Cluster diffusion at the gelation point

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We use molecular dynamics simulations to study a model of the gelation transition with a dynamic bond forming procedure. After establishing evidence for three-dimensional (3D) percolation as the static universality class, we turn our attention to the dynamics of clusters at the gelation point, focusing in particular on the behavior of the diffusion constant $D(s)$ as a function of cluster size s. We find a very clear power law behavior $D(s) \sim s^{-k}$ with a nontrivial exponent $k \approx 0.69$.

I. INTRODUCTION

Gelation is a phenomenon that continues to receive wide interest in the physics community [1–3]. It is a problem with relevance both from a fundamental physics point of view, but also from a more application oriented view due to the many uses of gels in industry. Despite a long-standing effort the underlying physics has still not received a complete explanation, in particular as far as the dynamical quantities are concerned.

In a solution of polyfunctional monomers irreversible chemical bonds may be formed via some external influence, e.g., irradiation with γ rays [4,5]. As the density p of bonds increases, the resulting macromolecules grow larger and larger, until at a critical density p_c (the gelation point) there is a cluster spanning the entire system, and a gel has formed. There are a number of static/thermodynamic quantities characterizing this transition, e.g., cluster size distribution, largest cluster, correlation length, and radius of gyration, that in many cases are believed to be well described by the three-dimensional (3D) percolation universality class [6]. Besides the appearance of a wide distribution of cluster sizes, the presence of the gel fundamentally changes many of the dynamic properties as well. For example, it has been found that the viscosity η diverges as $(p_c - p)^{-s}$ when $p \rightarrow p_c$, but there is still no general agreement on the value of the exponent s. However, there are many other quantities that probe the unique dynamics at the gelation point, and here we consider, among other things, the diffusion of clusters of different sizes. Diffusion in general is well known to be sensitive to geometry and topology as well as to the interactions with the environment, and in the case of gelation we expect the motion of the individual macromolecules to be strongly affected by their interaction with other macromolecules with a wide distribution of sizes.

Here we consider a model for polycondensation; using molecular dynamics we simulate a solution of hexafunctional monomers interacting via the Lennard-Jones potential and allow the particles to form permanent chemical bonds if they get close enough. After defining the model in Sec. II, we determine the static universality class by considering the behavior of several characteristic structural quantities aided by finite size scaling in Sec. III. Here we also measure the ra-

dius of gyration of the clusters as a function of cluster size at the gelation point allowing us to determine the fractal dimension. In Sec. IV we focus on the behavior of the self-diffusion constant of clusters at the gelation point, a quantity that has hitherto received little attention (see, however, Ref. [7]). Finally in Sec. V we give our conclusions.

II. MODEL

Our system is composed of $N = L^3$ ($L = 10$, 15, and 20) particles interacting pairwise through the shifted Lennard-Jones potential

$$U(\mathbf{r}) = \begin{cases} U_{LJ}(r) - U_{LJ}(2.5\sigma), & r \leq 2.5\sigma \\ 0, & \text{otherwise,} \end{cases} \quad (1)$$

where $U_{LJ}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$. All of our simulations are 3D constant energy simulations corresponding to an average temperature of $k_B T/\epsilon \approx 1$ and density $\Phi = 0.8\sigma^{-3}$. These choices ensure that the system is in the liquid-phase region of the phase diagram [8]. We use periodic boundary conditions and a time step of magnitude $dt = 0.004\sqrt{m\sigma^2/\epsilon}$. From a typical equilibrium state of this liquid we let the particles form permanent chemical bonds if they come closer than $r_c = 2^{1/6}\sigma \approx 1.12$ [coinciding with the minimum of $U(r)$], and the corresponding bond interaction is represented by a harmonic oscillator potential $U_{\text{harm}}(r) = 1/2 k r^2$; in our simulations we take $k\sigma^2/\epsilon = 120$. Note that this way of adding bonds breaks energy conservation; indeed we actually pump energy into the system when adding bonds. With this bonding procedure cross linking is very fast—the average distance between the particles is comparable to r_c, so a large number of particles will be available for bonding at a given instant. Each particle can bond to a total of $f = 6$ other particles, and the cross link density p is then given in terms of the number of bonds n as $p = 2n/fN$. Any number of particles, if fulfilling the conditions above, can be cross linked per time step, but we halt the bond formation when p reaches a predetermined value.

