Universality in Structure and Elasticity of Polymer-Nanoparticle Gels

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We propose a combination of polymer field theory and off-lattice computer simulations to study polymer-bridged gelation in polymer-nanoparticle mixtures. We use this method to study the structure of gels formed in attractive polymer-colloid systems. Our results indicate that such gels exhibit a universal structure with a fractal dimension $d_f \approx 2.5$ characteristic of random percolation. By mapping to an affine-network model, the enhancement in elastic moduli is predicted to follow a critical exponent $\nu_\eta \simeq 1.8$ characteristic of the resistor network percolation. We analyze selected experimental results to suggest the existence of a universality class corresponding to our results.

There has been a recent surge of interest in understanding gelation and clustering phenomena in colloidal systems [1]. Using model systems, experiments and theoretical studies have shed light on the origins of reentrant glass transitions, gelation, and their relationship to the percolation transitions in colloidal systems [1]. In addition to clarifying the interplay between interaction potentials and dynamics, such studies also possess implications for practical applications using colloidal suspensions.

Many of the above studies pertain to gelation involving the attractive component of the potential and have relied on the experimental model system of noninteracting (except by entropic exclusion or "depletion") colloid-polymer mixtures. The polymer-mediated colloidal interactions then closely resemble a square-well attractive potential, and the structure and properties of the resulting gel depend on the strength and range of this potential [1]. In contrast, many practical colloid-polymer mixtures involve polymers which are preferentially attracted to the colloids [2]. In such cases, the characteristics of the effective interactions have been predicted to be richer due to saturation of the surfaces [3,4], being purely attractive at low polymer concentrations, with a long-range attraction and a short-range repulsion at intermediate concentrations and purely repulsive at higher concentrations.

Attractive polymer-colloid systems constitute a unique model system for which gel-like structures can be formed by two distinct mechanisms. At dilute polymer concentrations, gels can result from attraction-induced aggregation of the colloids, and their characteristics can be expected to resemble those of the "energetic gels" discussed above [1,5]. In contrast, at higher polymer concentrations, polymer bridging can result in long-lived bonds between the particles and lead to gelation even when the effective interactions between the particles are purely repulsive [2,6]. We term the latter an "entropic gel," since the main source of elasticity arises from the polymer bridges. In a typical colloidal suspension, where the size of the particles is much larger than the polymers, entropic polymer-bridged gels (PBGs) are not expected to manifest until very high volume fractions of the colloids. However, for particle size regimes termed as the nanoparticle limit (where the colloid size becomes comparable to or smaller than the polymer), such as in micelles, proteins, and polymer nanocomposites, such gels can prevail at even very low particle concentrations [2,6,7].

There is a considerable motivation to understand the formation, structural, and universality characteristics of PBGs and the distinctions, if any, with their well-studied energetic counterparts. On the one hand, recent experiments have noted significant enhancements in the viscoelastic properties of polymers upon the addition of extremely low loadings of nanoparticles [7,8]. In many instances, it is still unresolved whether such enhancements result from gelation due to direct particle aggregation or due to the polymer-bridging (PBG) mechanisms. Second, recent simulations have considered schematic models of entropic and energetic gels to suggest that they fall in different universality classes [9,10]. Considering the richness of the effective interactions and polymer conformational characteristics, it is not evident if these considerations are equally applicable to the characteristics of PBGs resulting in polymer-nanoparticle systems.

In this Letter, we propose a computer simulation scheme combining polymer mean-field theory with Monte Carlo simulations and graph theory to delineate structural characteristics of PBGs resulting in systems such as polymer solutions, polyelectrolytes, polyampholytes, etc. We apply this method to address the following questions regarding attractive polymer-nanoparticle gels: What is the percolation threshold for such gels and how does it depend on physical parameters such as polymer concentration, adsorption strength, etc.? Is there a universality in the structure and elasticity of such gels? How do the characteristics of PBGs compare with the results of schematic simulation models of entropic gels? The results presented relate the structural and elasticity characteristics of PBGs to the thermodynamic and physical parameters while establishing the applicability of the entropic gel universality class to PBGs. Further, by analyzing published experimental re-

sults, we suggest that the results provide a means to understand (and control) the properties of polymer-nanoparticle mixtures. Our approach consists of three steps:

(a) We use a generalized McMillan-Mayer formalism to integrate out the polymer degrees of freedom from the description of the polymer-particle mixture. This allows a mapping of the two-component system onto a system of just the particles interacting via (polymer-mediated) effective interaction potentials. The latter are expressed in terms of the grand-canonical partition functions for the polymer in the presence of particles and are computed using polymer mean-field theory [11].

