Dynamic Scaling in an Aggregating 2D Lennard-Jones System

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The evolution of a 2D Lennard-Jones system, quenched from the fluid to below the triple point, is simulated by molecular dynamics. We show that the structure factor obeys the scaling relation $S(q/q_m(t)) \sim q_m(t)^{-d_f} \tilde{S}(q/\tilde{q}_m)$. Here q_m is the location of the low angle peak in $S(q)$, $d_f = 1.85 \pm 0.05$ is a fractal dimension, and $\tilde{S}(q/\tilde{q}_m)$ is a time-independent characteristic function which peaks at $\tilde{q}_m$. The quenching process is thermodynamically similar to the formation of a gel from a sol. Hence the relation suggests that a characteristic fractal dimension of even a dense gel can be derived from measurements of the time evolution of $S(q)$.

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This Letter reports a simulated quench of a fluid to a temperature below the triple point. Specifically, we describe a molecular dynamics [1,2] simulation of the evolution of a 14 336-particle two-dimensional Lennard-Jones system when quenched from a liquid state reduced temperature $T = 1.0$ to $T = 0.2$. The triple point for this system is approximately $T_{\text{tp}} \approx 0.41$. The system was allowed to evolve at a density $\rho = 0.325$ for a total reduced time of $t = 1000$, with an integration time step $\Delta t = 0.004$, and at a constant temperature maintained by a Gaussian isokinetic thermostat [1].

The behavior of the system is of interest since quenching to the solid has not been simulated before. Moreover, the change in morphology with time, mirroring the decomposition of the system from the spinodal region to a quasisolid, is of wider interest. We have argued [3] that quenching is thermodynamically similar to the formation of a gel from a sol. In fact, recent experiments on the structure of dense silica gels prompted this work [3,4]. The experiments indicated that a power-law form of the structure factor $S(q)$, where q is the scattering wave vector, does not necessarily reflect fractal aggregation when the sol is dense [5]. From simulations, however, we may unambiguously evaluate the structure factor. We will show that the evolution of $S(q)$ in this quenched Lennard-Jones system obeys a dynamic scaling relation from which a characteristic fractal dimension of the decomposing fluid can be derived—*regardless of the density*. We thus argue that the simulation provides invaluable insight into the interpretation of experiments designed to probe the gel mechanism.

The simulation results are presented in Fig. 1 for representative times. Shown are four snapshots taken at post-quench times $t = 8, 40, 200$, and 1000. At $t = 8$, the system, which was in an initial, disordered state at $T = 1.0$ before the quench, has formed two distinct phases: a solid (black regions formed of dense particle clusters)

and an extremely dilute gas (white regions essentially devoid of particles). The microstructure is characterized by finely dispersed clusters of particles that form thick filaments and is reminiscent of the structures observed in simulations of spinodal decomposition in liquids [6,7] and solids [8]. Figure 2 shows the corresponding computations of $S(q, t)$ (azimuthally averaged as the computed diffraction patterns displayed circular symmetry). A peak in $S(q)$ at low angles results from correlations in the positions of neighboring *clusters*, and its location provides a rough measure of the average cluster-cluster separation at
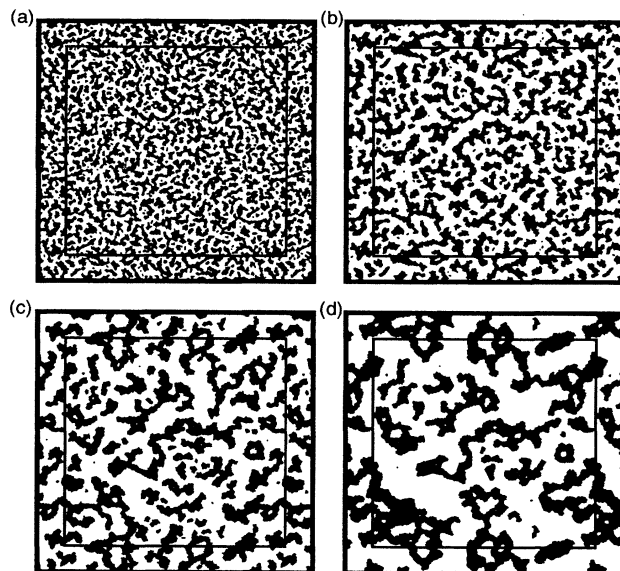

