Polymerization transitions in two-dimensional systems of dipolar spheres

Justin Stambaugh,[1] Kevin Van Workum,[2] Jack F. Douglas,[2,*] and Wolfgang Losert[1,†]
[1]*Department of Physics, IPST, and IREAP, University of Maryland, College Park, Maryland 20742, USA*
[2]*Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899, USA*
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We investigate the self-organization of dipolar spheres into polymer chains as a fundamental model of the self-assembly of particles having anisotropic interparticle interactions. Our study involves a combination of modeling with vertically vibrated magnetic beads simulating a quasi-two-dimensional fluid at equilibrium and corresponding Monte Carlo simulations of hard spheres with embedded extended dipoles. We find a transition from a gas-like phase to a polymerized phase upon cooling, in accord with the analytic theory of equilibrium polymerization.

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The self-assembly of anisotropically interacting particles is currently a topic of considerable interest in science and technology. The increasing demand to manufacture structures at the nanoscale has made this strategy for fabrication attractive, if not necessary. Moreover, numerous biological structures (e.g., actin filaments responsible for cell movement, viral capsids) involve the reversible self-assembly of proteins with anisotropic interactions. It is evidently important to have well-defined models of self-organization to study the essential characteristics of these systems.

Van Workum and Douglas [1] have advocated dipolar fluids as a prototypical model of self-organization and they have extensively investigated the polymerization transition (PT) which occurs in this model by Monte Carlo (MC) simulations in three dimensions. Stambaugh and Losert [2,3] have investigated the self-assembly of spherical particles containing small bar magnets of various length. They found the prevalence for dynamic polymer chain formation for highly extended magnets, while particles with short magnets tend to form compact clusters. There have been several recent computational studies of quasi-two-dimensional dipolar fluids (spheres confined to 2D, with dipolar orientation in 3D) [4,5] that demonstrate the occurrence of chain polymerization, as in the 3D dipolar fluid simulations [1,5].

In the present paper, we are concerned with generating a *real physical system* that exhibits reversible equilibrium polymerization that can be studied as a model system exhibiting self-assembly. We are also interested in testing theoretical predictions for the polymerization transition (PT) line describing this type of thermodynamic transition. For validation, we perform MC simulations in two dimensions that faithfully model the dimensional characteristics of the particles, the anisotropy of magnets involved, as well as the confinement effects of the cavities containing the dipolar particles so that a direct comparison between the simulations and experiments is possible.

Both the experiments and simulations are limited to small system sizes due to experimental limitations and our intrinsic interest in self-assembly acting under finite size constraints, characteristic of many biological self-assembly processes [6].

First, we establish that the simulations faithfully reproduce the morphology observed in PTs and then we determine the order parameter curve (extent of polymerization) to quantify the progress of the transition as a function of T. The average length of the polymers is determined for both the experimental and simulated fluids since this is a fundamental observable. After establishing a good correspondence between these observables in the simulated and experimental systems, we then determine the PT line (transition concentration as a function of temperature) for both fluids and find remarkably good agreement.

The magnetic particles used were cylindrical permanent magnets securely encased in spherical hard plastic shells (Safari Ltd.). The magnetic cores had length $l=1.42$ cm and diameter $d=0.94$ cm. The particles were 5.3 g in mass, the maximum strength of the magnetic field on the surface of a particle was 0.54 kG$\pm$16% (one standard deviation), and the particle diameter D was 1.69 cm. N particles were placed in a horizontal, cylindrical container of diameter 17.5 times the particle diameter (the size is limited to avoid exciting bending modes in the plate through shaking) and height 1.7 particle diameters, to give a system concentration C (measured as particle area fraction in our 2D system). The system was then sinusoidally vibrated vertically at 30 Hz. The system was imaged from above at a rate of 0.5 Hz with a CCD color camera.

