Specific heat anomaly at the glass transition

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A general frame work is devised to obtain the specific heat of nonequilibrium systems described by the energy-landscape picture, where a representative point in the phase space is assumed to obey a stochastic motion which is governed by a master equation. The specific heat depends on the observation time and becomes quenched one for short observation time and annealed one for long observation time. In order to test its validity, the frame work is applied to a two-level system where the state goes back and forth between two levels stochastically. The specific heat is shown to increase from zero to the Schottky form as the observation time is increased from zero to infinity. The anomaly of specific heat at the glass transition is reproduced by a system with a model energy-landscape, where basins of the landscape form a one-dimensional array and jump rate between adjacent basins obeys a power-law distribution. It is shown that the glass transition can be understood as a transition from an annealed to a quenched system and that the glass transition temperature becomes lower when the observation time is increased. [DOI: 10.1063/1.1519237]

I. INTRODUCTION

Much understanding of the glass transition has been achieved in recent years. The mode coupling theory based on the mean field treatment of liquid dynamics predicted a dynamical transition in which structural arrest occurs at a critical temperature T_c.[1] It is now believed that T_c is much higher than the glass transition temperature T_g identified by thermodynamic measurements. Recently, a replica method was introduced to calculate the configurational entropy on the basis of the energy-landscape picture, and it was argued that the Kauzmann temperature T_K where the configurational entropy vanishes is an ideal glass transition temperature.[2]

It has been shown that the specific heat of glass forming materials exhibits a slight increment when T_g is approached from above and an abrupt decrement at T_g.[3] This behavior of the specific heat is opposite to the well-known anomaly observed in the second order phase transition, where the lower temperature phase has higher specific heat than the higher temperature phase. Although the analysis of the configurational entropy in the equilibrium treatment based on the replica method reproduces the desired change in the specific heat,[2] the transition occurs at T_K and not at T_g. Thus, it is still an open and challenging problem to explain the anomaly of the specific heat at the glass transition which is believed to occur between T_K and T_c. It is worth mentioning that in the MCT approach the anomaly of the specific heat is regarded as an artifact due to slow relaxation.[1]

In this paper, we propose a possible explanation for the sharp change in the specific heat at the glass transition on the basis of the energy-landscape picture.[4] Treating the dynamics of a representative point in the phase space by a stochastic master equation and assuming the density of states for the collective dynamics in each basin, we obtain the specific heat as a function of the observation time. We prove that the specific heat is given by a quenched average for short observation time and by an annealed average for long observation time and show that the glass transition can be understood as a transition from the annealed average to the quenched average due to the increase of the structural relaxation time beyond the observation time.

We organize this paper as follows: In Sec. II, we present the general frame work for the calculation of the specific heat for systems described by the landscape picture. We also show rigorously that the specific heat in the short and long observation times reduce to the quenched and annealed expressions, respectively. In order to test its validity, we apply the frame work to a system consisting of two levels where the state makes stochastic transition between these levels. We consider in Sec. III a model energy-landscape consisting of one-dimensional array of basins and investigate the temperature dependence of the specific heat when the jump rate between two adjacent basins obeys a power law distribution function which has been shown to hold in general.[5] We show that the specific heat increases slightly before the glass transition and decreases sharply at the glass transition when the temperature is reduced. This behavior is due to the transition from the annealed average above T_g and to the quenched average below T_g. We give summary of the results and discussion in Sec. IV.

