Specific heat in a nonequilibrium system composed of Einstein oscillators

Toshiaki Tao, Akira Yoshimori, and Takashi Odagaki

Department of Physics, Faculty of Science, Kyushu University, Fukuoka 812-8581, Japan
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In order to understand the behavior of thermodynamic quantities near the glass transition temperature, we put the energy landscape picture and the particle's jump motion together and calculate the specific heat of a nonequilibrium system. Taking the finite observation time into account, we study the observation time dependence of the specific heat. We assume the Einstein oscillators for the dynamics of each basin in the landscape structure of phase space and calculate the specific heat of a system with 20 basins. For a given observation time, a transition from annealed to quenched system occurs at the temperature when the time scale of jumps exceeds the observation time. The transition occurs at lower temperature and becomes sharper for longer observation time.

I. INTRODUCTION

Statistical dynamics for sytems in equilibrium has been well established and thermodynamic properties can be calculated from microscopic informations. On the other hand, for systems in nonequilibrium, definitions for "thermodynamic" properties are unclear and the framework to calculate these propeties has not been established. Although we have had no way to obtain thermodynamic properties of systems in nonequilibrium, measurements of these properties such as specific heat, specific volume, etc. in supercooled liquids have been actually reported [1].

Many efforts for understanding the vitrification process have been done through experiments, theories, and numerical simulations in recent years [2]. Theoretical studies have clarified some characteristics in the vitrification process. The mode-coupling theory [3], a mean field approach to the liquid dynamics, showed that an ergodic-to-nonergodic transition occurs. In the trapping diffusion model [4], a power-law distribution of jump rates was shown to lead to a unified understanding of the dynamical singularities of the glass transition. The replica method [5], which is based on the energy landscape picture, has been applied to calculate thermodynamic properties of glasses such as free energy, internal enegy, and specific heat. In this approach, the Kauzmann temperature at which the excess entropy vanishes is an ideal glass transition point. This approach is, however, within the equilibrium framework.

Though these theoretical approaches have been clarified some aspects of the glass transition, the anomaly of the thermodynamic quantities at the glass transition, for example, an abrupt change of the specific heat and a cooling rate dependence of the glass transition temperature, cannot be understood by these approaches. So far there are no other theoretical studies trying to understand the anomaly of thermodynamic quantities at the glass transition. The purpose of this paper is to give a clear definition of the specific heat of a system in nonequilibrium and devise a theoretical method to evaluate it. We assume that a system in nonequilibrium can be described within the energy landscape picture. By considering the stochastic motion among basins in the energy landscape, we phenomenologically show the mechanism of the glass transition.

In this paper, we show that one can understand the anomaly of specific heat from the picture of particle's jump motion in landscape. In Sec. II, a general formalism of calculating specific heat in nonequilibrium systems is summarized [6]. In Sec. III, the results for the model composed of 20 basins, each of which is made of Einstein oscillators, are shown. We show that a transition from annealed to quenched system occurs and that the transition depends on the observation time. Conclusion and discussion are given in Sec. IV.

II. FORMALISM

From the direct observation of the particle's motion by means of molecular dynamic simulation for the supercooled state of a binary soft-sphere system, it was found that some particles change their location simultaneously [7]. This cooperative jump motion of particles became the base of the trapping diffusion model. Moreover it was reported that the kinetics in supercooled liquids can be separated into two motions, slow stochastic jump motion and fast localized motion [8]. Odagaki and Yoshimori [9] showed that the existence of fast and slow motions gives rise to the power-law jump rate distribution in the low jump rate limit. This power-law jump rate distribution leads to a unified understanding of the dynamical singularities of the glass transition [4]. Therefore, it is important for understanding the real glass transition to take the jump motion of particles into account. We put the energy landscape picture and the jump motion of particles together and assume that a representative point moves in the phase space which has a landscape structure. The motion in a basin in the landscape corresponds to the localized motion in the real space. The motion among basins in the landscape corresponds to the stochastic jump motion of particles in the real space. There are many works to treat the connected network of potential minima, and some [10] of them can give correctly long time dynamical behavior of the system out of equilibrium.

In order to distinguish these two motions, the motion in a basin and the motion among basins, it is required that characteristic time scales of fast and slow motions should be

apparently different. That is, the time scale of relaxing within a basin is much smaller than the time scale of jumping among basins. We assume that the system is locally in equilibrium, namely, the local system equilibrates instantly due to the fast motion.

