

Short-ranged attractions in jammed liquids: How cooling can melt a glass

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(Received 10 August 2004; revised manuscript received 26 January 2005; published 28 March 2005)

We demonstrate that an extended picture of kinetic constraints in glass-forming liquids is sufficient to explain dynamic anomalies observed in dense suspensions of strongly attracting colloidal particles. We augment a simple model of heterogeneous relaxation with static attractions between facilitating excitations, in a way that mimics the structural effect of short-ranged interparticle attractions. The resulting spatial correlations among facilitated and unfacilitated regions give rise to relaxation mechanisms that account for nonmonotonic dependence of relaxation times on attraction strength as well as logarithmic decay of density correlations in time. These unusual features are a simple consequence of spatial segregation of kinetic constraints, suggesting an alternative physical perspective on attractive colloids than that suggested by mode-coupling theory. Based on the behavior of our model, we predict a crossover from super-Arrhenius to Arrhenius temperature dependence as attractions become dominant at fixed packing fraction.

DOI: 10.1103/PhysRevE.71.031206

PACS number(s): 61.20.Lc, 61.43.Fs, 64.70.Pf

Homogeneous liquids with slowly varying intermolecular attractions are typically well represented by appropriate hard sphere reference systems [1]. The deeply supercooled regime of simple liquids appears to be no exception [2]. Computer simulations of hard sphere fluids at high packing fraction ϕ exhibit the canonical features of glass-forming materials, including dynamic heterogeneity, stretched exponential decay of dynamical correlators, and dramatic changes in relaxation times following small changes in density (corresponding in most experiments to small changes in temperature T) [3]. Confocal microscopy of colloids under conditions designed to maximally screen interparticle attractions confirms this fact [4]. Most of the theoretical approaches developed to rationalize sluggish dynamics take advantage of the fact that intermolecular structure at such high densities (or low temperatures) differs little from that of the standard liquid state near the triple point. It is exactly this spatially uniform structure that justifies a hard sphere representation.

Glass-forming liquids that do not fit into this van der Waals picture thus not only introduce the possibility of qualitatively different dynamical features but also provide a significant test of the flexibility of various theoretical perspectives. The simplest such material is a fluid of hard spheres that attract one another strongly over short distances, realized experimentally as a suspension of attractive colloidal particles. In this case attractive forces can play an important role in determining intermolecular structure. Experiments and computer simulations indicate that for small u/T (where u is the strength of attractions), overall relaxation rates exceed those of a hard sphere liquid at the same packing fraction [5–11]. For fixed u , one can thus view melting of the glass as a consequence of cooling. For large u/T , however, tight clustering of particles leads to rigid gel-like structures that rearrange extremely slowly. This second, attraction-driven glassy state would seem to differ qualitatively from the original jammed material ($u=0$) in both structure and dynamics [12].

Calculations based on mode-coupling theory have motivated much of the experimental study of slow dynamics in attractive colloids, predicting the existence of multiple glassy states and relaxation times that vary nonmonotonically with u/T at fixed ϕ [13–15]. The physical origins of these predictions, however, are difficult to assess. Attraction-driven changes in dynamics have been ascribed to loosening of the dense liquid environment that confines particle motion. But the mean field approximation underlying mode-coupling theory would seem unable to capture the inhomogeneous particle clustering necessary for such a mechanism. This mean field nature is most problematic in generating a spurious dynamical arrest at large u/T or ϕ . Nonetheless, many predictions of mode-coupling theory, including logarithmically slow relaxation near reentrance to the attractive glass, have been verified by dynamic light scattering [5–11].

A more intuitive, though less detailed, theory of deeply supercooled liquids has been constructed by considering *only* the inhomogeneous fluctuations that lie outside the scope of mode-coupling theory [16–19]. Jamming at high density prevents all but a small fraction of particles from moving a significant distance over any short time interval. The loose regions (or defects) which enable nearby relaxation are therefore sparse and essentially uncorrelated in space. Although the statistics and spatial patterns of these defects may be trivial, their dynamics are complicated by the fact that jammed regions cannot spontaneously loosen unless nearby motion provides space for them to do so. In other words, defects can only be created in the vicinity of other defects. Such a constraint greatly limits the accessible pathways for exploring phase space [18].