II. FRAMEWORK

A. Basic equations

In the energy-landscape picture, the energy of each basin is assumed to be well defined. We denote by $P(\mathbf{a},t)$ the probability that the system is in basin $\mathbf{a}$ at time t. Then the energy of the system at time t is given by

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$$\langle E(t)\rangle = \sum_{\mathbf{a}} E_{\mathbf{a}} P(\mathbf{a},t), \tag{1}$$

where $E_{\mathbf{a}}$ is the energy of basin $\mathbf{a}$. The probability distribution $P(\mathbf{a},t)$ depends on details of the temperature control for the measurement. Here, we consider the control that the temperature $\hat{T}(t)$ at time t is given by

$$\hat{T}(t) = \begin{cases} T & (t<0) \\ T' & (0\leq t) \end{cases}. \tag{2}$$

The specific heat for a given observation time t_o is defined by the ratio of the increase of the energy and the temperature jump when the jump is infinitesimal. Namely, the specific heat at T is defined by[6]

$$C(T,t_o) = \lim_{T'\to T} \frac{\langle E(t_o)\rangle - \langle E(0)\rangle}{T'-T}. \tag{3}$$

The probability function $P(\mathbf{a},t)$ can be assumed to obey the master equation

$$\frac{\partial P(\mathbf{a},t)}{\partial t} = \sum_{\mathbf{b}\neq\mathbf{a}} w_{\mathbf{ab}} P(\mathbf{b},t) - \sum_{\mathbf{b}\neq\mathbf{a}} w_{\mathbf{ba}} P(\mathbf{a},t), \tag{4}$$

where $w_{\mathbf{ab}}$ is the transition rate from basin $\mathbf{b}$ to basin $\mathbf{a}$. The initial condition for

$$\mathbf{P}(t) \equiv \begin{pmatrix} \vdots \\ P(\mathbf{a},t) \\ \vdots \end{pmatrix}$$

is the equilibrium distribution at T

$$\mathbf{P}(0) = \mathbf{P}_{\mathrm{eq}}^{T},$$

where

$$\mathbf{P}_{\mathrm{eq}}^{T} = \begin{pmatrix} \vdots \\ P_{\mathrm{eq}}^{T}(\mathbf{a}) \\ \vdots \end{pmatrix}$$

and $P_{\mathrm{eq}}^{T}(\mathbf{a}) = Z_{\mathbf{a}}(T)/\Sigma_{\mathbf{b}} Z_{\mathbf{b}}(T)$. Here $Z_{\mathbf{a}}(T)$ is the partition function of basin $\mathbf{a}$ at T. Note the jump rate in Eq. (4) must satisfy the detailed balance

$$w_{\mathbf{ab}} Z_{\mathbf{b}}(\hat{T}) = w_{\mathbf{ba}} Z_{\mathbf{a}}(\hat{T}). \tag{5}$$

B. Quenched and annealed limits

The master equation Eq. (4) can be solved readily by using the eigenvectors and eigenvalues of a matrix $\mathbf{W}$, $(\mathbf{a},\mathbf{b})$ element of which is given by

$$\mathbf{W}_{\mathbf{ab}} = \begin{cases} w_{\mathbf{ab}} & (\text{when } \mathbf{a}\neq\mathbf{b}), \\ -\sum_{\mathbf{c}} w_{\mathbf{ca}} & (\text{when } \mathbf{a}=\mathbf{b}). \end{cases} \tag{6}$$

We denote eigenvectors and eigenvalues of $\mathbf{W}$ by $\{\mathbf{x}_i\}$ and λ_i, respectively,

$$\mathbf{W}\mathbf{x}_i = \lambda_i \mathbf{x}_i. \tag{7}$$

It is known that the matrix $\mathbf{W}$ is negative semidefinite and the largest eigenvalue $\lambda_0 = 0$ is nondegenerate and the corresponding eigenvector $\mathbf{x}_0$ is given by $\mathbf{P}_{\mathrm{eq}}^{T}$.[7] It is straightforward to show that

$$\mathbf{P}(t) = \mathbf{P}(0) + [(\mathbf{x}_0,\mathbf{0},\cdots) - \mathbf{X}][\mathbf{E}-\Lambda]\mathbf{X}^{-1}\mathbf{P}(0), \tag{8}$$

where $\mathbf{X}$ is a matrix defined by

$$\mathbf{X} = (\mathbf{x}_0,\mathbf{x}_1,\mathbf{x}_2,\cdots),$$

and Λ is a diagonal matrix whose (i,i) element is given by $\exp(\lambda_i t)$. We find that this solution gives the two limiting behaviors correctly (see Appendix)

$$\lim_{t_o\to 0} \mathbf{P}(t_0) = \mathbf{P}_{\mathrm{eq}}^{T} \tag{9}$$

and

$$\lim_{t_o\to\infty} \mathbf{P}(t_0) = \mathbf{P}_{\mathrm{eq}}^{T'}. \tag{10}$$