The peak velocity of the vertically vibrated surface was varied from 1.6 to 3.6 m/s and was measured using an accelerometer. Earlier work has shown that a direct analogy can be made between the excitation of macroscopic particulate matter by vertical shaking and thermal excitations of microscopic matter [7]. For the range of driving amplitudes studied, this analogy can be quantified by the expression $T \propto v_p^2$ where T is the effective temperature and v_p is the peak velocity of the vertically vibrated surface. For the present, we define our experimental temperature as $T=v_p^2$. Below, we will linearly rescale our temperature through a matching to the MC simulation estimate of the polymer transition line as a function of C, thus fixing the constant.

The magnetic particles are modeled as hard spheres of

*Electronic address: jack.douglas@nist.gov
†Electronic address: wlosert@glue.umd.edu

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diameter σ containing two oppositely charged monopoles separated by a distance $dr=0.69\sigma$ and symmetrically situated about the center of the sphere, following earlier modeling of the particles in our measurements [2].

In order to mimic the quasi-two-dimensional nature of the experimental setup, the centers of the spheres are restricted to lie in a plane while the embedded dipole vectors are allowed to rotate in 3D. All the spheres also interact with a circular boundary having the same ratio of radius to that of the particle, as in our measurements.

Canonical ensemble MC simulations are used to generate equilibrium configurations and thermodynamic averages. In addition to the traditional translational and rotational MC moves, two advanced MC methods are implemented. The aggregate volume bias MC method [8] is used to enhance the dynamic formation and destruction of clusters. This method provides efficient phase space sampling in systems that form strong interparticle associations such as those present in this study. The parallel tempering MC method [9,10] is also used in these simulations to provide improved statistical sampling.

Based on previous analytical modeling [11] and MC simulations [1] of equilibrium polymerization of the Stockmayer fluid (dipolar spheres with additional isotropic Lennard–Jones van der Waals interactions), we anticipate a PT to occur at a fixed concentration as we decrease the temperature. At temperatures above the PT, the particles are largely dissociated from each other and exhibit gas phase characteristics, while at temperatures below the PT, the thermal (kinetic) energy of the particles is insufficient to overcome the attractive interactions and the particles form strongly bound clusters. The anisotropic nature of the dipolar interactions induce head-to-tail alignment resulting in the formation of linear, ring, or branched structures. Between these two limits lies a broad transition region in which these polymer-like structures continuously form and disappear in dynamic equilibrium. Three movies above, at and below the transition can be found as supplemental material to this paper. For the present, we loosely define the PT temperature, T_Φ, as the temperature at which the particles first begin to form clusters. A more precise definition of T_Φ based on the average cluster size follows.

As examples of the observed structures, Fig. 1 shows the experiment (a)–(c) for $C=0.026$ at $T/T_\Phi>1$, $T/T_\Phi\approx 1$, and $T/T_\Phi<1$, respectively. Figures 1(d)–1(f) are similar renderings of the simulations for $C=0.026$ at $T/T_\Phi>1$, $T/T_\Phi\approx 1$, and $T/T_\Phi<1$, respectively. For $T/T_\Phi<1$, a linear chain of head-to-tail aligned particles is observed and for $T/T_\Phi>1$ the particles are completely dissociated. Near the transition, $T/T_\Phi\approx 1$, a fraction of particles is associated while the remaining ones are dissociated. This is our first hint that the observed broad transition involves the dynamic formation and destruction of polymeric chains at equilibrium with larger chains forming as T decreases.

We further characterize the transition by monitoring the average fraction of particles that are members of a cluster, *i.e.* the extent of polymerization, Φ. The extent of polymerization is defined by $\Phi=N_p/N$, where N_p is number of polymerized (reacted) particles and N is the total number of particles in the system. Φ thus defines an order parameter for the PT where $\Phi=0$ corresponds to an entirely dissociated system, and $\Phi=1$ corresponds to a state where all the particles are in contact with at least one other particle.

