Quantitative theory of a relaxation function in a glass-forming system

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We present a quantitative theory for a relaxation function in a simple glass-forming model (binary mixture of particles with different interaction parameters). It is shown that the slowing down is caused by the competition between locally favored regions (clusters) that are long-lived but each of which relaxes as a simple function of time. Without the clusters, the relaxation of the background is simply determined by one typical length, which we deduce from an elementary statistical mechanical argument. The total relaxation function (which depends on time in a nontrivial manner) is quantitatively determined as a weighted sum over the clusters and the background. The "fragility" in this system can be understood quantitatively since it is determined by the temperature dependence of the number fractions of the locally favored regions.

Two fundamental riddles in glass-forming systems [1,2] are (i) what determines the spectacular slowing down of the relaxation to equilibrium when the temperature is lowered through a relatively short interval, and (ii) how to predict theoretically the functional forms of various relaxation functions. In practice, one usually fits the data to phenomenological relaxation functions [e.g., the Kohlrausch-Williams-Watt (KKW) law] without any theoretical justification. Here we employ a classical example of glass formation, i.e., a binary mixture of particles with different interaction diameters, to demonstrate unequivocally that the slowing down is due to the creation of clusters of local order; these are mechanically stable and slow to relax. We present a *quantitative* computation of a (functionally nontrivial) and strongly temperature-dependent relaxation function by presenting it as a weighted sum of cluster contributions, each of which decays as a simple relaxation function.

The model discussed here is the classical example [3,4] of a glass-forming binary mixture of N particles in a two-dimensional domain at constant pressure, interacting via a soft $1/r^{12}$ repulsion with a "diameter" ratio of 1.4. More or less related models can be found in [5–10]. We refer the reader to the extensive work done on this system [3,4,11–13]. The sum-up of this work is that the model is a *bona fide* glass-forming liquid meeting all the criteria of a glass transition. In short, the system consists of an equimolar mixture of two types of particles, "large" with "diameter" $\sigma_2 = 1.4$ and "small" with "diameter" $\sigma_1 = 1$, respectively, but with the same mass m. The three pairwise additive interactions are given by the purely repulsive soft-core potentials

$$u_{ab} = \epsilon \left(\frac{\sigma_{ab}}{r} \right)^{12}, \quad a,b = 1,2, \tag{1}$$

where $\sigma_{aa} = \sigma_a$ and $\sigma_{ab} = (\sigma_a + \sigma_b)/2$. The cutoff radii of the interaction are set at $4.5\sigma_{ab}$. The units of mass, length, time, and temperature are m, σ_1, $\tau = \sigma_1 \sqrt{m/\epsilon}$, and $T = \epsilon/k_B$, respectively, with k_B being Boltzmann's constant. The results presented below are extracted from molecular-dynamics simulations using 30 independent systems of 4096 particles each, using the Nose-Poincare-Andersen thermostat [15]. We em-ploy periodic boundary conditions on the torus with pressure $p = 13.5$.

The relaxation function. For the sake of this Rapid Communication, we introduce a relaxation function that is made as follows. At time zero every large particle i in the system is assigned a value $c_i = 1$ and a neighbor list consisting of its n (small or large) nearest neighbors. In time nearest neighbors wander into the yonder, and when the ith particle loses one (respectively, two and three) of its nearest neighbors, having at that time $n-1$ (respectively, $n-2$ and $n-3$) of the original list, it is assigned a value $c_i(t) = 2/3$, 1/3, and 0, respectively. The relaxation function that we monitor is $C(t) \equiv (2/N)\Sigma_i^N c_i(t)$. Figure 1 shows how the relaxation function decays in logarithmic time for different temperatures as indicated in the figure legend. While at high temperatures ($T > 0.56$) the function can be fitted to a stretched exponential, for lower temperatures a long tail develops (starting at $T = 0.56$), destroying any fit to a stretched exponential, as can be seen in the lower panel where the same data are presented in linear time. Note the extreme slowing down exhibited in the lowest eight temperatures.