Under the picture of a jumping representative point in the energy landscape, nonequilibrium energy of a system at time t is defined by

$$e(T,t)=\sum_i p_i(T,t)E_i(T), \quad (1)$$

where $p_i(T,t)$ denotes the probability that the system is in basin i and $E_i(T)$ is the energy of basin i in local equilibrium. Note that T is the temperature of environment (heat bath), and we have assumed that the local energy relaxes to an equilibrium value at this temperature without delay, but the probability distribution relaxes with some delay. It is important to note that the probability distribution depends on the history of temperature control (measurement procedure). Here we consider the following simple temperature control of heat bath,

$$T(t)=\begin{cases} T & (t\leqslant 0) \\ T' & (t>0), \end{cases} \quad (2)$$

where $T'=T+\Delta T$. Under this temperature control, we define nonequilibrium specific heat at temperature T and the observation time t_{obs} as follows [6],

$$c(T,t_{obs})=\lim_{\Delta T\to 0}\frac{e(T+\Delta T,t_{obs})-e(T,t_{obs})}{\Delta T}$$

$$=\sum_i\left(p_i(T,t_{obs})\frac{dE_i(T')}{dT'}\bigg|_{T'=T}\right.$$

$$\left.+\frac{dp_i(T',t_{obs})}{dT'}\bigg|_{T'=T}E_i(T)\right). \quad (3)$$

Note that we defined the difference of nonequilibrium energy of a system for the temperature control of heat bath by $\Delta e(T,t_{obs})=e(T+\Delta T,t_{obs})-e(T,t_{obs})$, and not by $\Delta' e(T,t_{obs})=e(T+\Delta T,t_{obs})-e(T,0)$. If the probability is not in equilibrium at time $t=0$, the specific heat using the energy difference $\Delta' e$ cannot be defined correctly unless two limits of $\Delta T\to 0$ and $t_{obs}\to 0$ are performed simultaneously and it does not coincide with an equilibrium value in the limit of $t_{obs}\to\infty$. In definition (3), we consider energy difference between the real nonequilibrium energy at time t_{obs} and the imaginary nonequilibrium energy at time t_{obs}. As a result, we can consistently define the specific heat at any time by using Δe and this is a natural definition for theoretical treatment. Note that, for the temperature control (2), the distribution at time $t=0$ is in equilibrium and the imaginary nonequilibrium energy at $t=t_{obs}$ coincides with that at $t=0$, $e(T,t_{obs})=e(T,0)$. In this case, the definition (3) coin-

cides with the experimental definition. The comparison with the definition of specific heat in the actual experiments is performed in Appendix.

Now we can argue the general behavior of the observation time dependence of nonequilibrium specific heat. In the limit of $t_{obs}\to 0$, the probability distribution stays in an equilibrium state at temperature T and the second term on the right-hand side (rhs) of Eq. (3), which is the derivative of T', disappears. Consequently, the specific heat becomes the quenched average $\sum_i P_i^{eq}(T)[dE_i(T)/dT]$ [11]. In the limit of $t_{obs}\to\infty$, the probability distribution is to be an equilibrium one at temperature T' and the specific heat becomes the annealed average with the second term on the rhs of Eq. (3). Therefore a system shows quenchedlike specific heat for the short time observation and annealedlike one for the long time observation. Here the contribution of the second term on the rhs of Eq. (3) represents the effect of jump motion among basins. In a previous work [6], we showed that this framework gives the valid specific heat for the gaseous hydrogen that was known to have two species, *ortho*-hydrogen and *para*-hydrogen, and considered to be a two-basin system.

III. CALCULATION AND RESULTS

With the formalism described in Sec. II, we can calculate the specific heat in nonequilibrium systems if the fast dynamics of each basin and the probability distribution $p_i(T,t)$ are given. In the supercooled liquid sufficiently close to the glass transition, a representative point jumps around among many basins, each of which is a quasistable state. We consider a system with many basins, each of which is made of Einstein oscillators. In this formalism, we expect that the qualitative nature of the specific heat is independent of the number of basins. Then we set up the number of basins as 20 for the sake of convenience. We assume that the Einstein frequency that characterizes the energy of basin i is expressed as $\omega_E^{(i)}=R_i\times\omega_E^*$, where R_i is a uniform random $R_i\in[1,3]$ and ω_E^* is a constant. Different basins have different configurations, and different configurations have different state densities. In general, the state density is approximated in the Einstein model by a δ function, where the δ function corresponds to an Einstein frequency. Therefore each basin would have a differnt Einstein frequecy from others. We assume the existence of minimum and maximum in Einstein frequencies, because amorphous nature cannot produce long wave length modes as long as system size and an Einstein frequency as an approximated frequency would be finite. The former corresponds to the minimum and the latter corresponds to the maximum. We set up values of the minimum and the maximum as ω_E^* and $3\omega_E^*$ for the sake of convenience. The flat distribution is just a model and different distributions can be considered. However, we do not expect significant change in the results.