The simplest model embodying this picture consists of noninteracting excitations whose dynamics are coupled together by kinetic constraints. Each cell of a lattice, with the size of a liquid's density correlation length, is thus designated as either excited, $n_i=1$, or jammed, $n_i=0$. Creating

defects in a liquid requires local reorganization of particles and thus costs entropy (or, in a thermal system, free energy). This cost is represented schematically by an external field $h > 0$, limiting the average concentration of mobile cells $\langle n_i \rangle \equiv c \ll 1$. The model system's total energy is then $\mathcal{H} = h \sum_{i=1}^N n_i$. (Throughout this paper we express all energies in units of T , distances in units of the lattice spacing, and frequencies in units of the rate at which an unbiased, unconstrained cell changes its excitation state.) Cell mobilities change with rates that preserve a canonical distribution, but are subject to a constraint of facilitation; namely, cell i is only free to change its state when one of its nearest neighbors is already excited. In the one-dimensional East model only cell $i-1$ can facilitate changes at cell i [20]. In the Fredrickson-Andersen (FA) model either neighbor ($i+1$ or $i-1$) can provide facilitation [21].

Despite their simplicity one-dimensional facilitation models exhibit remarkably nontrivial dynamics. Garrahan and Chandler have shown that kinetic constraints in these models confer special geometries on trajectories below a crossover value of c [18]. These spatiotemporal patterns result in sluggish relaxation with temperature dependences mirroring those of many glass-forming materials [19,22,23]. There are even indications that scaling of such geometric features near a dynamical critical point at $T=0$ may be universal among facilitation models and real liquids [24]. Nevertheless, a detailed relationship between between mobility-promoting defects and molecular degrees of freedom remains elusive.

It is not obvious that the kinetic facilitation picture is sufficiently flexible to account for the anomalous dynamical behavior reported for colloidal suspensions [25]. Basic facilitation models possess a single control parameter c , which seems best to correspond to the density (or temperature) of a real material. The monotonic growth of relaxation times with decreasing c in these models appears to prohibit a straightforward explanation of reentrance and multiple glassy states in terms of dynamic heterogeneities alone. In this article we describe a simple extension of the kinetic facilitation picture inspired by structural changes arising from short-ranged attractions. We then examine the dynamics of an appropriately modified one-dimensional East model and demonstrate striking agreement with the phenomenology of attractive colloids.

We assert that the primary effect of introducing short-ranged attractions in a dense, disordered material is to produce a gradual segregation of tightly clustered, immobile regions from loose regions enriched with facilitating defects. In the limit of very strong attractions such demixing produces gel-like structures and eventually macroscopic phase separation, as seems appropriate for strongly attractive colloids. In the context of one-dimensional facilitation models, gradual demixing is naturally generated by adding attractions between adjacent excitations:

$$\mathcal{H} = -\epsilon \sum_{i=1}^N n_i n_{i+1} + h(\epsilon, c) \sum_{i=1}^N n_i. \quad (1)$$

Although clusters and voids would certainly segregate as desired with increasing attraction strength ϵ , the average con-

centration of mobile cells would increase significantly if the external field h did not change. We imagine that increasing attraction strength in a liquid with fixed density, however, does not significantly change the concentration of facilitating defects (in a sense, the total free volume). If we view c as uniquely determined by ϕ , then the field strength h must be adjusted to maintain a desired value of c for any ϵ . With a routine change of variables, $s_i = 2n_i - 1$, Eq. (1) becomes (within an additive constant) the energy of a one-dimensional Ising model with exchange interaction $J = \epsilon/4$, magnetic field $H = -(h - \epsilon)/2$, and magnetization per spin $\langle s_i \rangle = -1 + 2c$. The required adjustment of external field given c and ϵ is thus a standard result [26]:

$$h(\epsilon, c) = \epsilon + 2 \sinh^{-1} \left(\frac{1 - 2c}{2\sqrt{c(1-c)}} e^{-\epsilon/2} \right). \quad (2)$$

This constraint on the density of excitations, motivated by the notion of conserved free volume at a specific packing fraction, distinguishes our approach from simply adding attractions to a conventional model of kinetic facilitation. It is an essential feature, without which dynamical anomalies such as reentrance would not be obtained.

We emphasize that the attraction between defects in our model does not represent a literal interaction energy between mobile regions in a liquid. In a liquid it is of course particles that attract one another, the effect of which is to drive mobile regions together. Attractions in Eq. (1) could thus be viewed as a potential of mean force between mobile regions, or simply as a measure of clustering tendency. For a fixed value of c , it is in fact energetically immaterial whether attractions act between adjacent excited lattice cells, n_i , or between adjacent jammed cells, $1 - n_i$.

