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Specific heat in nonequilibrium systems

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We propose a general framework of calculating the specific heat of the system in nonequilibrium, where the dynamics of the representative point can be separated into fast motion in a basin of energy landscape and the slow stochastic jump motion among basins. We apply this framework to gaseous hydrogen and obtain the observation time (t_{obs}) dependence of the specific heat. We find that the specific heat gives the quenched and the annealed one in the limit of $t_{obs}\rightarrow 0$ and $t_{obs}\rightarrow\infty$, respectively. We also investigate the waiting time and the observation time dependence of the specific heat and show that, for shorter waiting time, the observation time must be longer to obtain the same degree of annealing. This tendency is consistent with the observation that the glass transition temperature is higher for faster quenching.

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I. INTRODUCTION

Statistical dynamics for systems in equilibrium has been well established and thermodynamic properties of a system in equilibrium can be calculated from microscopic informations using the statistical dynamics. For systems in nonequilibrium, however, there are no clear definitions of ‘‘thermodynamic’’ quantities nor methods to evaluate them. Nevertheless, in some systems in nonequilibrium such as supercooled liquids, measurements of specific heat, specific volume, etc. have been reported [1]. For example, a recent analysis has shown the specific heat of a class of glass forming materials in the supercooled state can be scaled in a certain way near the glass transition temperature [2]. There are many origins that inhibit a system to relax to equilibrium and thus it is difficult to construct a theoretical framework to evaluate physical quantities for systems in nonequilibrium in general.

Recent progress of the study of spin glasses and structural glasses has revealed that the characteristic of these systems can be understood with the so called energy landscape picture [3,4]. The purpose of this paper is to give a clear definition of the specific heat of a system that can be described within the energy landscape picture and devise a theoretical method to evaluate it. The basic assumptions for the energy landscape picture is that the dynamics of the representative point in the phase space can be described by fast motion within a basin and slow stochastic motion among basins. This picture has emerged from extensive molecular dynamics simulations [5]. When the characteristic time τ_c of the stochastic motion becomes comparable to or exceeds the observation time t_{obs}, the system appears to be in nonequilibrium. Therefore we can consider the system as an annealed one when $\tau_c \ll t_{obs}$ and as a quenched one when $\tau_c \gg t_{obs}$.

We give the basic formalism of the evaluation of the specific heat in Sec. II. We assume that the energy of a system at a given temperature is well defined when the system is in one basin. After elevating the temperature by a certain amount, we observe the energy of the system that is given by the average of energies of basins that the system visits in t_{obs}. The specific heat is defined by the initial slope of the energy increment in the limit of the temperature rise being infinitesimal. In Sec. III apply the present formalism to gaseous hydrogen that is known to consist of ortho and para species. Since the conversion time of the nuclear spins is comparable to or larger than t_{obs} and the characteristic time of vibrational and rotational motion is much faster than t_{obs}, we consider the gaseous hydrogen as a two-basin system in the sense described above. We calculate the specific heat as a function of the waiting time t_w before starting the observation and the observation time. We observe that the specific heat changes continuously from the quenched one to the annealed one as a function of t_w and t_{obs}. We give discussion in Sec. IV where we argue the possibility of extending the present formalism to other physical quantities.

II. FORMALISM

In order to calculate the specific heat, we must take account of the measurement operation explicitly. Figure 1 shows a typical temperature control of the heat bath, where t_w and t_{obs} represent the waiting time and the observation time, respectively. First the temperature of the heat bath is decreased from T_0 to T by time t_1 (the cooling process) and we wait for t_w at T. In this process, the system is supposed to relax toward equilibrium, but it is not always in equilibrium at $t' = t_1 + t_w$. The state of the system depends on whether the time scale t' is longer than the characteristic time τ_c of the system or not. Next the temperature is increased to T_a by time $t' + t_2$ (the heating process) and is kept with T_a ever after. Here we assume to measure the specific heat by increasing temperature. The specific heat is measured by the energy change between the states at time t' and $t'' = t' + t_2 + t_{obs}$.