To gain a quick insight as to the nature of the slowing down, it is advantageous to watch a movie of the decay of the relaxation function. Such a movie is provided as supplementary information to this Rapid Communication [14]. Color coding in green every particle whose assigned value $c_i(t) > 0$, it is obvious from the movie that a fraction of particles lose their green color very rapidly, whereas the nonzero values of $C(t)$ at longer times are contributed entirely by *clusters* of large particles in local hexagonal order. These visual observations bring us to the central theme of this paper. We propose that the present glass-former belongs to a generic class of glass-forming systems that have competing states (of crystalline order or not) that are locally close in energy to the ground state (which is typically unique). Upon rapid cooling, such systems exhibit patches (or clusters) of these competing states, which become locally stable in the sense of having a relatively high local shear modulus. It is in between these clusters where aging, relaxation, and plasticity under strain can take place [16]. A still picture of a typical realization of this system is provided in Fig. 2, where the locally hexagonal clusters of large particles are highlighted
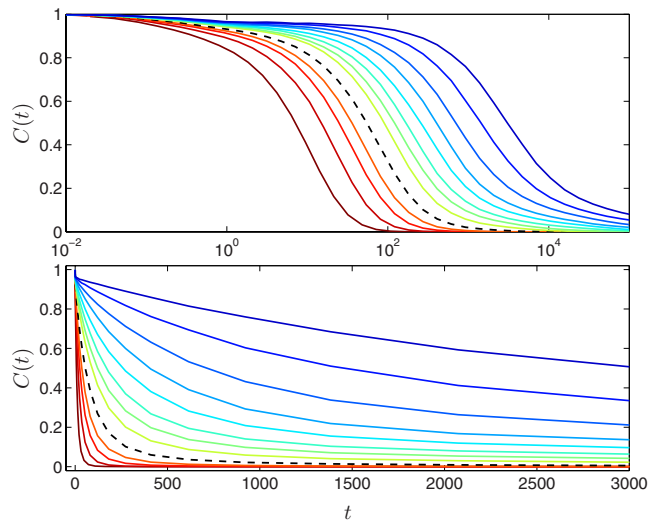
FIG. 1. (Color online) The relaxation function $C(t)$ as a function of logarithmic time (upper panel) and of linear time in the lower panel. The leftmost curve (in red) pertains to $T=1.0$, and in order to the right, the temperatures are $T=0.80$, 0.7, 0.65, 0.6, 0.56, 054, 0.52, 0.50, 048, 0.46, 0.44, and 0.42. Note the extreme slowing down in the range $0.56 < T < 0.42$. The black (dashed) line at $T=0.6$ separates "simple" time dependence at higher temperature, which can be well fitted to a stretched exponential function from "nontrivial" time dependence at lower temperatures, which is ill-fitted by any stretched exponential form. Our aim is to predict quantitatively the form and value of the relaxation function for all temperatures and times.

in color (no meaning to different colors). For clarity of presentation, we do not show in this figure the local hexagonal patches of small particles, or any other cluster of a competing phase.

Cluster decomposition formula. In the rest of this Rapid Communication, we show that this insight is the basis of a quantitative theory of the relaxation function. To this aim, we separate in our mind the clusters (here we only take into account the clusters of large particles in hexagonal local order, which are like curds) from the rest of the system, which
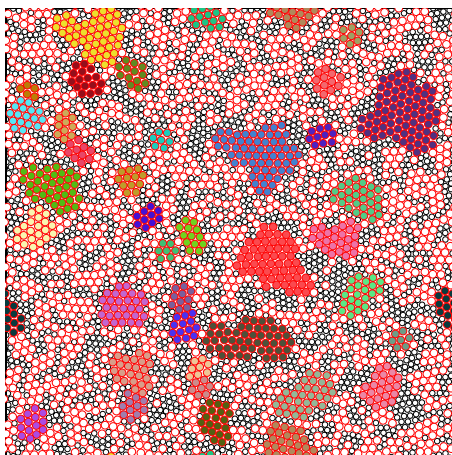