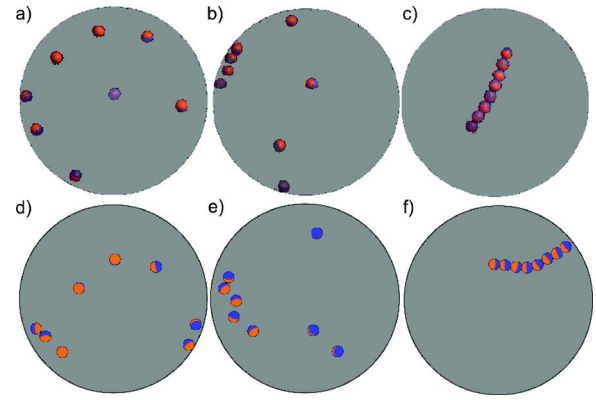

FIG. 1. (Color online) (a),(b),(c) Images of an experimental system where $C=0.026$ at three different temperatures: $T/T_\Phi>1$ (a), $T/T_\Phi\approx 1$ (b), and $T/T_\Phi<1$ (c). Particles were constructed to have differently colored northern and southern hemispheres so that dipole orientations could be discerned. (d),(e),(f) Simulated particle realizations with $C=0.026$ and: $T/T_\Phi>1$ (d), $T/T_\Phi\approx 1$ (e), and $T/T_\Phi<1$ (f).

Figure 2(a) is a plot of Φ versus T/T_Φ for experimental systems where $C=0.020$, 0.026, 0.039, 0.052, 0.078, and 0.104. A transition from $\Phi\approx 1$ to $\Phi\approx 0$ is seen with increasing T/T_Φ for $C<0.052$, while the transitions for $C\geqslant 0.052$ are partially captured for the T range studied. Figure 2(b) is a plot of Φ vs T for simulated systems where $C=0.020$, 0.026,

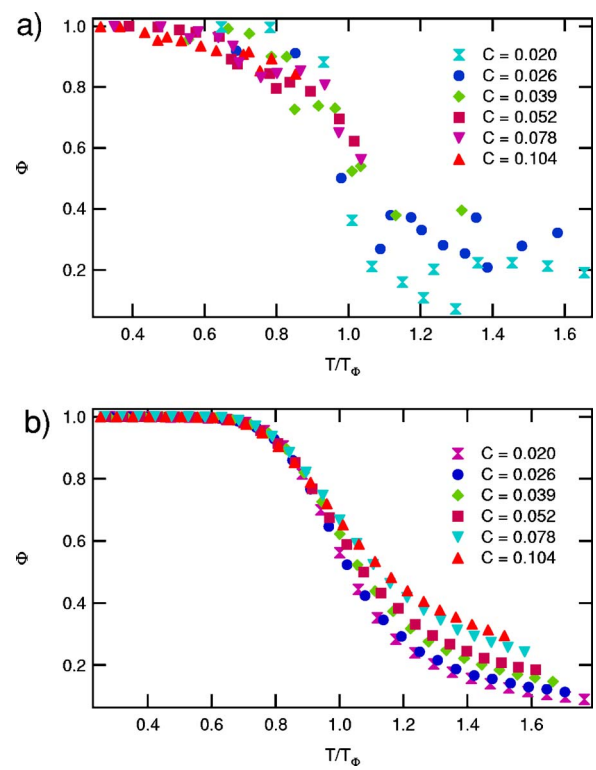

FIG. 2. (Color online) (a) A plot of Φ vs T/T_Φ for experimental systems where $C=0.020$, 0.026, 0.039, 0.052, 0.078, and 0.104; (b) a similar plot of Φ vs T/T_Φ for similar simulated systems.