As the temperature is decreased more, τ_c becomes longer. When τ_c is longer than the time scales t' and $t'' - t'$, systems cannot relax to equilibrium in these time scales. This situation can be understood as follows. There are many basins in the phase space. The representative point moves fast within a basin and jumps stochastically among basins. We denote the probability density of finding the system in basin i at time t'' by $p_i(T_a, t''-t'; T, t')$. Note $p_i(T_a, 0; T, t')$ is the distribution of the representative point among basins at $t'' = t'$ that depends on the preparation process of the system before t'. In the measurement of the specific heat, it is important whether

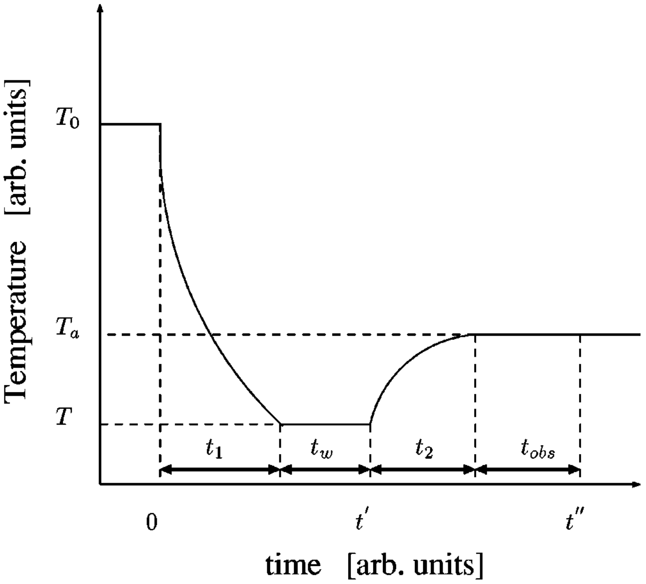

FIG. 1. Temperature control of the heat bath, where time and temperature are given in arbitrary units and $t' = t_1 + t_w$ and $t'' = t' + t_2 + t_{obs}$. The time scales t_w and t_{obs} represent the waiting and the observation time, respectively. The process between $[0, t_1]$ is the cooling process and the process between $[t', t' + t_2]$ is the heating process.

the time scales t' and $t'' - t'$ are larger than the system's relaxation time or not and we express the probability density as a function of t' and $t'' - t'$. In order to define the specific heat measured through the heating process, we consider the total energy of the system given by

$$e(\{p_i\}, T_a) = \sum_i p_i(T_a, t'' - t'; T, t') E_i(T_a), \tag{1}$$

where we denote equilibrium energy in a basin i as $E_i(T_a)$. Here, it should be emphasized that the energy of the system in each basin is assumed to be well defined, because the relaxation in a basin is much faster than the relaxation among basins. We consider the total energy of the system depends on time through the probability density for each basin. In most of real experiments the energy difference between the final state of the system at temperature T_a at time t'' and the initial state at temperature T at time t' is measured. Unless one can take $T_a \rightarrow T$ and $t'' \rightarrow t'$ limits simultaneously, the specific heat cannot be well defined. In our definition, we use the energy difference between the final state of the system at temperature T_a at time t'' and the virtual state of the system at time t'' if it is kept at temperature T. As a result, the specific heat defined by taking the limit $T_a \rightarrow T$ exists at any time and it is natural definition for theoretical treatment. Thus we define the specific heat of the system in nonequilibrium by

$$c(T, t', t'' - t') \equiv \left. \frac{de(\{p_i\}, T_a)}{dT_a} \right|_{T_a = T}. \tag{2}$$