Time evolution of the probability distribution is assumed to obey the master equation

$$\dot{p}_i(T,t)=-\sum_{j\neq i}^{20}\omega_{ij}(T)p_i(T,t)+\sum_{j\neq i}^{20}\omega_{ji}(T)p_j(T,t). \quad (4)$$
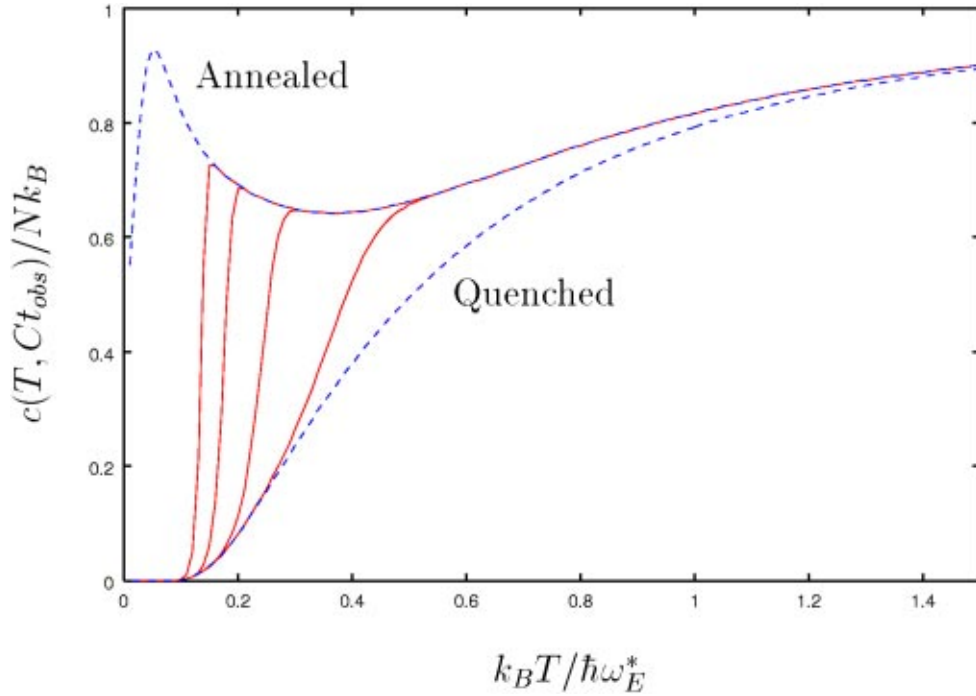
FIG. 1. (Color online only.) Observation time dependence of specific heat for a model composed of 20 basins, each of which is an Einstein oscilators system. The lines show specific heat for $Ct_{obs}=0$(quenched)$,10^2,10^4,10^6,10^8,\infty$(annealed) from right to left.

By solving this set of equations numerically, we obtain the probability distribution function at time $t=t_{obs}$, $p_i(T,t_{obs})$. We set a transition rate from basin i to j as follows,

$$\omega_{ij}(T)=C\exp\{-\beta[F_A(T)-F_i(T)]\}, \tag{5}$$

where $F_i(T)$ is a free energy of an Einstein oscillator in basin i, and $F_A(T)=\max\{F_i(T),F_j(T)\}+\hbar\omega_E^*\alpha$ is an activation free energy introduced between basins i and j. The quantity C^{-1} is the unit of time and α is a positive constant. We obtain the temperature derivatives of those distributions as $\partial p_i(T,t)/\partial T\simeq[p_i(T+\Delta T,t)-p_i(T,t)]/\Delta T$.

We can calculate the nonequilibrium specific heat of this system from Eq. (3). Figure 1 shows the observation time dependence of the nonequilibrium specific heat. In this figure, results are presented for observation times; $Ct_{obs}=0$(quenched system), $10^2,10^4,10^6,10^8,\infty$(annealed system). From this figure, we can see that, at a given temperature, the nonequilibrium specific heat is transformed from quenchedlike to annealedlike specific heat with increasing observation time. We can also see that, at a given t_{obs}, it is transformed from annealedlike to quenchedlike specific heat with decreasing temperature (glass transition).