FIG. 1. Evolution of the MD simulation after a quench from $T = 1.0$ to $T = 0.2$. The simulation contains 14 336 particles at a density $\rho = 0.325$. (a) $t = 8$, (b) $t = 40$, (c) $t = 200$, and (d) $t = 1000$.
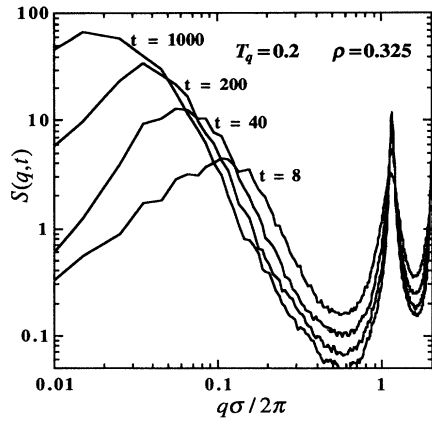
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FIG. 2. The structure factor $S(q,t)$ computed from the four simulations presented in Fig. 1. Note, as the simulation evolves, the peak maximum at low q increases and moves towards smaller q.
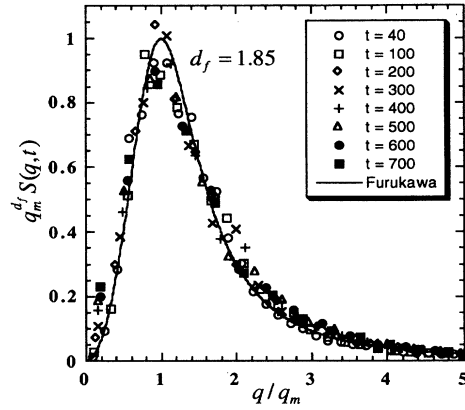

FIG. 3. The structure factor $S(q,t)$ for various times in the simulation since the temperature quench, scaled according to Eq. (3). The solid line is the phenomenological theory of Furukawa [11], which has no adjustable parameters.

a given time. As the simulation evolves, this peak moves to lower q and grows in height. The shift to lower q indicates increasing cluster-cluster separation; the height is related both to the degree of correlation between clusters and to the number of particles contained in an average cluster.

Inspection of the morphologies shown in Fig. 1 hints that the decomposition proceeds in a temporally self-similar manner. We, therefore, assume a form for the structure function that, except for the location and height of the peak maximum, is invariant during the coarsening process:

$$S(q/q_m(t)) = K(q_m(t)) \tilde{S}(q/\tilde{q}_m), \qquad (1)$$

where $q_m(t)$ is the location of the peak maximum, $\tilde{S}(q/\tilde{q}_m)$ is a characteristic structure function with a maximum at $\tilde{q}_m$, and $K(q_m(t))$ is a proportionality constant.

The form of $K(q_m(t))$ can be obtained as follows. The magnitude of the structure factor is proportional to the number of clusters N_c and the square of the number of particles per cluster n^2:

$$S(q/q_m(t)) \sim N_c n^2 \tilde{S}(q/\tilde{q}_m). \qquad (2)$$

We note that $n \propto L_c^{d_f} \propto q_m^{-d_f}$, where L_c is a characteristic linear dimension of the clusters, and, in general, d_f is a fractal dimension. Mass conservation requires $N_c n = N_p$, the total number of particles in the system. The scaling relation can thus be written as

$$S(q/q_m(t)) \sim q_m(t)^{-d_f} \tilde{S}(q/\tilde{q}_m). \qquad (3)$$

Equation (3) is, therefore, a more general form of the scaling relation normally given in the literature [9–11], where d_f has replaced D, the dimensionality of the system. Figure 3 is a plot of the scaled structure factor against q/q_m at times $t = 40$ to $t = 700$ after quench initiation, using an exponent $d_f = 1.85$ in Eq. (3). All

data fall essentially on a single curve. The hypothesis of temporal self-similarity thus appears justified. (Results corresponding to $t = 8$, and those after $t = 700$, are not included in the figure. For early times cluster growth does not follow a coarsening mechanism [6]. At later times the clusters reach a size which spans more than $\frac{1}{2}$ the simulation box length [see, e.g., Fig. 1(d)].)

Note that the exponent is not the Euclidean dimension $D = 2$. We verified that $d_f \neq D$ by constructing a plot of $q_m^{d_f} S(q_m)$ vs q_m for $d_f = 2, 1.85, 1.7$. If scaling holds and the fractal dimension is chosen properly, then this plot must give a horizontal line, otherwise there will be systematic deviations from the horizontal. Figure 4 is the
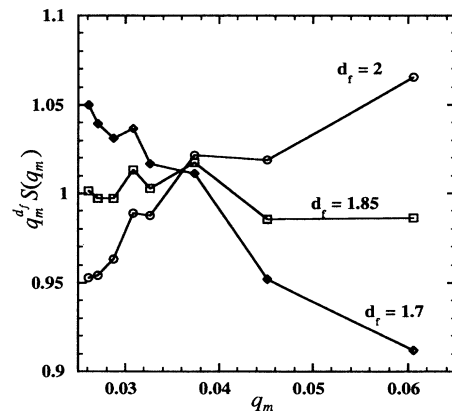