III. STATIC UNIVERSALITY CLASS

We begin by examining the geometric structure resulting from the cross linking procedure described above. First we need to know the location of the geometric percolation point p_c, and to this end we measure the fraction $W(L,p)$ of per-
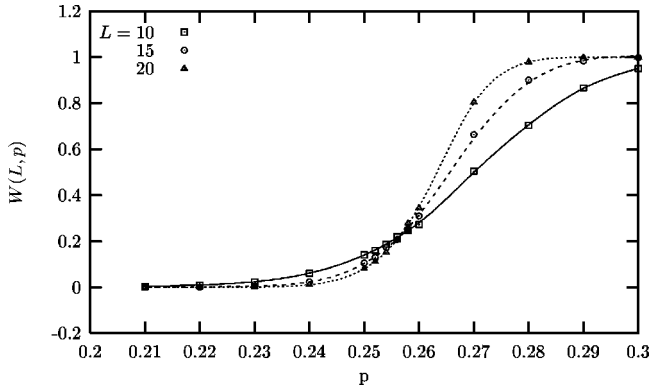
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FIG. 1. Fraction of systems, $W(L,p)$, percolating in the x direction as a function of p and for three different system sizes as indicated on the plot. The lines are guides for the eye. We estimate $p_c = 0.2565$.

FIG. 3. Here we plot the cluster size distribution $n(s)$ as a function of s for the same three system sizes at $p = p_c$ and based on 5000 samples. The straight line is a fit to a power law to the data from the $L=20$ system.

colating (in one direction) systems of size $N=L^3$ at a given cross link density p. In this context a system is considered percolating when a cluster connects a particle in the central computational box with its image in an adjacent box, and the corresponding cluster is called a spanning cluster. In the limit $N \to \infty$, $W(L,p)$ becomes the Heaviside step function $\theta(p - p_c)$. However, at finite N for any $p > 0$ below p_c, some realizations will contain a spanning cluster, and thus $W(L,p) > 0$. Similar reasoning allows us to conclude that $W(L,p) < 1$ for $p > p_c$. If we make the assumption that $W(L,p)$ converges monotonically to $\theta(p-p_c)$ for fixed p, it follows that for $L_1 > L_2$, $W(L_1,p) < W(L_2,p)$ if $p < p_c$, and likewise $W(L_1,p) > W(L_2,p)$ for any $p > p_c$. Therefore *at and only at* p_c the curves of $W(L,p)$ coincide, i.e., $W(L,p_c) = $ const. In Fig. 1 we plot $W(L,p)$ obtained from 5000 realizations as a function of p for $L=10$, 15, and 20, and we see that all the curves cross approximately at the same point: the value of p_c determined this way is $p_c = 0.2565$.

Finite size scaling theory predicts that $W(L,p)$ does not depend on L and p separately but only on the combination L/ξ (and the sign of $p-p_c$) where $\xi = |p-p_c|^{-\nu}$ is the correlation length and ν the correlation length exponent [9]. Thus we may write

$$W(L,p) = f(L^{1/\nu}(p-p_c)), \tag{2}$$

where $f(x)$ is a scaling function with the following limiting values:

$$\lim_{x \to \infty} f(x) = 1 \quad \text{and} \quad \lim_{x \to -\infty} f(x) = 0. \tag{3}$$