In the following we consider two limits; One is the $t' \rightarrow \infty$, $t'' - t' \rightarrow \infty$ limit, where the probability density depends only on the final temperature T_a, equilibrium state, $p_i(T_a, t'' - t'; T, t') = P_i^{eq}(T_a)$. The specific heat is given by

$$\lim_{t'' - t' \rightarrow \infty} \lim_{t' \rightarrow \infty} c(T, t', t'' - t') = \sum_i \left[\frac{dP_i^{eq}(T_a)}{dT_a} E_i(T_a) + P_i^{eq}(T_a) \frac{dE_i(T_a)}{dT_a} \right] \Bigg|_{T_a = T}.$$

This limit corresponds to the annealed system. The other is the $t' \rightarrow 0$, $t'' - t' \rightarrow 0$ limit, where the probability density of basin i becomes equilibrium one at temperature T_0 and independent of T_a, $p_i(T_a, t'' - t'; T, t') = P_i^{eq}(T_0)$. The specific heat is given by

$$\lim_{t'' - t' \rightarrow 0} \lim_{t' \rightarrow 0} c(T, t', t'' - t') = \sum_i \left[P_i^{eq}(T_0) \frac{dE_i(T_a)}{dT_a} \right] \Bigg|_{T_a = T}.$$

This limit corresponds to the quenched system.

III. APPLICATION

A. Gaseous hydrogen

As a simple application of the framework presented in the preceding section, we consider gaseous hydrogen that is known to have two species, ortho-hydrogen and para-hydrogen and the conversion time between two species can be as long as several days. Since the characteristic time scale of the rotational motion of molecules is much faster than the conversion time, we can consider molecular hydrogen as an assembly of the two-basin systems, provided that intermolecular interaction is negligible. Noting that the wave function should be antisymmetric under exchange of protons, partition function for rotation and nuclear spin, $j(T)$, is expressed as the sum of partition function of ortho-hydrogen $j_o(T)$ and that of para-hydrogen $j_p(T)$,

$$j(T) = j_o(T) + j_p(T).$$

It is known that the rotational contribution to the Helmholtz free energy of N gaseous hydrogen at temperature T is given by

$$A^A(T) = -Nk_B T \ln[j_o(T) + j_p(T)] \tag{3}$$

for annealed system and

$$A^Q(T) = -Nk_B T \left[\frac{3}{4} \ln j_o(T) + \frac{1}{4} \ln j_p(T) \right] \tag{4}$$

for quenched system. The specific heat for these systems divided by Nk_B are written as

$$c^A(T) = \frac{\partial}{\partial T} \left\{ T^2 \frac{\partial}{\partial T} \ln j(T) \right\}, \tag{5}$$

$$c^{Q}(T)=\frac{3}{4}C_o(T)+\frac{1}{4}C_p(T), \tag{6}$$

respectively, where $C_\alpha=\partial/\partial T\{T^2(\partial/\partial T)\ln j_\alpha(T)\}$ $(\alpha=o,p)$ is the specific heat of each species. The coefficients 3/4, 1/4 in Eq. (6) are probabilities for each species at $T=\infty$. Experimental observation is compatible with the behavior of the specific heat for quenched system [6].

Therefore when the time scale of spin conversion becomes comparable to the observation time, we can expect to obtain a crossover of the specific heat between quenched and annealed ones. In the following we apply the framework described in Sec. II to this system and study explicitly the crossover of the specific heat.

B. Two-basin system

We consider a simple relaxation process between these two basins that correspond to ortho and para species of a molecular hydrogen. Suppose that the temperature of the heat bath is changed according to $T(t)$. Denoting the probability density of a basin i at time t as $p_i(\hat{T},t)$, where $\hat{T}=T(t)$, time evolution of the probability density is assumed to obey the master equation

$$\begin{pmatrix}\dot{p}_o(\hat{T},t)\\ \dot{p}_p(\hat{T},t)\end{pmatrix}=\begin{pmatrix}-\omega_{op}(\hat{T}) & \omega_{po}(\hat{T})\\ \omega_{op}(\hat{T}) & -\omega_{po}(\hat{T})\end{pmatrix}\begin{pmatrix}p_o(\hat{T},t)\\ p_p(\hat{T},t)\end{pmatrix}, \tag{7}$$