The structural effect of nonzero ϵ for a particular value of c is clear: Excitations cluster together, and the average spacing between consecutive clusters, d , grows:

$$d \approx \begin{cases} d_0 + (e^\epsilon - 1), & \epsilon \ll h_0, \\ c^{-1/2} e^{\epsilon/2}, & \epsilon \gg h_0. \end{cases} \quad (3)$$

Here, $d_0 \approx c^{-1}$ and $h_0 \approx \ln(1/c)$ are the values of d and h at $\epsilon=0$. Just as short-ranged attractions enhance transient structural heterogeneity in a liquid, attractions in the East model generate nontrivial (i.e., nonideal gas) spatial patterns of defects. The dynamical consequences are more subtle. In a Metropolis Monte Carlo trajectory the rate of exciting a cell at the boundary of an excitation domain (or alongside a single excitation) is $e^{-(h-\epsilon)}$. Larger values of J in the isomorphic Ising model require weaker symmetry-breaking magnetic fields to maintain fixed magnetization, so that $h(\epsilon, c) - \epsilon$ decreases monotonically with ϵ :

$$h - \epsilon \approx \begin{cases} h_0 - \epsilon + 2c(e^\epsilon - 1), & \epsilon \ll h_0, \\ c^{-1/2} e^{-\epsilon/2}, & \epsilon \gg h_0. \end{cases} \quad (4)$$

Attractions therefore expedite fluctuations in the vicinity of excitations. This enhanced defect creation rate must be balanced, however, in order to preserve the proper equilibrium distribution. Here, balance is provided by the decline in number of excited clusters per lattice cell.

In the FA model defects may diffuse freely through the

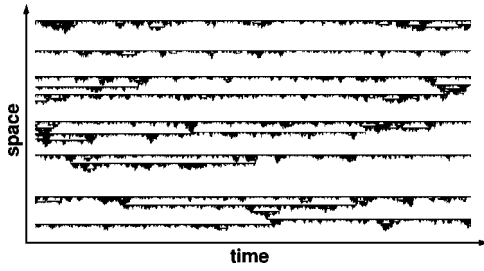


FIG. 1. A representative trajectory of the one-dimensional attractive East model with $c=0.10$ and $\epsilon=4.0$. Vertical cross sections are snapshots of a portion of the system (several hundred lattice cells), in which excited lattice cells are colored black. Unexcited cells are not shown. Time runs along the horizontal axis. The total duration of this trajectory segment is 1000 units of the relaxation time of a single facilitated cell. See Ref. [18] for a detailed discussion of this manner of depicting trajectories and the space-time geometry it reveals.

system through short sequences of local moves, e.g., $10 \rightarrow 11 \rightarrow 01$. The directionality of constraints in the East model gives rise to more complex, self-similar relaxation pathways when the density of excitations is low. In this case all excitation domains are pinned on one side, as is clear from the trajectory plotted in Fig. 1, and can fully relax only when contacted by another domain on that side. For $\epsilon=0$, the minimum energy path for connecting two defects separated by a distance $\ell=2^m$ establishes a set of isolated defects between them. These stepping stones are situated hierarchically, at $\ell/2, 3\ell/4, 7\ell/8, \dots, \ell-1$, giving rise to an energetic barrier $\Delta(\ell)=mh_0$ [27]. The overall relaxation rate is then $\Gamma_0 \approx e^{-\Delta(d_0)} = d_0^{-h_0/\ln 2}$.

Attractions establish a length scale $a \approx h/(h-\epsilon)$ below which it is energetically advantageous to fill immobile spaces between excitations with additional defects. Gap filling (clearly visible in the trajectory of Fig. 1) effectively renormalizes the basic hierarchical relaxation mechanism. Low energy pathways, such as that depicted in Fig. 2 for $a=8$, do not involve isolated defects separated by distances smaller than a . This change of scale, which grows monotonically with ϵ ,

$$a \approx \begin{cases} 1 + \epsilon/h_0, & \epsilon \ll h_0, \\ \epsilon c^{1/2} e^{\epsilon/2}, & \epsilon \gg h_0, \end{cases} \quad (5)$$

has two important consequences. First, the activation energy for pathways connecting subsequent excitations renormalizes. For $\ell=(2^m-1)a+1$, the barrier becomes $\Delta(\ell)=(m-1)h+a(h-\epsilon) \approx h \ln(\ell/a)/\ln 2$. Second, a new time scale τ_a emerges, corresponding to the frequency with which excitation domains spontaneously grow to size a .