To test this hypothesis we replot the data for $W(L,p)$ from Fig. 1 in Fig. 2 as a function of $L^{1/\nu}(p-p_c)$ with $p_c = 0.2565$ as determined above and $\nu = 0.9$. The curves collapse quite convincingly onto the same master curve with the limiting values given in Eq. (3), and the results are thus consistent with finite scaling theory. Moreover, the value of ν is in very good agreement with the correlation length exponent 0.88 of 3D percolation theory [6,9]. Thus we believe that in spite of using an off-lattice dynamic bonding method from an equilibrium liquid state, this system belongs to the universality class of 3D percolation. To further substantiate that claim, we have also considered the cluster size distribution at the critical point $p = p_c$ in Fig. 3. According to standard percolation theory the number $n(s)$ of clusters of size s is a power law $n(s) \sim s^{-\tau}$ with an exponent $\tau \approx 2.18$ [10]. Fitting the data from the largest system size to a power law
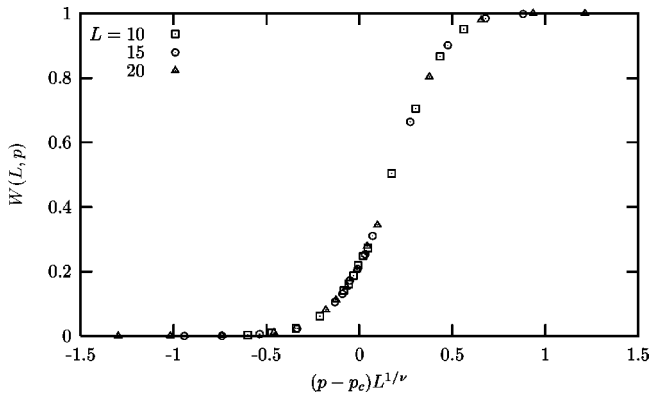

FIG. 2. Same as Fig. 1, except here $W(L,p)$ is plotted as a function of $L^{1/\nu}(p-p_c)$ with $p_c = 0.2565$ and $\nu = 0.9$. The data collapse very nicely in agreement with finite size scaling theory.
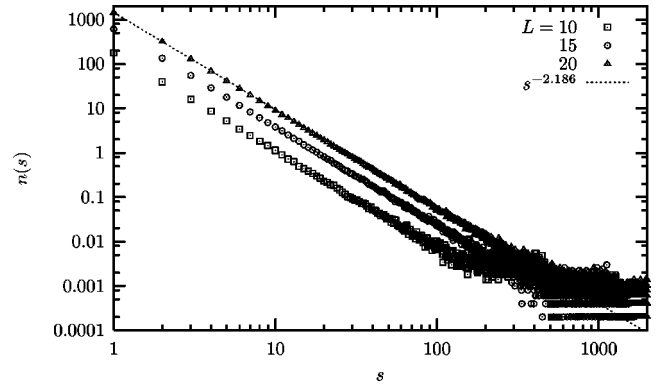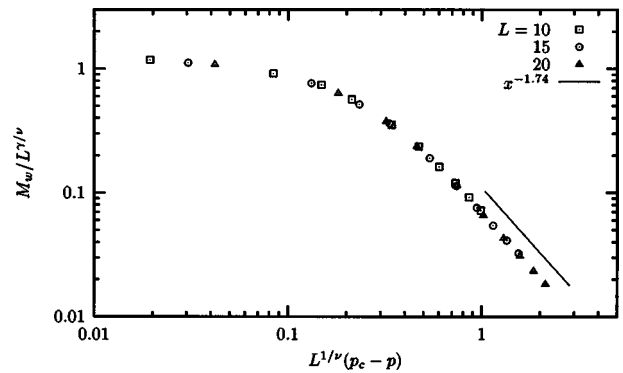