(b) We assume PBG to be a result of "equilibrium gelation" resulting from polymer bridges whose conformations correspond to the equilibrium statistics for the solution and interaction conditions (time scales involved in gel formation are ignored). Polymer mean-field theory is used to determine the numbers and size distributions of the polymer bridges between the particles for given parametric conditions [4,12]. If $M_{br}(r)$ denotes the *average* number of bridges at an interparticle distance r, then we assume that the probability to form interparticle bridges follows a Poisson distribution and deduce the probability of forming at least one interparticle bridge as $P_{br}(r) = 1 - \exp[-M_{br}(r)]$. $P_{br}(r)$ serves as the "gelation potential" in our simulations and quantifies whether two particles at a given distance are connected.

(c) We use Monte Carlo simulations of a canonical ensemble of particles interacting with the effective pair interaction potentials [13]. The direct connectivity of the particles is determined based on $P_{br}(r)$. The pairwise connectivity information is then transformed to incorporate indirect connectivities (i.e., through intermediate particles), and thereby the statistics of particle clusters are identified [14]. The percolation volume fraction η_c is determined by searching for a critical number of configurations (set as 50% in our simulations) wherein a particle in a cluster is connected to its replica in the neighboring simulation boxes [15]. The simulations were carried out for different system sizes (reported data are for 864 particles) in a cubic box with periodic boundary conditions. While the small system sizes preclude an accurate analysis of percolation characteristics, analysis of the simulation results suggests that the errors in the data and exponents reported are less than 10% in all instances.

The enhancement in elasticity resulting from polymer bridges is estimated using an analogy to the affine-network model for *unentangled* polymer gels [17]. We first identify the backbone of the percolating clusters, defined as the cluster excluding the dangling ends and loops which do not contribute to elasticity. The latter is obtained as the largest biconnected graph corresponding to a connectivity graph of the cluster [18]. The elastic modulus G is then ascribed to the total bridges in the backbone, i.e., $G \propto \sum_{ij}^{*} M_{br}(r)$, where $\sum_{ij}^{*}$ denotes summation over particles in the backbone.

While the preceding framework can be used for a variety of polymer-polymer and polymer-particle interactions, for illustration, we consider a model of a dispersion of nanoparticles in a polymer solution, where the polymers can adsorb onto the particles. We studied different ratios of particle (R) to polymer sizes (R_g) ranging from $R/R_g = 2.0$ to $R/R_g = 0.5$ (nanoparticle regime). Polymer concentrations were chosen in semidilute regimes [3,19] ($\phi > 1.0$, where $\phi = \rho_p/\rho_p^*$, with ρ_p the polymer concentration and ρ_p^* the overlap concentration) such that the polymer-particle mixtures correspond to the stable one phase region of the phase diagram. Excluded volume interactions between the polymer segments are characterized by a nondimensional parameter B [19], which was chosen as 10 in our simulations corresponding to the case of good solvents. We also considered the case of a polymer melt, where the excluded volume interactions are assumed to be screened and the effective colloidal interaction is just a hard sphere potential. Polymer adsorption on particles is characterized by a nondimensional inverse adsorption length $\lambda = u_0 N/R_g$, where u_0 (in $k_B T$ units) is a short-range potential acting on the polymer segments in direct contact with the surface. Surface capacity for adsorption is incorporated through an entropic term which restricts the maximum surface concentration as ϕ_m [4]. Figure 1 displays the effective interaction potential $U(r)$ and the bridging probabilities $P_{br}(r)$ for the different conditions considered. Note that different parameters which correspond to the
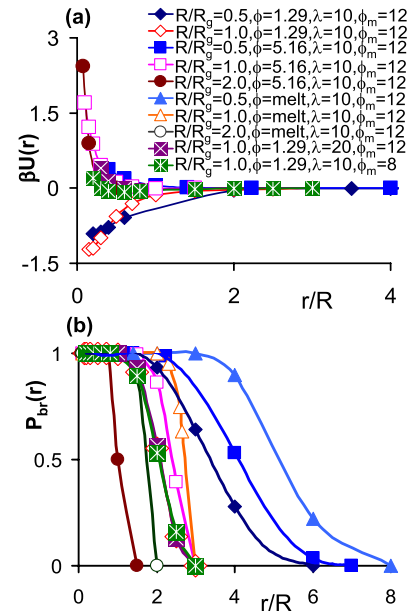