Because in the East model domains are bound on one side, fluctuations of the boundaries dividing excited domains from immobile domains (i.e., domain walls) are equivalent to the motion of a one-dimensional random walker. The potential energy of this walker at position x is $(h-\epsilon)x$, and a reflecting boundary restricts motion to $x>0$. Excursions for which the change in energy is comparable to T are essentially diffusive in nature, occurring with a frequency propor-

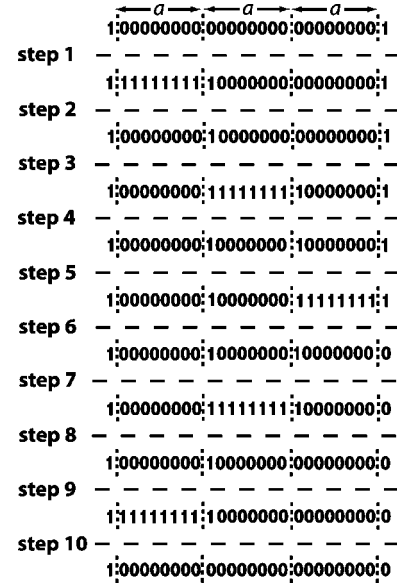


FIG. 2. Renormalization of the hierarchical relaxation mechanism characteristic of the East model. A small portion of the system is depicted horizontally at each step. Numbers (0 and 1) indicate the presence or absence of individual excitations in a sequence of configurations proceeding from top to bottom. Each of the ten steps comprising this schematic trajectory involves creating or (nearly) destroying blocks of $a=8$ consecutive excitations. (The simple sequences of single-cell changes that create and destroy these blocks are not shown.) This idealized example represents the lowest-energy pathway that results in elimination of the rightmost defect.

tional to $(h-\epsilon)^2$. Excursions of length $L>(h-\epsilon)^{-1}$ are less frequent by a factor of $\exp[(h-\epsilon)L-1]$. The basic time scale associated with steps of length $a \gg 1$ is therefore $\tau_a \approx (h-\epsilon)^{-2} e^h$.

Assembling these results, we estimate the relaxation rate for $\epsilon>0$ as

$$\Gamma \approx (h-\epsilon)^2 \exp\left[-h - \frac{h}{\ln 2} \ln(d/a)\right]. \quad (6)$$

This expression depends on attraction strength ϵ implicitly through h , d , and a . Each of these quantities grows with increasing ϵ , but their combination in Eq. (6) may be non-monotonic.

Through renormalization of the basic dynamical length scale, attractions aid the propagation of excitations. But for fixed c , attractions also increase the distance excitations must propagate to achieve relaxation. The quantity $h \ln(d/a)$ characterizes this competition. For weak attractions, $\ln(d/a) \approx \ln d_0 - \epsilon/h_0$ varies much more rapidly than $h \approx h_0 + 2c\epsilon$, and relaxation becomes more facile with increasing ϵ :

$$\ln\left(\frac{\Gamma}{\Gamma_0}\right) \approx \frac{\epsilon}{\ln 2}, \quad \epsilon \ll h_0. \quad (7)$$

The defect concentration c does not appear in this result, which should be accurate in the limit of small c . Terms of order $(\ln c)^{-1}$, which for moderately small values of c cause

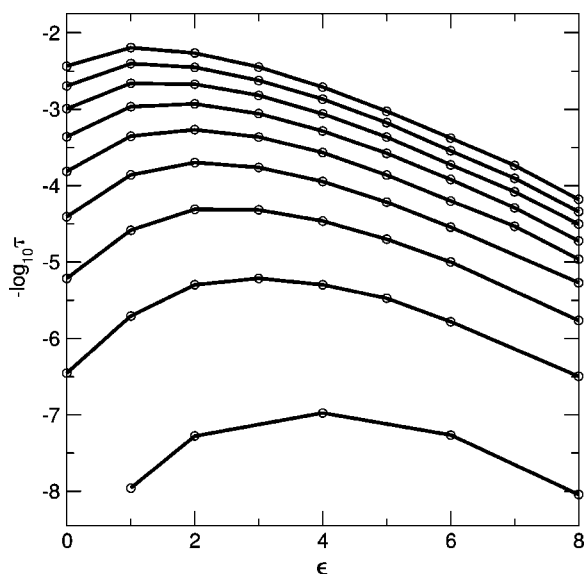


FIG. 3. Average time τ required for all but N/e cells to flip, as a function of attraction strength ϵ . The concentrations are, from bottom to top, $c=0.02, 0.04, 0.06, 0.08, 0.1, 0.12, 0.14, 0.16,$ and 0.18 . The continuous time Monte Carlo simulations that generated these results employed $N=10^5$ lattice cells.

the initial growth in $\ln \Gamma$ to differ for different attraction strengths, have been omitted.

