Inevitable Irreversibility Generated by the Glass Transition of the Binary Lattice Gas Model

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We numerically investigate the thermodynamic properties of the glass state. As the object of our study, we employ a binary lattice gas model. Through Monte Carlo simulations, we find that this model actually experiences a glass transition. We introduce a potential into the model that represents a piston with which we compress the glass. By measuring the work performed in this process, we find that irreversible works exist at the glass state even in the quasistatic limit. This implies that yield stress is created by the glass transition.

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Theoretically describing structural glass is a long-standing problem in statistical physics. As the temperature of a supercooled liquid is reduced, its molecular dynamics become slower, and eventually such motion ceases at a temperature $T_g$, which is called the glass transition temperature. Below this temperature, the glass is usually considered to be a solid in the sense that its molecules are trapped within a cage formed by their neighbors from which they cannot escape, at least within the experimental time scale. However, a glass is never a solid in the true sense, but out of equilibrium.

Significant effort has been devoted to understanding the nature of glasses, with theoretical studies employing mode coupling theory, the replica model, and the trap models. However, in spite of these attempts, a unified picture and satisfactory understanding have not yet been obtained. The main source of the difficulty in obtaining a theoretical description is that we cannot use the universal measure (i.e. the canonical measure) in treating the glass state. Since the glass state is not an equilibrium state, the Boltzmann-Gibbs ensemble does not apply. Without the framework of statistical mechanics, we are powerless to theoretically treat a large number of degrees of freedom. To allow for the treatment of glass forming materials, it is thus necessary to construct an extended form of statistical mechanics. With this goal, as a first step, it is wise to first consider the thermodynamic concept of a glass state. After confirming the important macroscopic nature, we hope to connect the macroscopic picture to the microscopic picture. In this letter, we report the numerical investigation of the thermodynamic properties of the glass state in a lattice gas model.

Since a glass represents a nonequilibrium state, it is not definite whether thermodynamic structure exists in this state. For this reason we first reconsider the thermodynamic concept of a glass state. After confirming the important macroscopic nature, we hope to connect the macroscopic picture to the microscopic picture. In this letter, we report the numerical investigation of the thermodynamic properties of the glass state in a lattice gas model.

Lattice gas models are very simple and easy to treat computationally. For this reason, if a lattice gas model possesses a glass state, it would be convenient for the theoretical study of this state. Several lattice gas models have been proposed as models of the glass transition. The most commonly used models are the lattice gas models with kinetic constraints proposed by Jäckel, Palmer, Kob and Andersen, and Kurchan et al., among others. However, because these models possess no energy, there are not suited to our thermodynamic study. Despite this fact, we are interested in lattice-gas models because Fuchizaki and Kawasaki assert that such a model with a repulsive interaction displays glassy dynamics. Since a lattice gas model of this type does possess an energy, it would seem to be a possible model with which to carry out our study. However, in our simulations, we have not found a glass transition in this model. (We give detailed discussion regarding this point below.) Therefore, we must make a new lattice model with energetic constraints. In this letter, we extend the lattice gas model to a two component model. Using Monte Carlo simulations, we find that our extended lattice gas model indeed exhibit a glass transition. Finally, we carry out thermodynamic operations within the model and investigate its macroscopic properties so revealed.

We first introduce our extended lattice gas model. We consider a system defined on a 2-dimensional lattice of size $L \times L$. We assume that there are two types of particle, A and B, on the lattice, and that all particles interact repulsively. The strengths of the interactions differ for different pairs, A and A, B and B, and A and B. The interactions are restricted to nearest neighbors, and there is no more than one particle at each site. These conditions are satisfied by the Hamiltonian

$$\mathcal{H}_0 = -J^{AA} \sum_{(ij)} n_i^A n_j^A - J^{BB} \sum_{(ij)} n_i^B n_j^B - J^{AB} \sum_{(ij)} n_i^A n_j^B,$$