FIG. 1 (color online). (a) Interaction potentials $U(r)$ and (b) probability of bridging $P_{br}(r)$ as a function of the interparticle distance r normalized by the radius of the particle R for the different parametric conditions considered (notations explained in the text).

similar $U(r)$ can result in a vastly different gelation potential $P_{br}(r)$.

The simulation methodology allows us to characterize the dependence of percolation threshold η_c on different physical parameters [Fig. 2(a)]. It is first observed that, in the nanoparticle regime ($R \simeq R_g$), PBGs can form at even extremely dilute particle concentrations, confirming the speculations on the occurrence of PBGs. However, it is also seen that the percolation thresholds are extremely sensitive to the ratio R/R_g where even a small increase beyond $R/R_g = 1$ leads to a shift in percolation thresholds to much higher particle volume fractions. This can be understood by noting that the bridging probabilities which drive gelation have a range of approximately R_g. Indeed, it is seen from Fig. 1 that, with an increase in the size of the particles, $P_{br}(r)$ decays to zero at much smaller interparticle distances (relative to the particle size) which results in significantly higher percolation thresholds.

Formation of PBGs involves a subtle interplay between interaction potentials and polymer-bridging probabilities. For instance, by comparing the η_c values for a fixed size $R/R_g = 1$, it is seen that increasing the surface capacity ϕ_m (from 8 to 12) leads to an attractive interaction which clusters the particles and results in a lower percolation threshold. In contrast, an increase in polymer concentration ϕ (from 1.29 to 5.16) leads to a repulsive potential but no corresponding change in the η_c value. This can be understood by noting that an increase in ϕ leads to an increase in the range of the $P_{br}(r)$ [cf. Fig. 2(b)] which compensates for the decreased tendency to cluster. Such trends contrast with energetic gels where the thresholds are expected to be correlated directly with the strength and the range of interaction [1].

A main objective of this study was to analyze the structural characteristics of PBGs and identify their universality features. In Fig. 2(b), we present the results for the fractal dimension d_f of clusters defined through $R_{gc} \propto n^{1/d_f}$, where R_{gc} is the radius of gyration of the cluster of size n. We observe that, for all the parameters considered, close to the percolation transition, the fractal dimensions show a nearly universal value of $d_f \approx 2.2$–2.45. A similar universality is also observed in the cluster size distribution exponent α in the scaling of the number of clusters of size n, $m(n)$, as $m(n) \propto n^{-\alpha}$. At the onset of percolation, the value of α is approximately 2.0–2.2 [cf. Fig. 2(c)]. Figure 2(d) displays the variation in the elastic modulus in a similar representation. We observe again that the results for the elastic moduli could be fitted into a single universal scaling law of the form $\beta G' \simeq G_0(\eta - \eta_c)^{\nu_\eta}$, where $\nu_\eta = 1.8$. Remarkably, the exponents appear to be independent of the nature of $U(r)$ and $P_{br}(r)$, displaying the same magnitudes for attractive and repulsive interactions, independent of the range of $P_{br}(r)$ and the magnitude of $M_{br}(r)$, suggesting a universal trend in PBGs of spherical particles.

The above exponents, $d_f = 2.5$ and $\alpha = 2.2$, match with the exponents noted for random percolation models and for polymers resulting through step growth reactions [20]. The elasticity exponent $\nu_\eta = 1.8$ is identical to that predicted for the random resistor network models and matches with the recent results of schematic models of entropic gels [9,21]. While models of entropic gels and PBGs share many features, it is still remarkable that our approach, which retains the thermodynamical features of the polymer-nanoparticle system and incorporates information on the interparticle bridging, results in the same universality exponents. In contrast, the elastic exponents resulting from purely energetic interactions are predicted to be 2.1 for central force networks and 3.75 for bond-bending interactions [9,22].