where $\omega_{ij}(\hat{T})$ is the transition rate from basin i to j at temperature $\hat{T}$. Here we have assumed that the transition rate depends only on the temperature of heat bath at time t. The transition rate can be expressed as $w_{ij}(\hat{T})=C\exp\{-\beta(F_A(\hat{T})-F_i(\hat{T}))\}$, where $F_A(\hat{T})$ is the free energy of the transition state and $F_i(\hat{T})$ is that of basin i, and C is a constant. Since partition functions of both species are known, free energies of both species can be calculated and these are shown in Fig. 2, where $F_o(\hat{T})$ and $F_p(\hat{T})$ are free energy of the ortho and para species. To take account of the activated process, we introduce free energy of the transition state as the form

$$F_A(\hat{T})=F_o(\hat{T})+k_B\alpha, \tag{8}$$

where $k_B\alpha$ is the activation free energy. Then transition rates between ortho and para species are expressed as

$$\begin{aligned}w_{op}(\hat{T})&=C\exp(-\alpha/\hat{T}),\\ w_{po}(\hat{T})&=C\exp(-\alpha/\hat{T})j_o(\hat{T})/j_p(\hat{T}).\end{aligned} \tag{9}$$

Since the stationary probability of state i is denoted as $P_i^{eq}(\hat{T})=j_i(\hat{T})/\{j_o(\hat{T})+j_p(\hat{T})\}$, we find that the detailed balance is satisfied.

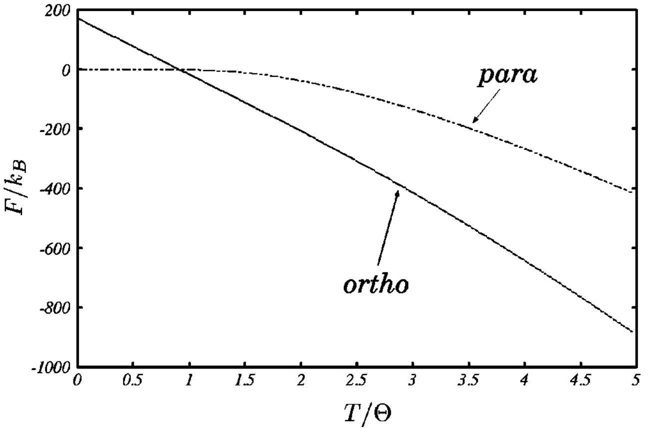

FIG. 2. Free energies of both species. Θ is the characteristic temperature for rotation. The full line is free energy of ortho state F_o/k_B and the dashed line is that of para state F_p/k_B, where k_B is the Boltzmann constant. The ortho state is the global minimum at high temperatures, on the other hand, the para state is the global minimum at low temperatures.

As a specific temperature control, we consider the following two-step process;

$$T(t)=\begin{cases}T_0 & (t<0)\\ T & (0\leq t<t_w)\\ T_a & (t_w\leq t),\end{cases}$$

which is shown in Fig. 3, where we set $t_1=t_2=0$ assuming an ideal condition. Note that t is scaled by a constant C^{-1} for later convenience. It is straightfoward to solve Eq. (7) for this temperature control. Noting that the eigenvalues of the matrix on the right hand side of Eq. (7) are 0 and $-\Lambda(\hat{T})$, where

$$\begin{aligned}\Lambda(\hat{T})&=\omega_{op}(\hat{T})+\omega_{po}(\hat{T})\\ &=Ce^{-\alpha/\hat{T}}\left\{1+\frac{j_o(\hat{T})}{j_p(\hat{T})}\right\}\equiv C\lambda(\hat{T}),\end{aligned} \tag{10}$$