In order to quantify how the system approaches an annealed system at a given temperature and a given observation time, we define degree of annealing by

$$S(T,t_{obs})\equiv\frac{c(T,t_{obs})-c^Q(T)}{c^A(T)-c^Q(T)}, \tag{6}$$

where $c^A(T)$ is the specific heat of the annealed system and $c^Q(T)$ is that of the quenched system. The degree of annealing becomes $S(T,t_{obs})=0$ for the quenched system and

$S(T,t_{obs})=1$ for the annealed system and thus we can quantify the state of a system by the parameter that varies in between [0,1]. The observation time dependence of the degree of annealing is shown in Fig. 2. In this figure, the behaviors of $S(T,t_{obs})$ are shown for observation times; $Ct_{obs}=10^2,10^4,10^6,10^8$. We can see that as the temperature is reduced, a transition from the annealed to quenched systems occurs at lower temperatures and the transition becomes sharper for longer observation times. This might be related to the cooling rate dependence of the glass transition temperature.

IV. CONCLUSION AND DISCUSSION

We have given a framework for understanding the behavior of specific heat in nonequilibrium systems like supercooled liquids with the existence of fast modes and slow modes. Under the picture of a jumping representative point in the landscape, we defined the specific heat depending on temperature history and suggested a general formalism to calculate specific heat in nonequilibrium systems.

Comparing our work with the work of Angelani *et al.* [10], we found that the picture of energy landscape and a jump dynamics described by the master equation were same in both works. Angelani *et al.* gave correctly long time dynamical behavior of the system out of equilibrium by means of the connected network of basins. On the other hand, we aimed to evaluate thermodynamic quantities of the system out of equilibrium by means of the similar picture. Differences were that we assumed dynamics of a minimum in the landscape and that we simply defined transition rate between two minima. The significance of our work was to take the
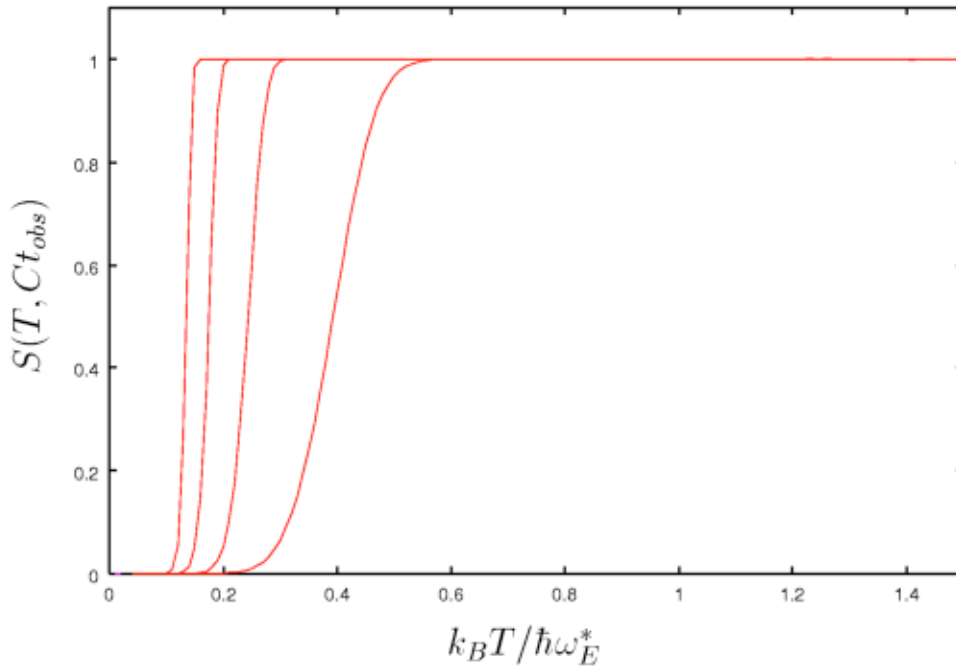
FIG. 2. (Color online only.) Observation time dependence of the degree of annealing. The lines are behavior for $Ct_{obs} = 10^2, 10^4, 10^6, 10^8$ from right to left.

temperature control of heat bath into account and to calculate the specific heat out of equilibrium which depends on the waiting time and the observation time. In this paper, we considered the case of infinite waiting time limit and showed the observatiion time dependence of specific heat. Then an abrupt change of specific heat from annealed to quenched state was shown in the case of finite observation time.

Calculating the nonequilibrium specific heat of a model system with 20 basins, each basin being made of the Einstein oscillators, we obtained the following results. (i) Glass transition is a transision from annealed to quenched systems, (ii) glass transition occurrs at lower temperatures and becomes sharper for longer observation times.

We can qualitatively understand the anomaly of specific heat near the glass transition point, even if we use a simple model system. Basically, localized equilibrium in each basin of the landscape and jump motion of a representative point among basins are important for our calculation. Note that the motion within a basin may clarify the nature of the boson peak.