Therefore, the specific heat defined by Eq. (3) becomes the quenched value for the short observation time $t_o = 0$

$$C(T,0) = \lim_{T'\to T} \sum_{\mathbf{a}} \frac{E_{\mathbf{a}}(T') - E_{\mathbf{a}}(T)}{T'-T} P_{\mathrm{eq}}^{T}(\mathbf{a}) = \langle C_{\mathbf{a}}^{\mathrm{eq}}(T)\rangle, \tag{11}$$

and the annealed one for the long observation time $t_o = \infty$

$$\begin{aligned} C(T,\infty) &= \lim_{T'\to T} \frac{\Sigma_{\mathbf{a}} E_{\mathbf{a}}(T') P_{\mathrm{eq}}^{T'}(\mathbf{a}) - \Sigma_{\mathbf{a}} E_{\mathbf{a}}(T) P_{\mathrm{eq}}^{T}(\mathbf{a})}{T'-T} \\ &= \lim_{T'\to T} \frac{\langle E_{\mathbf{a}}(T')\rangle - \langle E_{\mathbf{a}}(T)\rangle}{T'-T}. \end{aligned} \tag{12}$$

Generally speaking, observation is made for a finite observation time. Therefore, if the characteristic time scale of the relaxation process becomes longer than the fixed observation time as the temperature is reduced, we expect that the specific heat undergoes a transition from the annealed value to the quenched value.

In order to quantify the observation time dependence, we introduce the degree of annealing defined by

$$S(T,t_o) = \frac{C(T,t_o) - C(T,0)}{C(T,\infty) - C(T,0)}. \tag{13}$$

Note that $S(T,t_o) = 0$ for the quenched system and $S(T,t_o) = 1$ for the annealed system.

C. Schottky and Zeller–Pohl specific heats

To test the preceding formalism, we first apply it to a two level system consisting of two levels at $E_1 = 0$ and $E_2 = \varepsilon$. The probabilities that the system is in each level is assumed to obey the master equations

$$\frac{dP(\mathbf{1},t)}{dt} = w_{12} P(\mathbf{2},t) - w_{21} P(\mathbf{1},t), \tag{14}$$

$$\frac{dP(\mathbf{2},t)}{dt} = w_{21} P(\mathbf{1},t) - w_{12} P(\mathbf{2},t). \tag{15}$$

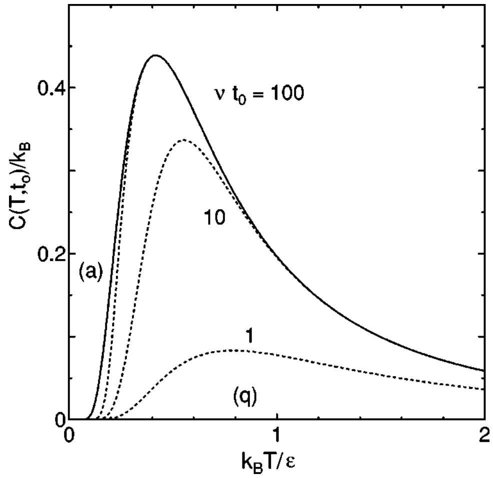

FIG. 1. Temperature dependence of the specific heat of a two level system for three observation times $\nu t_o = 1,10,100$. For simplicity, we set $\Delta = \varepsilon$ in this plot. (a) and (q) denote the annealed and quenched cases.