FIG. 4. Scaling plot of the weight average molecular weight M_w. The quality of the data collapse confirms $\gamma = 1.74$ in accordance with the 3D percolation value.
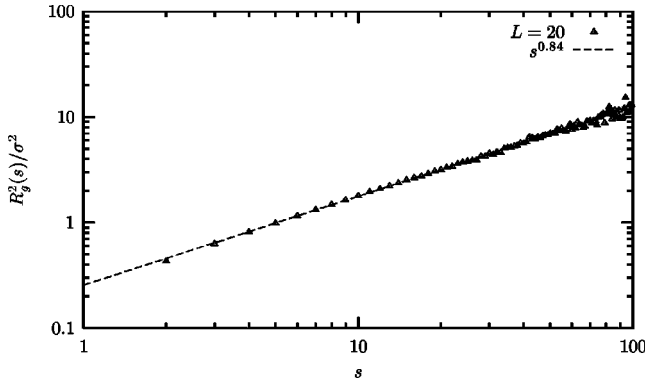
FIG. 5. Radius of gyrations R_g (squared) as a function of cluster size s for $L=20$ and $p=p_c$.

we find the exponent $\tau\approx2.19$, which is within 0.5% of the 3D percolation value quoted above.

For the universality class of 3D percolation there are in principle only two independent exponents, but to establish even more confidence in our conclusions and because we need part of the data later, we determine two more exponents.
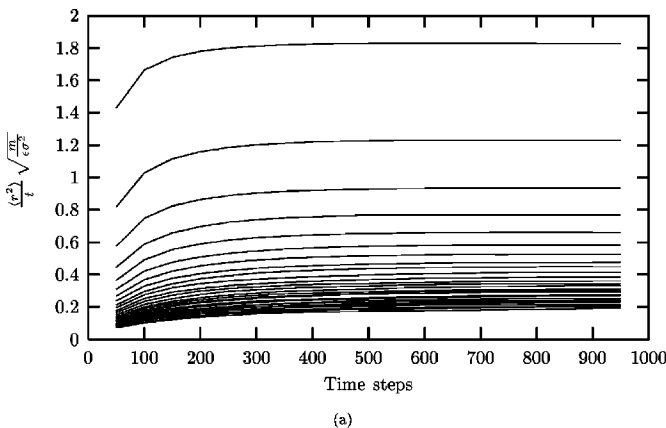
The weight average molecular mass M_w for $p<p_c$ defines the exponent γ by the relation $M_w\sim(p_c-p)^{-\gamma}$. Again, for finite systems, finite size scaling theory predicts the scaling form

$$M_w=L^{\gamma/\nu}g(L^{1/\nu}(p_c-p)),\tag{4}$$

where $g(x)$ is a scaling function with the following asymptotic behavior:

$$g(x)\sim\begin{cases}x^{-\gamma}, & x\to\infty\\ \text{const}, & x\to0.\end{cases}\tag{5}$$

Therefore we compute M_w as a function of p for different system sizes, and in Fig. 4 we plot the results in the form of $M_w/L^{\gamma/\nu}$ versus $L^{1/\nu}(p_c-p)$ with $\gamma=1.74$ being the expected 3D percolation value [9,11] and ν and p_c as deter-

mined previously. Again there is a very nice data collapse reinforcing our statement about the validity of 3D percolation exponents.

The last static exponent we wish to consider is the fractal dimension D of the clusters at the gelation point. During the simulations we maintain a list of all particles belonging to a given cluster, and this enables us to calculate the radius of gyration of a given cluster. At a given instant $R_g(s)$ ($s\geq2$) is found from Ref. [12],

$$R_g^2(s)=\frac{1}{s(s-1)}\sum_{i,j=1}^{s}(\mathbf{r}_i-\mathbf{r}_j)^2,\tag{6}$$

where the sum is over all particles in the cluster and $\mathbf{r}_i$ is the position of particle i at that instant. To calculate its thermal average we average over time. However, we have also averaged over 100 samples to get better statistics for the individual cluster sizes. We find that the results are independent of the system size (up to a cutoff) and do not significantly depend on the value of p close to p_c, and therefore we plot here only the results from the largest system, i.e., $N=20^3$. We focus on the properties of the system at the percolation point $p=p_c$ and the corresponding data are plotted in Fig. 5.