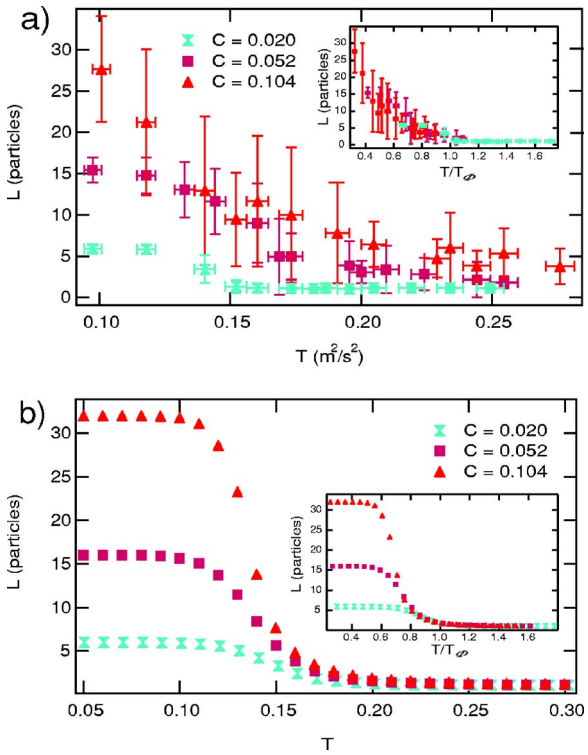

FIG. 3. (Color online) (a) A plot of L as a function of T for experimental systems where $C=0.020$, 0.052, and 0.104. Inset is a plot of L vs T/T_Φ; (b) plot of L as a function of T for similar simulated systems. Inset is a plot of L vs T/T_Φ.

0.039, 0.052, 0.078, and 0.104. A transition from $\Phi \approx 1$ to $\Phi \approx 0$ is seen with increasing T/T_Φ for all C, and for both simulations and experiments, the data roughly follow a similar pattern for all C.

The average cluster size L as a function of T is another property of polymerizing systems that characterizes the progress of the transition. Two particles are considered to be part of the same cluster when their interparticle distance is less than $r_a=1.125\sigma$. Based on previous work [12], the observed average cluster size is expected to be relatively independent to small changes in r_a. The average cluster size is then defined by

$$L = \sum_{i=1}^{N} iN_i \Big/ \sum_{i=1}^{N} N_i, \tag{1}$$

where i is the number of particles in a given cluster and N_i is the number of chains of length i. In Fig. 3, we show L as a function of T for the experiments (a) and the simulations (b) for a range of C. We find a family of curves describing the general increase of L upon cooling. At higher C, the increase in $L(T)$ occurs faster as T is lowered, reflecting the concentration dependence of the PT. The curves in Fig. 3 notably have a similar shape, and it is natural to seek a reduced variable description.

Previous simulations of the PT in the Stockmayer fluid have demonstrated that a universal reduced variable description of the T dependence of L can be obtained by expressing T relative to its value at the PT, T_Φ, defined by an inflection point in Φ. We also found that L at this temperature is nearly universal, taking a value 2.1 regardless of C. This constancy of L is predicted also by the analytic theory of equilibrium polymerization [11]. We checked this relation for the simulated analog of our experimental system and found that L at T_Φ again lies in a narrow range for the concentrations we consider. This universality in the magnitude of L at T_Φ suggest that we should similarly be able to reduce the scatter in the measurements in Fig. 3 by simply normalizing T by the temperature where $L=2$, to obtain an approximate equation of state description of the T dependence of L. This procedure is motivated by the comparatively noisy nature of our Φ data.

We see from the inset in Fig. 3(a) that this procedure indeed reduces the scatter considerably and the reduction is quite good for the approach to the PT temperature $T \to T_\Phi$ where $L=2$. Note that the simulation data in the inset of Fig. 3(b) exhibits a tendency to saturate to a finite value, which is simply the number of particles in the system. This feature is a finite size effect and the growth of L at low T is apparently unbounded in the thermodynamic limit, as found before for the 3D Stockmayer fluid [1]. The chains in the experiment also visually exhibit a saturation of chain length to a size corresponding to the number of particles in the system at low T, but the particle tracking algorithm cannot follow these large clusters reliably, giving rise to the residual scatter in the inset of Fig. 3(a) and the absence of a discernible plateau. Nevertheless, the inset of Fig. 3(a) clearly indicates the sharp rise in L at lower T and the significance of $L(T_\Phi)=2$ in defining a reduced variable description of these observations. We also note that our determination of $\Phi(T)$ below is consistent with $L(T_\Phi)\approx 2$ within experimental uncertainty in our experimental system and we could equally as well have reduced our L data by T_Φ values determined directly from the inflection point of Φ.