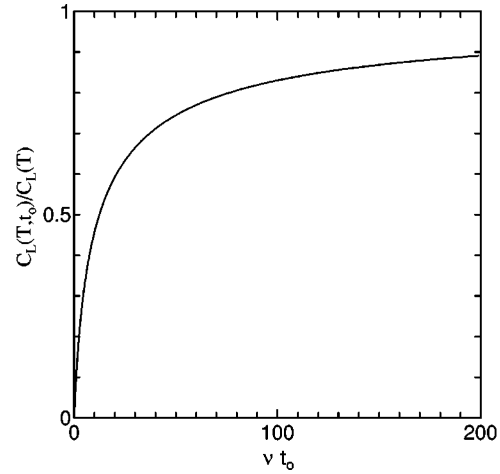

FIG. 2. The observation time dependence of the linear coefficient for the Zeller–Pohl specific heat obtained by the present method.

We assume a potential barrier between two levels of height Δ above level 2 and set

$$w_{12} = \nu e^{-\Delta/k_BT}, \quad w_{21} = \nu e^{-(\Delta+\varepsilon)/k_BT},$$

where ν is the attempt frequency serving as the scale of time, k_B is the Boltzmann constant. Solving the master equations (14) and (15) under the initial conditions

$$P(\mathbf{1},0) = P_{\rm eq}^T(\mathbf{1}) = \frac{1}{1+e^{-\varepsilon/k_BT}},$$

$$P(\mathbf{2},0) = P_{\rm eq}^T(\mathbf{2}) = \frac{e^{-\varepsilon/k_BT}}{1+e^{-\varepsilon/k_BT}},$$

we find $P(\mathbf{2},t)$, which determines the average energy as $\langle E(t)\rangle = \varepsilon P(\mathbf{2},t)$,

$$P(\mathbf{2},t) = P(\mathbf{2},0) + \left[P(\mathbf{1},0) - \frac{1}{1+e^{-\varepsilon/k_BT'}} \right] \times [1 - \exp\{-(1+e^{-\varepsilon/k_BT'})e^{-\Delta/k_BT'}\nu t\}]. \quad (16)$$

With use of the definition of the specific heat (3), we finally obtain

$$C(t_o) = k_B \left(\frac{\varepsilon}{k_BT}\right)^2 \frac{e^{-\varepsilon/k_BT}}{(1+e^{-\varepsilon/k_BT})^2} [1 - \exp\{-(1+e^{-\varepsilon/k_BT}) \times e^{-\Delta/k_BT}\nu t_o\}]. \quad (17)$$

Figure 1 shows the temperature dependence of the specific heat for several observation times. We can see that the specific heat changes gradually from the quenched value $C(T,0) = 0$ to the annealed one, i.e., the Schottky specific heat

$$C(T,\infty) = k_B \left(\frac{\varepsilon}{k_BT}\right)^2 \frac{e^{-\varepsilon/k_BT}}{(1+e^{-\varepsilon/k_BT})^2},$$

as the observation time is increased from 0 to ∞.

An immediate application of the two level system is the low temperature specific heat of glasses which has been shown by Zeller and Pohl[8] to depend linearly on temperature. This temperature dependence has been explained on the basis of the two level system as follows.[9] Let $n(\varepsilon)$ denote the density of states of two levels with energy separation ε. Then the specific heat of the system is given by

$$C_L = k_B \int_0^\infty n(\varepsilon) \left(\frac{\varepsilon}{k_BT}\right)^2 \frac{e^{-\varepsilon/k_BT}}{(1+e^{-\varepsilon/k_BT})^2} d\varepsilon. \quad (18)$$

