dimensions. Living polymers with a network topology having many loops (“sponges”) are expected to be common, so that a typical value of d_f for many associating systems at equilibrium should be near $d_f = 15/7$ (see Refs. 16–28).
- ⁸⁶A. N. Semenov and M. Rubinstein, *Macromolecules* **31**, 1373 (1998).
- ⁸⁷I. Y. Erukhimovich, *JETP* **81**, 553 (1995).
- ⁸⁸S. Kumar and A. Z. Panagiotopoulos, *Phys. Rev. Lett.* **82**, 5060 (1999).
- ⁸⁹P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953).
- ⁹⁰F. S. Dainton and K. J. Ivin, *Nature (London)* **162**, 705 (1948).
- ⁹¹H. Yamakawa, *Modern Theory of Polymer Solutions* (Harper and Row, New York, 1971).
- ⁹²K. F. Freed, *Renormalization Group Theory of Macromolecules* (Wiley, New York, 1987).
- ⁹³A. E. Larson and D. G. Greer, *Nature (London)* **385**, 230 (1997).
- ⁹⁴J. C. Crocker and D. G. Greer, *Phys. Rev. Lett.* **73**, 352 (1994).
- ⁹⁵K. S. Schmitz, *Langmuir* **13**, 5849 (1997).
- ⁹⁶A. P. Andrews, K. P. Andrews, S. C. Greer, F. Boue, and P. Pfeuty, *Macromolecules* **27**, 3902 (1994). Some differences exist between our calculations of $I(0)$ and the spin model calculations of $I(0)$ by Andrews *et al.* The two mean-field models coincide in very high and low tempera-

- tures, but discrepancies remain at intermediate temperatures. Unfortunately, Ref. 96 provides insufficient details for us to recognize the source of this discrepancy.
- ⁹⁷W. H. Stockmayer, *J. Phys. Chem.* **96**, 4048 (1992).
- ⁹⁸D. Dijkstra, J. P. Hansen, and P. A. Madden, *Phys. Rev. E* **55**, 3044 (1997).
- ⁹⁹A. Mourchid, A. Delville, J. Lambard, E. L  colier, and P. Levitz, *Langmuir* **11**, 1942 (1995).
- ¹⁰⁰K. S. Pitzer, *J. Am. Chem. Soc.* **77**, 3427 (1955).
- ¹⁰¹K. S. Pitzer and J. R. F. Curl, *J. Am. Chem. Soc.* **79**, 2639 (1957).
- ¹⁰²E. A. Guggenheim, *J. Chem. Phys.* **13**, 253 (1945).
- ¹⁰³J. G. Powles, *J. Phys. C* **16**, 503 (1983).
- ¹⁰⁴There are fluctuation corrections to the ratio T_θ/T_c in the absence of association (i.e., when $\Delta h \rightarrow 0$) where the ratio is exactly 4 in lattice mean-field theory. However, Douglas and Ishinabe [*Phys. Rev. E* **51**, 1791 (1995)] show that fluctuations should generally modify this ratio to a value near 16/3 for a nearest-neighbor interaction lattice model of small molecule phase separation in three dimensions. Mean-field and measured values of T_θ/T_c for fluids are summarized in Refs. 102 and 103.
- ¹⁰⁵S. Wiegand, J. M. H. Levelt Sengers, K. Zhang, M. E. Briggs, and R. W. Gammon, *J. Phys. Chem.* **106**, 2777 (1997).
- ¹⁰⁶M. S. Wertheim, *J. Stat. Phys.* **35**, 19 (1984); **35**, 35 (1984); **42**, 459 (1986); **42**, 477 (1986); *J. Chem. Phys.* **85**, 2929 (1986); **87**, 7323 (1987).
- ¹⁰⁷M. Buback and E. U. Franak, *Ber. Bunsenges. Phys. Chem.* **76**, 189 (1972).
- ¹⁰⁸J. M. H. Levelt Sengers, A. H. Harvey, and S. Wiegand, *Equations of State for Fluids and Fluid Mixtures*, edited by J. V. Sengers, R. F. Kaiser, C. K. Peter, and H. J. White (Elsevier, Amsterdam), Chap. XVII (to be published).
- ¹⁰⁹H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* (Oxford University Press, New York, 1971).
- ¹¹⁰J. Dudowicz and K. F. Freed, *Macromolecules* **24**, 5076 (1991).
- ¹¹¹J. C. Wheeler and P. M. Pfeuty, *Phys. Rev. Lett.* **71**, 1653 (1993).
- ¹¹²S. J. Candau, E. Hirsch, and R. Zana, *J. Phys. (France)* **45**, 1263 (1984).
- ¹¹³S. Ikeda, S. Ozeki, and M. Tsunoda, *J. Colloid Interface Sci.* **73**, 27 (1980).
- ¹¹⁴The concept of a phase transition is an ideal "Form" in the sense of Plato [*Phaedo* (Oxford University Press, New York, 1999)]. Forms are never realized in the physical world, but can be approximated to a greater or lesser degree by a physical system.
- ¹¹⁵M. C. Grant and W. B. Russel, *Phys. Rev. E* **47**, 2606 (1993).
- ¹¹⁶H. Verduin and J. K. G. Dhont, *J. Colloid Interface Sci.* **172**, 425 (1995).
- ¹¹⁷J. Bergenholtz and M. Fuchs, *J. Phys.: Condens. Mat.* **11**, 10171 (1999).