FIG. 2. (Color online) A snapshot of the system at $T=0.44$. In colors we highlight the clusters of large particles in local hexagonal order. The colors have no meaning.
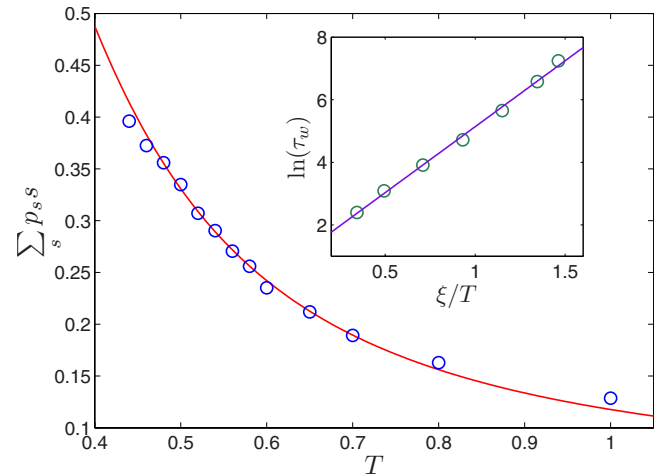

FIG. 3. (Color online) A test of Eq. (3) with $\Delta=1.31$. In the inset we demonstrate Eq. (2) with $\mu=4.212$. Here τ_w was measured directly as the decay time of the relaxation function of the whey Eq. (5), and $\xi(T)$ was computed from Eq. (4).

we refer to as the whey. In the whey, the relaxation process is dominated by "defects," mainly large particles in pentagonal cages and small particles in heptagonal cages [11,12]. If the average distance between such "defects" is a temperature-dependent typical $\xi(T)$, the analysis of [17,18] showed that the relaxation of such defects is determined by a typical relaxation time $\tau_w(T)$, which depends on the temperature according to

$$\tau_w(T) \propto e^{\mu\xi(T)/T}, \qquad (2)$$

where μ is a constant having dimensions of k_B. Clearly, in order to estimate the typical distance between such defects, we need to know how many particles belong to clusters. Denote the number of clusters of size s by N_s; then $sp_s = sN_s/N$ is the probability to find a large particle in a cluster of size s. The number density of large particles in the whey is $n_w = 1 - \Sigma_s p_s s$. To estimate ξ, we denote by H_c and H_w the average enthalpy of a large particle inside a cluster and in the whey, respectively, and $\Delta = H_w - H_c$. There are $g_w \approx (2^6 - 1)/6 + 2^7/7$ ways to organize the neighbors of a large particle in the whey (neglecting the rare large particle in the heptagonal neighborhood), but only one way in the cluster. Thus the number density n_c of particles in the clusters is

$$n_c \equiv \sum p_s s \approx \frac{1}{1 + g_w e^{-\Delta/T}}. \qquad (3)$$

This estimate, with $\Delta=1.31$, agrees very well with the measured value of n_c, as can be shown in Fig. 3. From here we can determine $\xi(T)$, the typical distance between "defects," as

$$\xi \sim \sqrt{n_c}. \qquad (4)$$

To demonstrate the usefulness of this equation, we have computed the relaxation function $C(t)$ only for particles in the whey, calling it $C_w(t)$, and found that it can be excellently fitted to the simple relaxation function
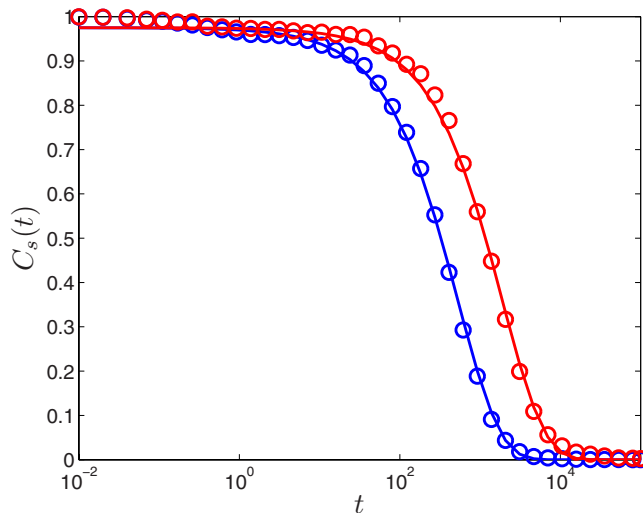
FIG. 4. (Color online) Demonstration that the relaxation of individual clusters of size s (circles) follows the same relaxation function as the whey (continuous line), but with a different relaxation time τ_s. In blue (left) we show $s=7$ at $T=0.5$, and in red (right) $s=10$ at $T=0.46$. Note that we do not have similar fits for large clusters, and Eq. (6) is proposed as a model for all s.