At sufficiently low temperatures one can assume $n(\varepsilon) \simeq n(0)$ for ε's which contribute to the integral. Thus one finds the linear temperature dependence

$$C_L \simeq \frac{\pi^2}{6} n(0) k_B^2 T.$$

Using the observation-time dependent specific heat in Eq. (18), we find that the observation time dependence of the low temperature specific heat is written as

$$C_L(T,t_o) = C_L \left[1 - \frac{6}{\pi^2} \int_0^\infty \frac{x^2 e^x}{(e^x+1)^2} \times \exp\{-(1+e^{-x})e^{-\Delta/k_BT}\} t_o dx \right]. \quad (19)$$

Figure 2 shows the observation time dependence of $C_L(T,t_o)/C_L(T)$ where we assumed $\Delta = \varepsilon$ for simplicity of calculation.

III. GLASS TRANSITION IN A MODEL ENERGY-LANDSCAPE

A. Array of Einstein oscillators

We consider an energy-landscape in which basins form a one-dimensional array. We also assume that the dynamics within a basin is described by a set of oscillators and the density of states of basin $\mathbf{a}$ is denoted as $D_{\mathbf{a}}(\omega)$. Then the energy of basin $\mathbf{a}$ is given by

$$E_{\mathbf{a}}(T) = \int \frac{\hbar\omega}{2} \coth \frac{\hbar\omega}{2k_BT} D_{\mathbf{a}}(\omega) d\omega. \quad (20)$$

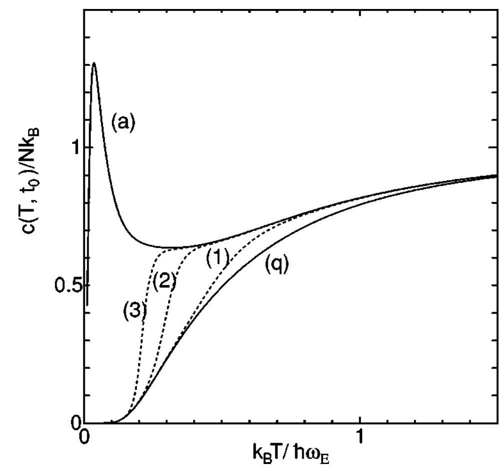

FIG. 3. The specific heat of a model energy-landscape consisting of 50 Einstein oscillators. The solid curves represent (q) the quenched system $t_o=0$ and (a) the annealed system $t_o=\infty$. The dotted curves correspond to (1) $\nu t_o=10^2$, (2) $\nu t_o=10^4$, and (3) $\nu t_o=10^6$. In this plot, we set $\Delta=3\hbar\omega_E$.

The probability distribution $P(\mathbf{a},t)$ obeys the master equation

$$\frac{dP(\mathbf{a},t)}{dt}=w_{\mathbf{aa-1}}P(\mathbf{a-1},t)+w_{\mathbf{aa+1}}P(\mathbf{a+1},t)-(w_{\mathbf{a-1a}}+w_{\mathbf{a+1a}})P(\mathbf{a},t). \tag{21}$$

We assume the jump rate from basin **a** to basin **b** is given by

$$w_{\mathbf{ba}}=\nu\exp\left(-\frac{F_A(T)-F_{\mathbf{a}}(T)}{k_BT}\right), \tag{22}$$

where $F_{\mathbf{a}}(T)$ is the local free energy of basin **a** and $F_A(T)=\max\{F_{\mathbf{a}}(T),F_{\mathbf{b}}(T)\}+\Delta$ is the free energy of the transition state. Here Δ is a positive constant introduced as an energy barrier. As an example, we employed the density of state of the Einstein oscillator and assumed that the Einstein frequency of each basin is distributed uniformly between ω_E and $3\omega_E$. We solved numerically the master equation (21) for 50 basins with the periodic boundary condition under the initial condition

$$P(\mathbf{a},0)=\frac{Z_{\mathbf{a}}(T)}{\Sigma_{\mathbf{b}}Z_{\mathbf{b}}(T)},$$

where $Z_{\mathbf{a}}(T)$ is the partition function of basin **a**. The specific heat is calculated from Eq. (3) for several observation times which is shown in Fig. 3. For a given observation time, the specific heat shows a sharp drop at a critical temperature with slight increase before the drop. This behavior of the specific heat is qualitatively the same as the system in which all basins are mutually connected.[10]

Figure 4 shows the temperature dependence of the degree of annealing for several observation times. At the temperature where the specific heat decreases sharply, the degree of annealing shows a transition from the annealed state to the quenched state.