For strong attractions, $\ln(d/a) \approx \ln(\epsilon/c)$ varies instead more slowly than $h \approx \epsilon$, so that Γ decreases with increasing ϵ . In this regime the change of dynamic length scale is insufficient to offset the enhanced sparseness of excitation domains. Relaxation rates should thus be maximum at the crossover from small- ϵ to large- ϵ behavior, i.e., near $\epsilon=h_0$.

The hierarchical mechanism we have described is sensible only for $a < d$. When the renormalized length scale is comparable to or larger than d , there are few consecutive defects separated by distances larger than a . For $\epsilon \gg c^{-1}$ the minimum energy pathway connecting defects simply excites all intervening lattice cells. Domain wall fluctuations are then the only relevant dynamics. A domain wall excursion of length d requires activation energy $d(h-\epsilon)$, which approaches c^{-1} in the limit of large ϵ . Relaxation rates for $a \gtrsim d$ vary with attraction strength (at fixed c) in a simple Arrhenius fashion, $\Gamma \approx [(h-\epsilon)]^2 e^{1/c} \approx c^{-1} e^{-\epsilon+1/c}$.

Numerical simulations of the East model defined by Eqs. (1) and (2) verify these expected features. The relaxation time τ is plotted in Fig. 3 as a function of ϵ for several values of c between 0.01 and 0.2. We define τ through the persistence function $\pi(t)$, i.e., the average fraction of cells that do not change over a time interval of length t [23]. Specifically, $\pi(\tau) = 1/e$, so a majority of cells have undergone fluctuations within time τ . Most importantly, numerical results confirm the existence of reentrant dynamics as attraction strength increases. The maximum relaxation rate can be nearly two orders of magnitude larger than its value at $\epsilon=0$ in this range of defect concentration. As expected, this maximum occurs near $\epsilon = \ln(1/c)$. Reentrance should become still more dramatic for smaller values of c .

For the larger values of c we have considered, the

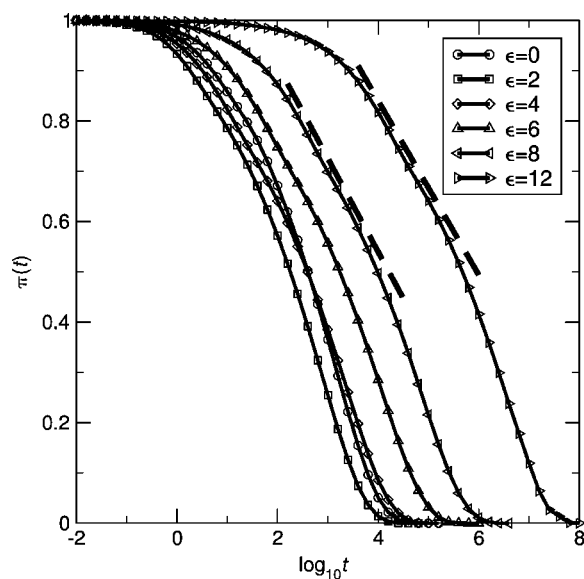


FIG. 4. Persistence $\pi(t)$ as a function of time t for several values of ϵ with $c=0.14$. Dashed lines highlight regions where logarithmic relaxation is noticeable.

asymptotic behavior for $a \gtrsim d$ begins to appear in our simulation results at large ϵ . (For smaller c , the corresponding range of ϵ is numerically inaccessible.) Several results point to dominance of activated domain wall fluctuations in this regime. First, the Arrhenius behavior of $\ln \Gamma$ evident in Fig. 3 is consistent with our analysis. Interestingly, although the hard sphere liquid (and the $\epsilon=0$ East model) is a fragile glass-former [28], our results suggest that the reentrant glass state is instead strong. This prediction seems reasonable, given that gel-like structures have much in common with conventionally strong, network-forming materials [29]. It would be straightforward to test in experiments or molecular dynamics simulations by varying the temperature at fixed packing fraction and attraction strength.