$$C_w(t) = \alpha \exp\left[-\left(\frac{t}{\tau_w(T)} \right)^\beta \right] \qquad (5)$$

with $\alpha=0.95$ and $\beta=0.83$. The values of $\tau_w(T)$ were extracted from such measurements at different temperatures, and plotted as $\ln[\tau_w(T)]$ versus $\xi(T)/T$. The results are shown as the inset in Fig. 3 in very satisfactory agreement with Eq. (2) with $\mu=4.212$. Note that it is highly nontrivial that exactly the same relaxation function describes the dynamics in the whey at all temperatures. We will see that this changes dramatically when the clusters are added to the picture. The coefficient of 0.95 represents an almost T-independent drop in $C_w(t)$, which results from thermal vibrations on the scale of one τ. The exponent 0.83 is a fit that appears to be specific to the present relaxation function.

Having understood the relaxation function of the whey, we turn now to the relaxation function of the clusters. Our best statistics is for relatively small clusters, and we demonstrate in Fig. 4 that the small clusters relax again *as the same simple function of time as the whey*, but with $\alpha \to \alpha'=0.98$ and an s-dependent relaxation time τ_s which can be fitted to

$$\tau_s = \tau_w \exp\left(\frac{\sigma s}{T} \right) = \exp\left(\frac{\mu\xi + \sigma s}{T} \right). \qquad (6)$$

Note that this typical relaxation time for clusters of size s goes smoothly to the whey when $s \to 0$. For larger clusters it is more difficult to say anything precise since the statistics deteriorates very rapidly. Nevertheless, we will show now that the model (6) is sufficient for our purposes, and that we can compute the total relaxation function quantitatively using this simple model. To do so, we present the relaxation func-
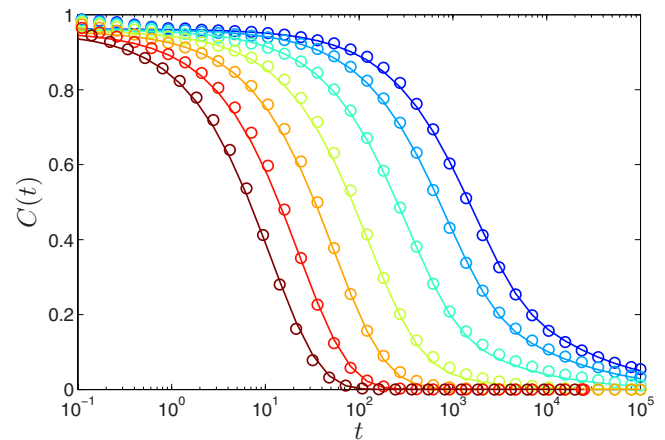

FIG. 5. (Color online) Comparison of the measured relaxation functions with the theoretical prediction on the basis of the cluster decomposition formula (7). From left to right, the temperatures are $T=1$, 0.8, 0.65, 0.56, 0.50, 0.46, and 0.44. Note the quantitative agreement at all times and temperatures. The only parameter fitted here is σ of Eq. (6).

tion $C(t)$ as a sum over the whey and the clusters in the "cluster decomposition formula (CDF),"

$$C(t) = n_w C_w(t) + \sum_s p_s \alpha' \exp\left[-\left(\frac{t}{\tau_s(T)} \right)^\beta \right]. \qquad (7)$$

It is important to note that at this point there is only one parameter left to fit, which is σ in Eq. (6). The best fit is $\sigma=0.031$ with which we predict the relaxation functions as shown in Fig. 5. It is obvious that the CDF captures quantitatively both the time and the temperature dependence of the relaxation function. We submit to the reader that a comparison of data and theory of this quality had been quite rare in the subject of glass-forming systems.