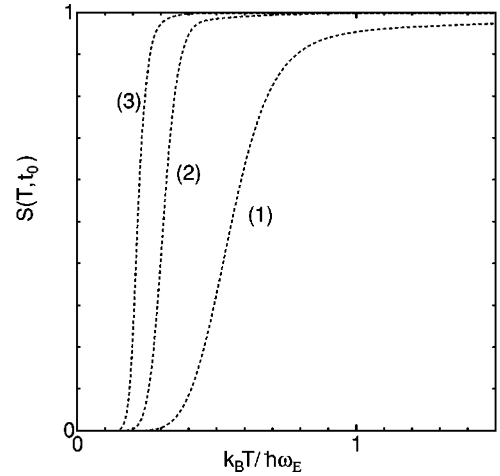

FIG. 4. Temperature dependence of the degree of annealing for three observation times shown by the dotted curves in Fig. 3: (1) $\nu t_o=10^2$, (2) $\nu t_o=10^4$, and (3) $\nu t_o=10^6$.

B. Power law distribution

On the basis of the analysis of single particle dynamics in the supercooled liquid, Odagaki has proposed a unified view for the glass transition singularities.[11,12] In the trapping diffusion model, it is concluded that the jump rate for a single particle dynamics obeys a power law distribution[5,11,12]

$$\Phi(w)=\begin{cases}\dfrac{s+1}{w_0}\left(\dfrac{w}{w_0}\right)^{\rho}, & (\text{ for } 0\leqslant w\leqslant w_0)\\ 0 & (\text{otherwise}),\end{cases} \tag{23}$$

where the exponent parameter is related to the configurational entropy $s_c(T)$ as

$$\rho=\frac{Ts_c(T)-T_gs_c(T_g)}{T_gs_c(T_g)}. \tag{24}$$

In the actual calculation, we simplify this expression to

$$\rho=\frac{T-T_g}{T_g-T_0}, \tag{25}$$

assuming that $Ts_c(T)\propto T-T_0$ with the Vogel–Fulcher temperature $T_0\sim T_K$. We consider the factor $\nu e^{-\Delta/k_BT}$ in Eq. (22) is distributed according to Eq. (23) with exponent (25).

Figure 5 shows the temperature dependence of the specific heat for several observation times. We again observe a transition compatible with the glass transition. As we show in Fig. 6, the transition is considered as one from the annealed state to the quenched state.

IV. SUMMARY AND DISCUSSION

In this paper we have presented a frame work for calculation of the specific heat of systems described by the energy-landscape picture. The essential point in this frame work is in the assumption of separation of dynamics, one for the fast dynamics within a basin of the landscape and the other for the slow dynamics between basins described by a stochastic model. This view has been supported by a recent computer simulation.[13] The dynamics within a basin can be