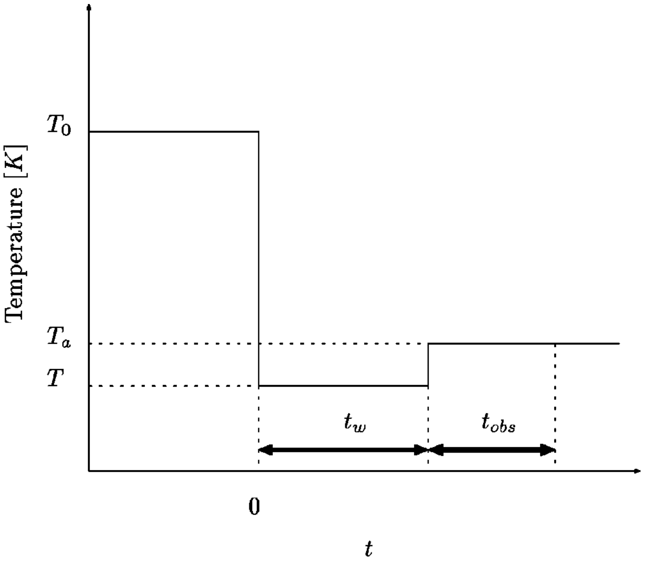

FIG. 3. Temperature control of the heat bath (two-step temperature shift process), where t is scaled by a constant C^{-1}.

we find for $t<t_w$,

$$p_i(T,t)=P_i^{eq}(T)+[P_i^{eq}(T_0)-P_i^{eq}(T)]e^{-\lambda(T)t}. \tag{11}$$

For $t>t_w$, the probability density relaxes to a new equilibrium state $P_i^{eq}(T_a)$ from the initial destribution $p_i(T,t_w)$. The probability density for this two-step temperature control process at time t_w+t_{obs}, $p_i(T_a,t_{obs};T,t_w)$, is expressed as

$$p_i(T_a,t_{obs};T,t_w)=P_i^{eq}(T_a)+[p_i(T,t_w)-P_i^{eq}(T_a)] \times e^{-\lambda(T_a)t_{obs}}. \tag{12}$$

We calculate the specific heat of the system in nonequilibrium using expressions (11) and (12) as

$$\begin{aligned} c(T,t_w,t_{obs}) &= \sum_i P_i^{eq}(T)C_i(T)\{1-\exp[-\lambda(T)(t_w+t_{obs})]\} \\ &+\sum_i P_i^{eq}(T_0)C_i(T)\exp[-\lambda(T)(t_w+t_{obs})] \\ &+\sum_i \frac{dP_i^{eq}(T)}{dT}E_i(T)(1-e^{-\lambda(T)t_{obs}})-t_{obs}\frac{d\lambda(T)}{dT} \\ &\times\sum_i \{P_i^{eq}(T_0)-P_i^{eq}(T)\}E_i(T) \\ &\times\exp[-\lambda(T)(t_w+t_{obs})], \end{aligned} \tag{13}$$

where $E_i(T)$ and $C_i(T)$ are the energy and the specific heat of each species, and both of them can be calculated from partition function $j_\alpha(T)$ $(\alpha=o,p)$. We find that the specific heat depends on two time scales, t_w and t_{obs}, and two temperatures, T_0 and T. Here we set $\alpha=3$, $T_0=\infty$ that are needed for numerical calculation.

The specific heat could be negative when t_w and t_{obs} are in an appropriate finite range, because of the fourth term on the right hand side of Eq. (13). This is due to the following reason: when the waiting time t_w is not long enough, the system cannot catch up with the temperature change and stay in nonequilibrium state, and then the system continues to release energy even after the observation is started.

C. Results

We first discuss two limiting behaviors of the specific heat obtained above. It is easy to show the following limits.