In order to directly compare T_Φ in our experiments and simulations, we rescale our experimental T using the expression $\tilde{T}=AT+B$ where A and B are constants to be determined. This method of rescaling is consistent with the thermal relation for vertically vibrated systems described in earlier work [7]. A and B are determined from a linear best fit to a plot of the T_Φ values from the experiment (at $C=0.020$, 0.026, 0.039, 0.052, 0.078, and 0.104) vs the T_Φ values from the simulation at similar C. For our experiments we find: $A=13.8$ and $B=0.151$. Figure 4 shows the PT temperatures, T_Φ and $\tilde{T}_\Phi$ ($\tilde{T}_\Phi$ are the rescaled experimental T_Φ values), as a function C for the experiment (filled circles) and the simulation (open circles). It has been shown that for living polymerization, the transition temperature is related to the concentration of monomers through the Dainton-Ivin (DI) equation [13]:

$$T_\Phi = \frac{\Delta h_p}{\Delta s_p + k \ln C}, \tag{2}$$

where Δh_p is the change in enthalpy upon polymerization, Δs_p is the change in entropy upon polymerization, and k is Boltzmann's constant. Dudowicz *et al.* [1] have shown that the DI equation also approximately describes T_Φ for freely

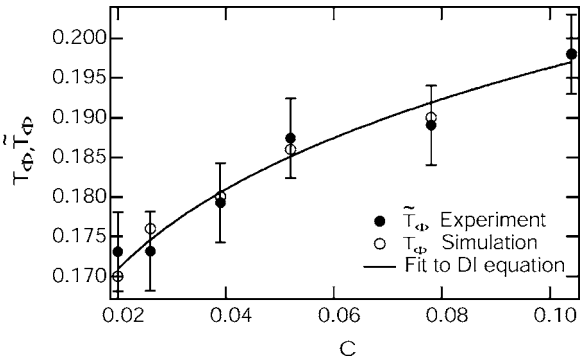

FIG. 4. T_Φ for the simulation (open circles) and the experiment (filled circles). Solid line is a fit of T_Φ to the Dainton-Ivin equation.

associating monomers, as in our measurements and simulations. In Fig. 4, we also show a fit of the DI equation to the simulation data, where $\Delta h_p = -2.13 \pm 0.19$, and $\Delta s_p/k = -8.5 \pm 1.0$. A similar fit to the experimental data gives $\Delta h_p = -2.20 \pm 0.34$, and $\Delta s_p/k = -8.9 \pm 1.8$. Note that T_Φ and $\tilde{T}_\Phi$ increase with increasing C, in a similar fashion for both the experiment and the simulation. Also, it has been shown in the PT observed in the Stockmayer fluid [13] that Δh_p is equal to the minimum of the interaction potential between two monomers, $U_{\min}$, in ideal equilibrium polymerization. In the case of our simulations, $U_{\min} = -1.8$, which is within 15% of the fitted Δh_p. Previous work on Stockmayer fluids in 3D [1] have also exhibited close agreement between $U_{\min}$ and Δh_p estimated from the the DI equation.

We have determined that a mechanically "thermalized" system of shaken hard spheres with embedded magnets exhibits self-assembly into linear polymer chains and have reproduced essential features of this system by MC simulations that faithfully model the experimental system. Our determination of the PT line from the inflection point of the order parameter Φ as a function of temperature coincides within numerical uncertainty in both the experimental and simulated systems and the results obtained are in accord with the analytic theory of equilibrium polymerization developed by Dudowicz *et al.* [1]. This is the first experimental system of dipolar particle fluids that has allowed the investigation of the reversible polymerization that occurs in these fluids and we expect this type of model to offer fundamental insights into both the dynamics and thermodynamics of self-assembly in biological systems where anisotropic interparticle interactions and geometrical confinement effects are prevalent.

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