The origin of the peak of the specific heat in annealed systems can be understood as follows. There are many energy levels in each basin. For sufficiently low temperatures, the representative point moves mostly among the lowest levels in each basin. If these levels have an energy gap, the specific heat for an annealed system shows a peak as a function of temperature. For a quenched system, the motion among basins will not occur and thus the peak disappear. Note that this picture depends on the distribution of energy levels. If there are not gaps among the lowest levels, then the peak of the specific heat disappears.

In the realistic systems, there exist many kinds of relaxation times. The essence of the transition from annealed to quenched state is that some of those relaxation times exceed the observation time (t_{obs}). In this paper, we assume the two-time scale hypothesis on the basis of the result of mo-

lecular dynamic simulations [7], and it is reasonable for temperatures sufficiently close to the glass transition point. To simplify the behavior of growing relaxation times, we employ the two-time scale hypothesis, where one is zero and the other is finite but grows with decreasing temperature. For high temperatures, these two time scales are by far less than t_{obs}. Then the system is always in an annealed state at the observation time. For temperatures close to the glass transition point, one relaxation time is finite but less than t_{obs}. Then these two time scales are distinguishable macroscopically. For temperatures less than the glass transition point, one relaxation time is finite but larger than t_{obs}. Then a successive transition between annealed and quenched system occurs. This kind of transition would be critical for the glass transition.

Various control of temperature and various distribution of activation energies must be considered for more generalized calculations. These works will be studied in a forthcoming paper.

APPENDIX

We consider a measurement operation of specific heat as follows. Suppose that a system in equilibrium at temperature T becomes that in equilibrium at temperature T' after adding energy ΔE. The experimental definition of specific heat in this case can be written as

$$c^E(T) \equiv \frac{\Delta E}{T' - T}, \tag{A1}$$

where $c^E(T)$ represents the specific heat at constant volume. Moreover one can extend the definition (A1) to the system in nonequilibrium. The definition is expressed as

$$c^{NE}(T,t) \equiv \frac{\Delta E}{T_f(t) - T}, \tag{A2}$$

where $T_f(t)$ is a fictive temperature and becomes equilibrium temperature T' at $t=\infty$. When the relaxation time exceeds the observation time and a system is out of equilibrium, one measures the fictive temperature as the temperature of the system. Then the specific heat of this system deviates from that in equilibrium.

Now we consider the following case. The system, which is the same as the former one, is in contact with a heat bath at temperature T. When the temperature of the heat bath is changed to T' at time $t=0$, the energy of the system changes from $e(T,0)$ to $e(T',t)$, where $e(T,t)$ is nonequilibrium energy. According to our formalism, specific heat in this case is defined as

$$c(T,t) \equiv \frac{e(T',t) - e(T,0)}{T' - T}. \tag{A3}$$

This coincides with the definition (3) in the limit of $T' \to T$. The nonequilibrium energy can be expressed as

$e(T(t),t) = \Sigma_i p_i(T(t),t) E_i(T(t))$ under the picture of energy landscape, where $T(t)$ is the temperature of environment (heat bath) at time t, and the energy $e(T(t),t)$ depends on the temperature control of heat bath. On the assumption that the system is in equilibrium at $t=0$, it is expressed that $e(T,0) = \Sigma_i P_i^{eq}(T) E_i(T) \equiv E(T)$, where $E(T)$ is the equilibrium energy of the system at T. On the other hand, the nonequilibrium energy can also be expressed as

$$e(T(t),t) = E(T) + \{E(T') - E(T)\}\{1 - \phi(T(t),t)\}, \tag{A4}$$

where $\phi(T(t),t)$ is a relaxation function satisfying with $\lim_{t\to 0}\phi(T(t),t) = 1$ and $\lim_{t\to\infty}\phi(T(t),t) = 0$. The energy variation between two equilibrium states is written as $E(T') - E(T) = \Delta E$. With the expression (A4), the specific heat in nonequilibrium system can be expressed as follows,

$$c(T,t) = \frac{\Delta E}{T' - T}\{1 - \phi(T(t),t)\} \equiv \frac{\Delta E}{T' + \psi(T(t),t) - T}, \tag{A5}$$

where $\psi(T(t),t)$ is an adequate function for holding this equation. Then the form of the definition (A5) coincides with the definition (A2).

From these considerations, we found that the theoretical definition (A3) is compatible with the experimental definition (A2). Therefore it seems to be valid to describe nonequilibrium systems by using the definition (A3).

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