The decay of the persistence function exhibits a more direct signature of domain wall fluctuations. For small values of c , a great majority of lattice cells are unexcited at any time. The average fraction of relaxed spins, $1 - \pi(t)$, should thus be largely determined by the growth of excited domains. (Relaxation of the initially excited minority contributes only weakly and at early times.) Recall that the time required for a typical domain wall excursion of length L is $t \approx (h-\epsilon)^{-2} e^{(h-\epsilon)L}$. In other words the typical extent of domain growth at time t is $L \sim (h-\epsilon)^{-1} \ln[(h-\epsilon)^2 t]$. As a result, the persistence function

$$\pi(t) \approx 1 - L/d \tag{8}$$

$$\approx \text{const} - c \ln(t) \tag{9}$$

decays logarithmically. Equation (9) suggests that the coefficient of logarithmic relaxation for $\pi(t)$ and related correlation functions should not change significantly with u/T for fixed packing fraction. $\pi(t)$ is plotted in Fig. 4 for $c=0.14$ and several values of ϵ . A period of logarithmic decay, with a slope on the order of c , appears as attractions are intro-

duced and becomes more prominent as ϵ increases. Since the average spacing between excited domains still exceeds a in this case, the terminal decay of $\pi(t)$ maintains a form characteristic of hierarchical relaxation. Logarithmic decay should extend over longer time spans for smaller c and larger ϵ . The two decades of such decay apparent in Fig. 4 for $\epsilon \geq 6$ reflect only the limit of our computational resources.

In summary, the simplest physically motivated modification of the East model reproduces the principal dynamical anomalies of attractive colloidal suspensions. In contrast to mode-coupling theory, our model suggests simple physical origins of these features. It is the combination of static and dynamic heterogeneity in our picture that generates additional dynamical features. Clustering of mobility renormalizes the relaxation mechanism that predominates in the absence of attraction. Reentrance results directly from a competition between a growing dynamic length scale a and a growing static length scale d . When the scale of uninterrupted defect propagation exceeds the typical separation between defect domains, the primary mode of relaxation crosses over to simple domain wall fluctuations, whose dynamics give rise to logarithmic relaxation. Although we have presented results only for a modified East model, an equivalently modified FA model shares much of the same behavior. Basic relaxation pathways are similarly renormalized, leading to reentrance of comparable magnitude. Logarithmic relaxation is less pronounced in this case, since excitation domains are not pinned on one side. At long times, fluctuations of a domain's two walls become correlated, and our arguments for the decay of $\pi(t)$ do not strictly apply.

Based on the dynamics of the attractive East model we make several predictions that may be tested by experiment or by numerical simulation of colloid dynamics. Most significantly, our results imply for increasing attraction strength not only a transformation from strong to fragile glass but also rapid growth of the length scale associated with dynamic

heterogeneity. Recent computer simulations [30,31] are consistent with this latter prediction.

We are aware of another effort to rationalize the behavior of attractive colloids within the kinetic facilitation picture [32]. This approach, in contrast to our own, preserves a lack of static spatial correlations between defects. It achieves reentrance by instead modulating the details of facilitation constraints. The two pictures are most distinct for very strong attractions, where spatial correlations between defects in our model become long ranged. In our view this behavior naturally reflects the growing range of correlated density fluctuations in a disordered material as the strength of interparticle attractions increases (or temperature decreases). Detailed experiments or computer simulations should be sufficient to assess the relative validity of these approaches by characterizing spatial distributions of dynamic heterogeneities on short time scales.

Although the kinetic facilitation picture is most sensible at high density, it is interesting to consider the implications of our results for low packing fraction and very large attraction strength. In a version of the attractive East model in more than one dimension, nearly irreversible aggregation of immobile regions would describe the growth of sparse fractal patterns similar to those observed in experiments [33,34]. It may therefore be possible to map the entire phase diagram of our model (in the plane of c^{-1} and ϵ) onto that of a real attractive colloidal suspension (in the plane of ϕ and u/T).

We would like to acknowledge D. Chandler, D. Fisher, and E. Rabani for useful discussions. We would especially like to thank J.-P. Garrahan for useful discussions that guided some of the analytical arguments used in this work, and D. Weitz for introducing us to this problem. We acknowledge the NSF (D.R.R.) and DOE (P.L.G.) for financial support. D.R.R. acknowledges partial financial support from the Camille Dreyfus Foundation and the Alfred P. Sloan Foundation.

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