There is a clear power law behavior $R_g^2(s)\sim s^{2/D}$, and from a least squares fit we deduce the value $D=2.38$. Here D is the fractal dimension of the clusters (since $s\sim R_g^D$) at the gelation point, and for this exponent 3D percolation theory predicts the value $D\approx2.5$. Our value is about 5% lower, but this small discrepancy may be due to lack of data for sufficiently large s. However, it may also be due to the interaction of the polymers with one another and with the leftover monomers.

Therefore regarding the static exponents we presented evidence that our model of the gelation transition, which uses a Lennard-Jones force-shifted intermolecular potential and a liquid state bond forming procedure, is consistent with the universality class of 3D percolation.
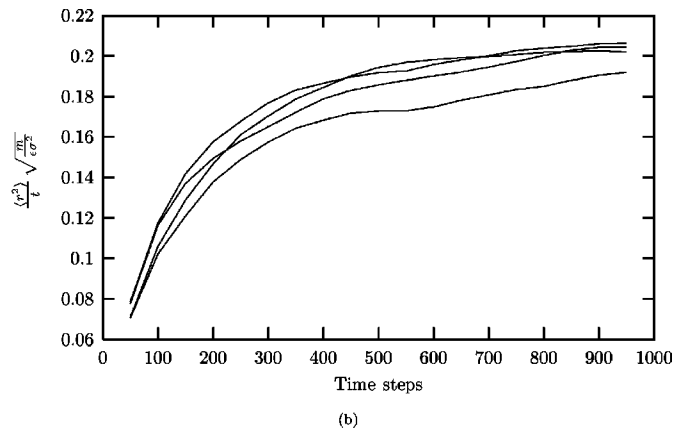

(a)

(b)

FIG. 6. Mean square displacements divided by time for the individual clusters of the $N=20^3$ system at $p=p_c$. (a) Clusters of size $1,\ldots,29$ from top to bottom. The asymptotic convergence to horizontal lines indicates normal diffusion, cf. Eq. (7). (b) Close up of (a) for the four largest clusters. They have all reached an almost constant value, except perhaps the largest cluster, that therefore represents the "worst case."
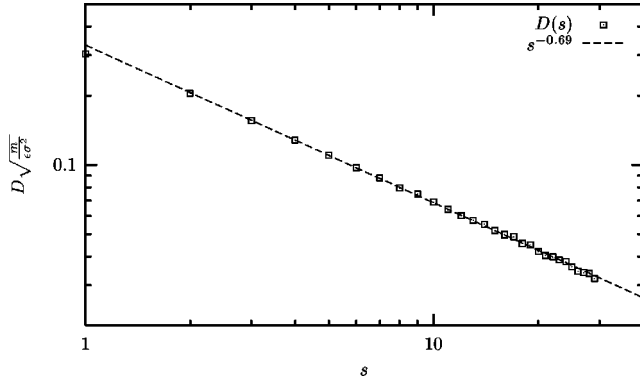
FIG. 7. Diffusion constant $D(s)$ as a function of the mass s (or size) of the cluster for the $N = 20^3$ system at $p = p_c$. The solid line is a power law $s^{-0.69}$ obtained from a least squares fit to the data in the region [3:30].

IV. CLUSTER DIFFUSION

We now turn to the measurement of a dynamic cluster specific quantity, namely, the diffusion coefficient $D(s)$ as a function of cluster size s at the percolation threshold $p = p_c$. We measure the mean square fluctuations of the center-of-mass position $R_s^{c.m.}(t)$ for each cluster of size s, and for large times we find a linear behavior

$$\langle [R_s^{c.m.}(t) - R_s^{c.m.}(0)]^2 \rangle \sim 6D(s)t, \qquad (7)$$

allowing us to extract the diffusion constant $D(s)$ as a function of cluster mass s. Again the average $\langle \cdots \rangle$ is performed over both time (thermal average) and over realizations, and here we have found it sufficient to use 80 samples.