FIG. 4. The small angle peak maximum scaled according to Eq. (3) for various fractal dimensions d_f. Note that when a fractal dimension of 2 or 1.7 is assumed there is a systematic deviation away from the horizontal, indicating that these fractal dimensions will not give an accurate fit to the assumed scaling law.

result. For $d_f = 2$ there is a clear systematic increase with q_m, for $d_f = 1.7$ there is a systematic decrease, but for $d_f = 1.85$ the curve is close to horizontal. Hence, Fig. 4 demonstrates that the exponent is indeed less than $D = 2$, and, by our estimation, is accurate to within ± 0.05.

As a matter of interest, Furukawa's phenomenological form [11]

$$\tilde{S}(q/\tilde{q}_m) = \frac{(1 + \gamma/2)(q/\tilde{q}_m)^2}{\gamma/2 + (q/\tilde{q}_m)^{2+\gamma}} \qquad (4)$$

for the characteristic structure function is plotted in Fig. 3, using $\gamma = 3$ to ensure that Porod's law is obeyed at high q. Agreement between our simulation data and Eq. (4) is impressive especially because the only variables required to construct Fig. 3 are the locations q_m for each snapshot (determined using a least-squares fitting procedure), the fractal dimension d_f, and a single, universal, normalizing constant to place the peak height at 1. Alternatives for the characteristic structure function can be considered, for example, Schätzel and Ackerson's equation [12] was shown to work well in colloidal systems. Here, however, the particular form of Eq. (4) is not central to our arguments.

Scaling using a form of Eq. (3) with $d_f = D$ is well known [6,10], but simulation results in which $d_f \neq D$ have apparently not been observed before. Here, however, we simulated decomposition into the solid, and this mechanism might be slightly different from previous studies that investigate decomposition into the liquid and which used D in the scaling. Also, here, the system contained 14 336 particles. In a smaller system [6,10], it is difficult to detect a small difference between D and d_f. For example, the simulations were repeated with 3584 particles, and it was impossible to distinguish scaling with the exponent $d_f = 1.85$ from $d_f = D = 2$. A large system was needed to confirm details of the fractal scaling because (a) it allows us to investigate a sufficiently wide range of times and scattering vectors, and (b) $S(q)$ can then be calculated to sufficient precision.

Finally, we connect the simulation results with experimental diffraction studies of aggregation and gelation in general and of gelation of silica spheres in particular [4,5]. Most gelation diffraction experiments have concentrated on dilute samples (volume fraction $<1\%$ of a precursor) where the structure factor displays a well-known power-law rise with decreasing wave vector [13]. This power-law growth has been demonstrated convincingly to result from fractal aggregation [14–16]. Recent experiments [4] with dense systems of colloidal silica (volume fraction $>10\%$) also suggested a power-law behavior of $S(q)$. It is, however, not necessarily valid to interpret a power-law slope in terms of a characteristic fractal dimension because the slope may have a contribution from cluster-cluster correlations [5,17]. Our simulations here of dense systems, for example, show a power-law rise in $S(q)$ with decreasing wave vector over a significant range of q (see

Fig. 2 in the region $0.05 < q\sigma/2\pi < 0.5$). This rise, however, is from a peak in $S(q)$ which we know originates from cluster-cluster correlations. It cannot be interpreted in terms of a fractal dimension. In fact, the slope in Fig. 2 is near 3—clearly nonsensical if interpreted in the normal way. It would seem, therefore, that it is not possible to derive a fractal dimension from scattering data on dense systems. This is true for a single measurement of $S(q)$, but the results of this paper indicate that if gelation at high density produces temporally self-similar structures, then measurements of the evolution of $S(q)$ could be used to derive a fractal aggregation dimension in the same way Fig. 3 was constructed.

Experimental evidence has indeed already demonstrated that an analysis of the time evolution of $S(q)$ can be fruitful. In their light-scattering experiments of aggregating polystyrene spheres, Carpineti and Giglio [18] estimated a dimension $d_f = 1.9$ from the standard power-law slope analysis, justified in their case because their system was sufficiently dilute. They then showed that this fractal dimension, when inserted into Eq. (3), scaled the time dependence of their $S(q)$. Equations (1)–(3) justify why a fractal dimension in the exponent is appropriate in their experiment rather than using $D = 3$. Moreover, our results demonstrate that it would be equally valid to determine a fractal dimension from the scaling relation itself. Furthermore, *the scaling law analysis will work in all systems regardless of the density*. The result of this paper may, therefore, indicate an important new way of unambiguously interpreting data taken from dense aggregating systems.

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