(i) Short waiting and observation time limit ($t_w\to 0$, $t_{obs}\to 0$);

$$\lim_{t_{obs}\to 0}\lim_{t_w\to 0} c(T,t_w,t_{obs})=\sum_i P_i^{eq}(T_0)C_i(T).$$

(ii) Long waiting and observation time limit ($t_w\to\infty$, $t_{obs}\to\infty$);

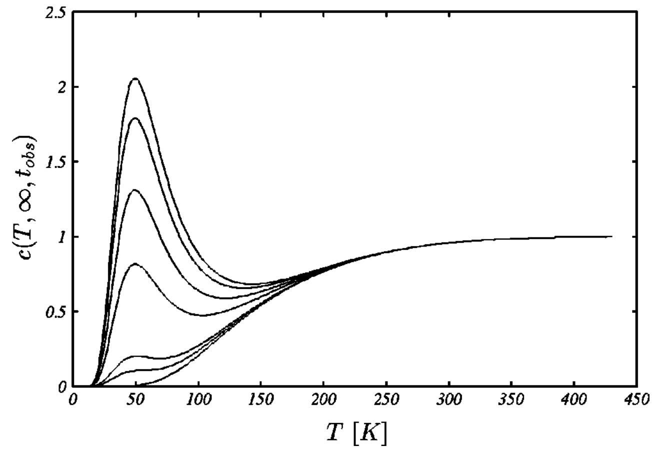

FIG. 4. Observation time dependence of $c(T,\infty,t_{obs})$, where $c(T,\infty,t_{obs})$ is the specific heat divided by Nk_B. The lines represent the specific heat for different observation times. They are $t_{obs}=1\times10^{-3}$, 5×10^{-2}, 1×10^{-1}, 5×10^{-1}, 1.0, 2.0, 5.0 from below. There are no differences for high temperatures.

$$\lim_{t_{obs}\to\infty}\lim_{t_w\to\infty} c(T,t_w,t_{obs})=\sum_i P_i^{eq}(T)C_i(T) +\sum_i \frac{dP_i^{eq}(T)}{dT}E_i(T).$$

The case (i) corresponds to the quenched expression Eq. (6) because $P_o^{eq}(T_0)=3/4$, $P_p^{eq}(T_0)=1/4$ for $T_0=\infty$. The case (ii) agrees with the annealed expression Eq. (5).

Second, we obtain the dependence of the specific heat on the observation time. Suppose that we wait for a long time after cooling, that is, we set $t_w=\infty$, then the specific heat becomes

$$c(T,\infty,t_{obs})=\sum_i P_i^{eq}(T)C_i(T)+\sum_i \frac{dP_i^{eq}(T)}{dT} \times E_i(T)(1-e^{-\lambda(T)t_{obs}}). \tag{14}$$

The behavior of the specific heat Eq. (14) is shown in Fig. 4. From this figure one can find that the system behaves as quenchedlike for a short time observation, while it behaves as annealedlike for a long time observation.

Third, to see whether the observation time is long enough or not, that is, whether the system is near the annealed one or not, we quantify an intermediate state between the quenched and the annealed systems. To quantify the degree of annealing, a new quantity $S(T,t_w,t_{obs})$ is introduced by

$$S(T,t_w,t_{obs})\equiv\frac{c(T,t_w,t_{obs})-c^Q(T)}{c^A(T)-c^Q(T)}. \tag{15}$$

From this quantity we can find that the system is the quenched one for $S=0$ and that it is the annealed one for $S=1$. The behavior of $S(T,t_w,t_{obs})$ at $T=40$ K on the t_w-t_{obs} plane is shown as a contour plot in Fig. 5. This figure shows that the narrow region where $S\simeq 0$ of this plane cor-