The above confirmation of universality in PBGs can be used to identify the origins of gelation in experiments of polymer-nanoparticle mixtures. For this, we consider the plateau moduli reported in a number of experiments involving colloidal suspensions in polymer matrices [23]. It is observed from Fig. 3 that the experimental results in stable polymer-particle mixtures, where PBGs had been suggested, indeed follow a scaling with an exponent $\nu_\eta \approx 1.88$. In contrast, situations where stronger energetic interactions manifest are seen to follow much higher exponents characteristic of energetic gels. Despite the statistical errors in this exercise, the excellent agreement between the results of this work and experimental data suggests that universality scaling of elastic moduli can provide a quantitative approach to delineate the mechanisms of gelation in polymer-nanoparticle systems.

In summary, we propose a new simulation framework which retains the thermodynamical features of polymer-particle mixtures while enabling the prediction of the
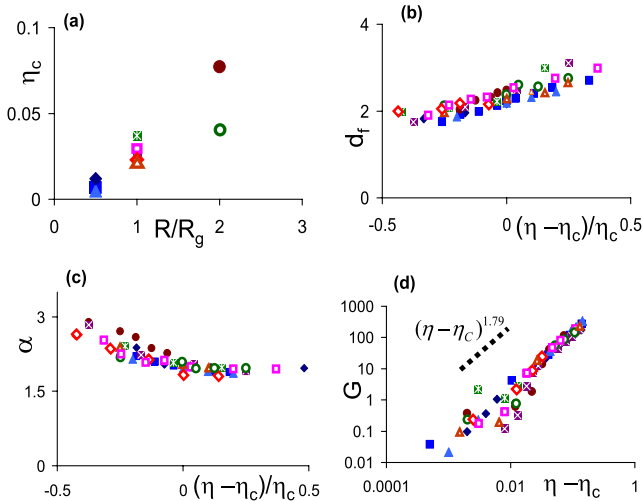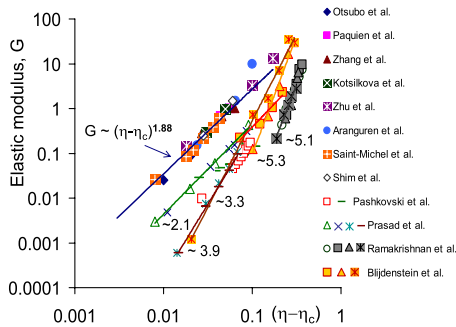

FIG. 2 (color online). Cluster statistics for different parametric conditions. The legend for the symbols is same as that in Fig. 1(a): (a) Percolation thresholds η_c; (b) fractal dimension d_f; (c) cluster scaling exponent α; (d) elastic modulus G.

FIG. 3 (color online). Scaling of published experimental data (sources listed in Ref. [24]) for elastic modulus G. For each data set, the G values are scaled by a single parameter to render them on the same plot. The experimental results for systems where formation of PBGs is speculated follow an exponent $\nu_\eta \approx 1.88$. For systems which deviate from situations considered here, depletion interactions (Prasad *et al.*, Ramakrishnanan *et al.*, Blijdenstein *et al.*, Pashkovski *et al.*) are observed to show significantly higher ν_η values.

structural, elasticity features of polymer-bridged gels resulting in such systems. For illustration, we adapted this method to study gelation in attractive polymer-nanoparticle mixtures. Our results indicate that, while the percolation thresholds are determined by a subtle interplay between interaction potentials and bridging probabilities, the overall structural features of the gel resemble those of the random percolation models with the entropic elasticity exponent identical to resistor network percolation. An analysis of experimental results suggests the existence of a universality class corresponding to our predictions. More generally, the present simulation approach can be adapted to systems such as polyelectrolytes, polyampholytes, etc., to study the formation and characteristics of polymer-bridged gels in such systems. Therein, interplay between the effective interactions and bridging probabilities can be expected to lead to nontrivial features.

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