where $n_i^A = 1$ and $n_i^B = 0$ if site $i$ is occupied by a particle of type A, while $n_i^A = 0$ and $n_i^B = 1$ if it is occupied by a particle of type B, with $i = 1, 2, \cdots L \times L$ labeling the $L \times L$ lattice points. Here, $(ij)$ denotes nearest neighbor pairs. The quantities $J^{AA}, J^{BB}, J^{AB}$ are the coupling constants between A and A, B and B, and A and B. We call this model the "binary lattice gas model". The model of Fuchizaki and Kawasaki is single component version of...
FIG. 1: Monte Carlo simulation results for the density-density correlation function \( \phi(t + \tau_w, t_w) \) of the binary lattice gas. Correlations are plotted for several waiting times \( t_w \): \( t_w = 0, 10^3, 10^4, 10^5, 10^6 \). (a) The parameter values are here \((N^A, N^B, T) = (65, 65, 1000)\). The unique curve in the long waiting time limit has a finite Debye-Waller factor defined by \( f_D = \lim_{\tau_w \to \infty} \lim_{t_w \to \infty} \phi \). The nature of the correlation dynamics in this case indicates that the system is in the gas state. (b) The parameter values are here \((N^A, N^B, T) = (55, 55, 1000)\). In this case, the unique curve in the long waiting time limit has a vanishing Debye-Waller factor. The nature of the correlation dynamics in this case indicates that the system is in the gas state.

We stipulate that the dynamics of the system are conservative by enforcing the conditions

\[
\sum_i n_i^A = N^A, \quad \sum_i n_i^B = N^B. \tag{2}
\]

To enforce these conditions, we adopted the Kawasaki (spin-exchange) dynamics for the numerical simulations. Thus, the system is parametrized by the set of quantities \( J^{AA}, J^{BB}, J^{AB}, N^A, N^B, T \) and \( L \), where \( T \) is the temperature of the system. In our simulations, negative coupling constants were used in order to preclude the gas-liquid transition. We set \((J^{AA}, J^{BB}, J^{AB}) = (-1, -4, -2)\) and \( L = 15 \), and employed periodic boundary conditions. The results of our Monte Carlo simulations indicate that this model possesses a glass phase when the particle concentration is sufficiently high. In Fig. 1(a) we show the results for the density-density correlation functions with several waiting times for the case \( T = 1000 \) and \( N^A, N^B = 65 \). We see that the correlation functions exhibit an aging dynamics, that is, the correlation depends explicitly on the observation time and on the time at which the perturbation is applied. We note that when the waiting time is sufficiently long, the correlation function converges to a universal form, which has a finite Debye-Waller factor. Thus we conclude that the system is in the glass phase in this case with \( N^A, N^B = 65 \). In Fig. 1(b), we show the density-density correlation functions for the case \( T = 1000 \) and \( N^A, N^B = 55 \). We see that again in this case, the correlation function converges to a universal form, but here it has a vanishing Debye-Waller factor, so that the system is concluded to be in the gas state in this case with \( N^A, N^B = 55 \). We can hence conclude that the transition between the gas state and the glass state occurs at a concentration in the range \( C = 0.42 - 0.51 \). The precise determination of the transition point is difficult, because the relaxation becomes very slow near the transition point. However, fortunately a precise determination is not necessary for the thermodynamic study we wish to carry out. For this purpose, it is only important that our binary lattice gas model has a concentration glass transition. (We have found that this model has another type of transition, a glass transition as a function of temperature. However, this transition is not involved in the present work.)

Now we investigate the thermodynamics of the model. For this purpose, it is convenient to slightly modify the model described above. First, we change the boundary conditions. Among the four boundaries \( i_x = 0, i_y = 0, i_x = L + 1 \) and \( i_y = L + 1 \), we consider the pair of boundaries \( i_y = 0 \) and \( i_y = L + 1 \) to be still periodic, while we consider the other pair \( i_x = 0 \) and \( i_x = L + 1 \) to be perfectly impermeable. Next, we introduce a potential which represents a movable piston into the model. The piston potential, denoted by \( V_a(t) \), is added to the original, "bare" Hamiltonian \( \mathcal{H}_0 \), so that the full Hamiltonian \( \mathcal{H} \) is given by

\[
\mathcal{H} = \mathcal{H}_0 + \sum_i V_a(i)(n_i^A + n_i^B). \tag{3}
\]