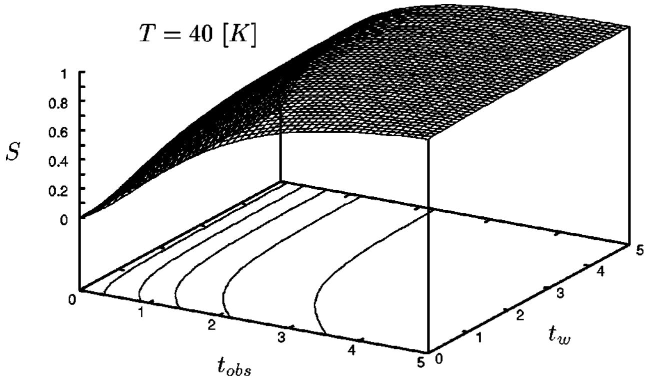

FIG. 5. The degree of annealing, $S(T,t_w,t_{obs})$, in the t_w-t_{obs} plane. This figure is contour plot of $S(40,t_w,t_{obs})$. The lines represent $S(40,t_w,t_{obs})=0.1$, 0.3, 0.5, 0.7, and 0.9 from left to right.

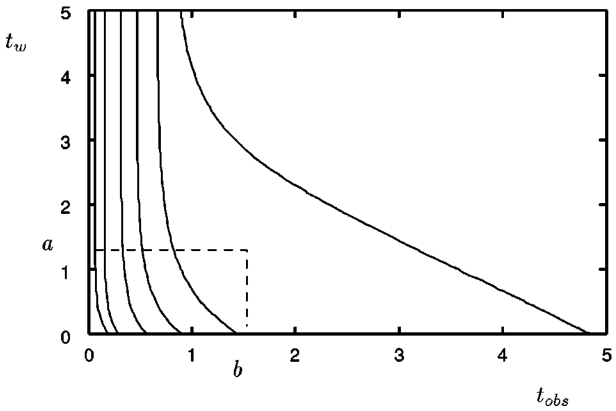

FIG. 6. The $S=0.5$ lines for $T=200$, 120, 80, 60, 40, and 20.25 from left to right. The temperature of $T=20.25$ corresponds to the boiling point of hydrogen. The quantities a,b correspond to a certain waiting time and a certain observation time, respectively.

responds to the quenched system and the wide region where $S\simeq 1$ to the annealed one. Moreover, we notice that the same degree of annealing can only be obtained for longer t_{obs} when t_w is short. Therefore it can be stated that the faster the system is cooled the easier it becomes the quenched one. It would correspond to the cooling rate dependence of the glass transition.

IV. CONCLUSION AND DISCUSSION

On the assumption that relaxation process is separated into fast and slow processes, we proposed a method to calculate the specific heat of the system in nonequilibrium. In this framework, we took account of the activated process of the representative point in the phase space and the temperature control of the heat bath, which play crucial roles. Since the calculated specific heat depends on two time scales, the waiting time t_w and the observation time t_{obs}, we can investigate the dependence of the specific heat on these times. We applied this method to the gaseous hydrogen system, which could be regarded as a two-basin system. The calculated specific heat of this system exhibited the quenchedlike specific heat when the observation time is short and the annealedlike one when the observation time is long. In addition, time regions corresponding to the quenched system and the annealed system are distinguished in the t_w-t_{obs} plane.

Now we draw lines of $S=0.5$ for various temperatures as shown in Fig. 6. We find that the $S=0.5$ line shifts from left to right with the temperature decrease. Here we consider a measurement that can be characterized by a set of two time scales, $(t_w,t_{obs})=(a,b)$. Supposing the line $S=0.5$ is a demarcation line between annealed and quenched systems, the point (a,b) in the t_w-t_{obs} plane shown in Fig. 6 corresponds to the annealed case for high temperatures, and it corresponds to the quenched case for low temperatures. Then the temperature at which the $S=0.5$ line passes the point (a,b) corresponds to the glass transition temperature T_g. As a result, we can conclude that the glass transition temperature depends on the procedure of a measurement.

Moreover, in a series of continuous measurements, the cooling rate is expressed as the function of two time scales, $v=v(t_w,t_{obs})$. If the cooling rate is changed, these two time scales will change and then the glass transition temperature T_g will also change. This situation corresponds to the cooling rate dependence in the glass transition. Details will be studied in a forthcoming paper.

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