We strongly believe that a similar approach should be relevant for a whole class of glass-forming systems where clusters of competing phases can form upon rapid cooling [19–25]. It does not mean, however, that one can automatically apply what had been done here to other cases. In each case, the physics of the glass former should be carefully understood to identify what are the clusters that dominate at longest times. For example, in hydrogen bonded systems these may be compact clusters, fractal clusters, or chains of molecules, giving difficult to guess formulas for τ_s as a function of the size s of the cluster and of the temperature T. In addition, we should stress that in the present case we have measured the distribution p_s; it is very desirable to derive this distribution from statistical mechanical first principles, as well as to provide a theoretical background to the fitted law (6). Notwithstanding these issues that remain for future research, we propose that this example provides unequivocal evidence that the existence of locally favored structure whose relaxation is much slower than the whey is fundamental to the understanding of the phenomenology of the glass transition.

[1] For a balanced review on glass formers in which many of the common concepts and terminologies are well spelled out, see M. D. Ediger, C. A. Angell, and S. R. Angell, J. Phys. Chem. **100**, 13200 (1996).

[2] See E. Donth, *The Glass Transition* (Springer, Berlin, 2001), and references therein.

[3] D. Deng, A. S. Argon, and S. Yip, Philos. Trans. R. Soc. London, Ser. A **329**, 549 (1989); **329**, 575 (1989); **329**, 595 (1989); **329**, 613 (1989).

[4] D. N. Perera and P. Harrowell, Phys. Rev. E **59**, 5721 (1999), and references therein.

[5] G. H. Frederikson and H. C. Andersen, Phys. Rev. Lett. **53**, 1244 (1984).

[6] L. Davison and D. Sherrington, J. Phys. A **33**, 8615 (2000).

[7] D. Sherrington, L. Davison, A. Buhot, and J. P. Garraham, J. Phys.: Condens. Matter **14**, 1673 (2002).

[8] G. Schliecker, Adv. Phys. **51**, 1319 (2002).

[9] S. Léonard, P. Mayer, P. Sollich, L. Berthier, and J. P. Garrahan, J. Stat. Mech. (to be published).

[10] G. Ben Arous and J. Černý, *Mathematical Statistical Physics, Les Houches, Session LXXXIII*, edited by A. Bovier, F. Dunlop, A. van Enter, and J. Dalibard (Elsevier, Amsterdam, 2006).

[11] E. Aharonov, E. Bouchbinder, H. G. E. Hentschel, V. Ilyin, N. Makedonska, I. Procaccia, and N. Schupper, Europhys. Lett. **77**, 56002 (2007).

[12] H. G. E. Hentschel, V. Ilyin, N. Makedonska, I. Procaccia, and N. Schupper, Phys. Rev. E **75**, 050404 (2007).

[13] H. G. E. Hentschel, V. Ilyin, N. Makedonska, I. Procaccia, and N. Schupper, Phys. Rev. E **76**, 052401 (2007).

[14] The movie is provided as Supplementary Information, temporarily available at http://www.weizmann.ac.il/chemphys/cfprocac/home.html

[15] J. B. Sturgeon and B. B. Laird, J. Chem. Phys. **112**, 3474 (2000).

[16] V. Ilyin, I. Procaccia, I. Regev, and N. Schupper, Phys. Rev. E **77**, 061509 (2008).

[17] V. Ilyin, E. Lerner, T.-S. Lo, and I. Procaccia, Phys. Rev. Lett. **99**, 135702 (2007).

[18] J.-P. Eckmann and I. Procaccia, e-print arXiv:0802.4346.

[19] A. Geiger and H. E. Stanley, Phys. Rev. Lett. **49**, 1749 (1982).

[20] R. V. Chamberlin, Phys. Rev. B **48**, 15638 (1993).

[21] D. Kivelson and G. Tarjus, Philos. Mag. B **77**, 245 (1998).

[22] G. Tarjus, D. Kivelson, and P. Viot, J. Phys.: Condens. Matter **12**, 6497 (2000).

[23] J. S. Langer, Phys. Rev. Lett. **97**, 115704 (2006); Phys. Rev. E **73**, 041504 (2006).

[24] H. Shintani and H. Tanaka, Nat. Phys. **2**, 200 (2006).

[25] H. G.E. Hentschel and I. Procaccia,Phys. Rev. E **77**, 031507 (2008).