To demonstrate the asymptotic normal diffusion we plot for the $N = 20^3$ system in Fig. 6(a) $\langle [R_s^{c.m.}(t) - R_s^{c.m.}(0)]^2 \rangle / t$ as a function of time steps for several cluster sizes $s = 1, \ldots, 29$, and part (b) shows a magnification for the largest clusters of $s = 26, \ldots, 29$. As can be seen all the curves approach constant values for large times, and it is from these values that we calculate the diffusion constant using Eq. (7). We have checked that the results below do not change if we extend the length of the sampling time to much longer times (5000 time steps).

For monodisperse polymers in a dilute solution, Rouse dynamics predicts the power law dependence $D(s) \sim s^{-1}$. Taking hydrodynamic interactions into account, Zimm dynamics predicts $D(s) \sim R_g^{-1} \sim s^{-1/D} = s^{-0.4}$ [13]. For the present model we observe a very clear power law, $D(s) \sim s^{-k}$, as can be seen in Fig. 7, where we have plotted $D(s)$ as a function of s. We consider again only the largest system size $N = 20^3$ at $p = p_c$, and $D(s)$ is found from Eq. (7) based on the data from Fig. 6. The exponent of the power law is approximately $k \approx 0.69$, and is thus described neither by pure Rouse nor by Zimm dynamics. Instead, the exponent is intermediate between the values for Rouse and Zimm dynamics.

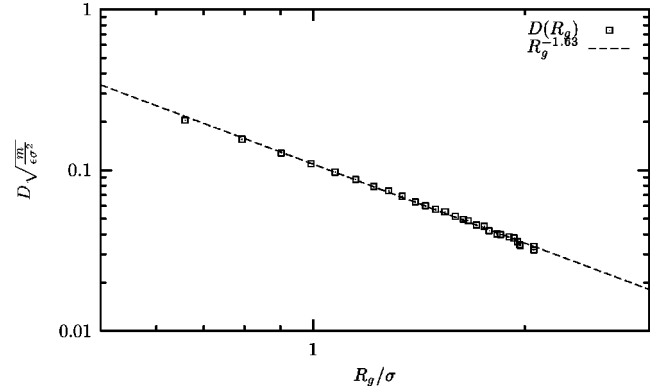Having measured the radius of gyration in Fig. 5, we can convert the above result into a dependence of D on R_g,

FIG. 8. Diffusion constant as a function of radius of gyration for $N = 20^3$ and $p = p_c$.

$D(R_g) \sim s^{-0.69} \sim R_g^{-0.69D} = R_g^{1.64}$, and the corresponding data are plotted in Fig. 8. Also shown is a power law fit to the data yielding an exponential value of 1.63. Again we emphasize the clear deviation from a Stokes-type law, $D(R_g) \sim R_g^{-1}$, as obtained from the Zimm dynamics for polymers. Moreover our result is in sharp contrast to a corresponding result in a recent paper [14] for a lattice model of gelation in which it was found that $D(R_g) \sim R_g^{-2.4}$ using bond fluctuation dynamics.

V. CONCLUSIONS

Using extensive molecular dynamics simulations of a system of Lennard-Jones particles we studied a specific model for the gelation transition. An important feature of our model is that particles are allowed to form permanent chemical bonds from the Lennard-Jones liquid state when they get close together. For this model we determined a number of exponents characterizing the geometry and polydispersity of the system, and this information allowed us to conclude that 3D percolation theory is the appropriate static universality class. We went on to discuss the radius of gyration of the clusters at the gel point resulting in the determination of their fractal dimension. Afterwards we focused on the self-diffusion constant of individual clusters as a function of their size. We found strong indications for a power law behavior with an exponent described neither by Rouse nor by Zimm dynamics. In future work we intend to study, e.g., the shear viscosity of this model in order to measure the corresponding dynamic exponents. As mentioned in the Introduction there is a considerable disagreement as to the values of these exponents, and numerical results for models such as the present one will allow us to discriminate between some of the proposed dynamic universality classes for gelation.

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