We represent the piston as a quadric potential:

\[
V_a(i) = \begin{cases} 
K (i_x - a)^2 & (i_x > a) \\
0 & (i_x \leq a). 
\end{cases} \tag{4}
\]

By changing the value of \( a \), we carry out the operation of compressing or expanding the system, and we refer to its value as the "piston position". In our numerical simulations, \( a \) was changed as follows. The piston position is initially \( L \), and at this time, the system is in the gas state. Then we compress the system gradually until \( a \) is \( L_0 \). It is then gradually returned to \( L \). We used the
following simple form of $a(t)$:

$$a(t) = \begin{cases} -vt + L & (0 \leq t \leq T) \\ v(t - T) + L_0 & (T \leq t \leq 2T), \end{cases}$$  \hspace{1cm} (5)$$

where $v$ is a parameter that represents the speed of the operation and $T$ is defined by $T = (L - L_0)/v$. When we make $L_0$ sufficiently small, the system experiences the glass transition during the compression. With the transition between the gas and glass states caused in this manner, we investigate the thermodynamic properties of the glass state. The quantity that we measure in the simulation is the work performed on the system, defined by

$$W[a(t)] = \int \frac{\partial V_a}{\partial a} (n^a_i + n^B_i) \, da.$$  \hspace{1cm} (6)$$

We are particularly interested in the quasistatic limit of this function, and we write this limiting form as $W_{qs}$. In equilibrium, $W_{qs}$ is equal to the Helmholtz free energy difference between the initial and final configurations. However, because a glass state is non-equilibrium in nature, it is not certain if $W_{qs}$ also can be used to construct the free energy in this case. (Here, we note that we use the word "quasistatic" to mean simply that the process is carried out sufficiently slowly compared to the $\beta$-relaxation time scale.) The main question we wish to answer in this letter is whether $W_{qs}$ is a useful thermodynamic function in the description of the glass state. For this purpose, we investigate the $v$ dependence of the work $W[a]$ in a complete cycle of compression and expansion defined by (5). If $\lim_{v \to 0} W[a] = 0$ in this cycle, $W_{qs}$ constitutes a thermodynamic function of the glass state, as it is in equilibrium thermodynamics.

In this simulation we set the parameters as $L = 15$, $T = 1000$ and $N^A, N^B = 30$. $L_0$ is taken sufficiently small as the system becomes a dense packing state at $a = L_0$. With the parameter values given above, the glass transition occurs at approximately $a = 9$. In Fig. 2 (a) we display simulation results for $W[a]$ as a function of $v$. For comparison, in the same figure, we also plot the results obtained using a Fuchizaki-Kawasaki type system with $N^A = 60, N^B = 0$. As we see, in this case the system always remains in the gas state. We can clearly see the effect of the glass transition from this comparison. For each case, we see that the work converges to a finite value in the quasistatic limit, but we see that the irreversible work performed in the two component case is much larger than that in the single component case. In the single component case, the amount of irreversible work is very small, and it appears to be due to a lattice effect. This is demonstrated by the fact that the amount of this work does not change when we set the values of coupling constants to zero. Thus we presume a slight amount of the work of the single component case to be almost zero. Contrastingly, in the two component case, irreversible work is essential to the glass transition. This implies that there is no thermodynamic function on characterizing the glass state.

The effect of the glass transition is seen more explicitly when we consider the dependence of the quasistatic irreversible work on the system size. In Fig.2 (b) we display the simulation results for $W[a]$ as a function of $v$ for two systems with four times more lattice points, but the same density: $L = 30$ and $(N^A, N^B) = (120, 120)$ for the two component case, and $L = 30$ and $(N^A, N^B) = (240, 0)$ for the single component case. We find larger difference here between the value of $W_{qs}$ for the one component and two component systems than in the $L = 15$ case. In Fig.3 we display the system size dependence of $W_{qs}$ for the two component system, with equal densities in each case. We find that the the irreversible work exhibits an anomalous and nonextensive system size dependence: $W_{qs} \sim (L \times L)^2$. The reason for this dependence is not yet clear.

From these results, we conclude that the glass state does not conform to conventional thermodynamics laws. We cannot define a thermodynamic function describing the glass state, and we need a theory which deals with the inevitable irreversibility directly. We point out here that approximately a decade ago, Langer and Sentma reported that the glass transition exhibits a hysteresis of the entropy [10]. Our results may be considered the free energy version of their results.

We have arrived at an interesting conclusion. From the operational point of view, the glass transition can be described as a generation of irreversibility, even in the quasistatic limit. For the description of a glass, it is thus not possible to use a simple extension of conventional thermodynamics. It is interesting that the macroscopic nature of our lattice gas may be represented by the transition between a Newtonian fluid and a Bingham fluid [7], because the inevitable generation of irreversibility in our system can be regarded as a generation of yield stress. In fact, we can determine the yield stress from Fig.2. However, at present we do not know of a clear relation between a glass and a Bingham fluid. The most important properties of glasses are disorder and metastability, and it is possible that these properties correspond to properties of Bingham fluids, but this correspondence is yet to be found. In any case, it may be productive to recognize that the glass transition may be one of the route to Bingham nature.

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[1] M. D. Ediger, C. A. Angell and S. R. Nagel, J. Phys. Chem. 100, (1996), 13200.
[2] F. H. Stillinger, Science 267, (1995), 1935.
[3] C. A. Angell, Science 267, (1995), 1924.
[4] R. Richert and A. Blumen, Disorder Effects on Relaxational Processes - Glasses, Polymers, Proteins, Springer-Verlag, Berlin, 1994.
[5] U. Bengtzelius, W. Götze and A. Sjölander, J. Phys. C: Solid State Phys. 17 (1984) 5915. cond-mat/9702070.
[6] G. Parisi, cond-mat/9905310.
[7] M. Mezard, Physica A 265 (1999) 352.
[8] J. P. Bouchaud, A. Comtet and Cecile Monthus, J. Phys.
[9] P. Sollich, F. Lequeux, P. Hebraud and M. E. Cates, PRL 78 (1997) 2020.
[10] W. Kob and H. Andersen, Phys. Rev. E, 48 (1993) 4364.
[11] J. Kurchan, L. Peliti and M. Sellitto, Europhys. Lett., 39 (1997) 365.
[12] K. Kawasaki, K. Fuchizaki and S. Miyazima, Prog. Theor. Phys. Suppl. 305 (1997) 126.
[13] K. Fuchizaki and K. Kawasaki, J. Phys. Soc. Jpn. 67, (1998), 1505.
[14] Stariolo and Arenson, Physica A 283, (2000) 74.
[15] K. Binder, Monte Carlo Methods in Statistical Physics, Springer-Verlag, Tokyo, (1986).
[16] S. A. Langer and J. P. Sethna, PRL 61 (1988) 570.
[17] J. D. Ferry, Viscoelastic Properties of Polymers, Wiley, 1980.
FIG. 2: The irreversible work as a function of the speed of the compression-expansion operation for both lattice gases. The speed of operation \( v \) is measured in units of the inverse of the time needed to change the system length by the inter-site distance. (a) The parameter values are here \( L = 15, T = 1000 \), and the particle numbers are \((N^A, N^B) = (60, 0)\) and \((N^A, N^B) = (30, 30)\). For each case, the amount of work converges to a finite value in the quasistatic limit. The amount of quasistatic irreversible work in the two component case is much larger than that in the single component case. (b) Here the parameter values are \( L = 30, T = 1000 \), and the particle numbers are \((N^A, N^B) = (240, 0)\) and \((N^A, N^B) = (120, 120)\). We see a more distinct difference between the two component and single component cases here than in (a).
FIG. 3: Log-log plot of the system size dependence of the quasistatic irreversible work in the two component case. The density is the same in each case. System size is normalized as $15 \times 15$ is equal to 1. The dashed line represents the fitting function $W \sim (\text{system size})^2$. 