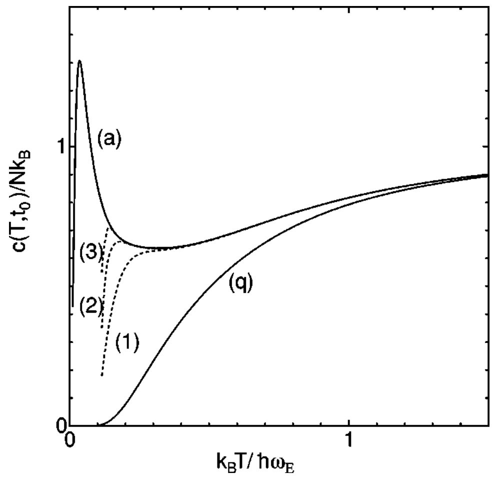

FIG. 5. The specific heat of a system described by a model energy-landscape consisting of 50 Einstein oscillators with power law distribution. In this plot, we set $T_0=0.1\hbar\omega_E/k_B$ and $T_g=0.2\hbar\omega_E/k_B$. The solid curves represent (q) the quenched system $t_o=0$ and (a) the annealed system $t_o=\infty$. The dotted curves correspond to (1) $\omega_0 t_o=10^2$, (2) $\omega_0 t_o=10^4$, and (3) $\omega_0 t_o=10^6$.

characterized by the density of states. For the density of states we selected the Einstein model in this paper for simplicity, but it can be easily generalized to more general cases, including the density of states consistent to the Boson peak. In general, the characteristic time for the stochastic dynamics becomes slower and slower as the temperature is reduced and could exceed the observation time at a characteristic temperature. Above this characteristic temperature, the system can survey many basins and the observed value of a physical quantity is given by the average over these basins, that is by the annealed average. Below the characteristic temperature, the representative point in the phase space hardly moves out from the initial basin in the observation time and the observed value is determined by the basin, that is by the quenched average. Thus we can expect a transition from the annealed average to the quenched average at the characteristic temperature which can be considered as the explanation for the glass transition.

The frame work was applied for a few model systems. First we analyzed effect of the slow transition rate on the specific heat of a two level system and obtained the observation time dependence of the T-linear Zeller–Pohl specific heat of glasses. We also studied the specific heat of a model energy-landscape and showed that the specific heat behaves consistently to observations for the glass transition,[3] which includes the slight increase of the specific heat just above the transition. In particular, it is important to note that the power law distribution of jump rates can explain the dynamic singularities[11,12] as well as the thermodynamic singularity and thus the energy-landscape picture gives a basis for the unified concept for understanding the glass transition.[14]

In the present paper, we consider a simplified setting of the temperature control. We can easily generalize the frame work for more realistic temperature control, which includes measurements along a cooling process or a heating process after quenching. Analysis in this line will be presented elsewhere.[15]

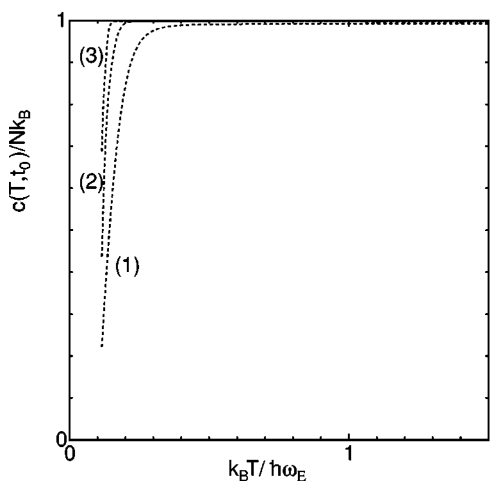

FIG. 6. Temperature dependence of the degree of annealing for three observation times shown by the dotted curves in Fig. 5: (1) $\omega_0 t_o=10^2$, (2) $\omega_0 t_o=10^4$, and (3) $\omega_0 t_o=10^6$.

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APPENDIX: LIMITING BEHAVIOR

It is self-evident that the second term on the right-hand side of Eq. (8) vanishes at $t=0$ since $\Lambda=\mathbf{E}$ at $t=0$. In the limit of $t=\infty$, all elements of Λ vanishes except for $\lambda_{11}=1$. Thus

$$\mathbf{P}(\infty)=(\mathbf{x}_0,\mathbf{0},\cdots)\mathbf{X}^{-1}\mathbf{P}(0).$$

We can easily show that the first row of $\mathbf{X}^{-1}$ is $(1,1,1,\cdots)$. Therefore, we have

$$\mathbf{P}(\infty)=\mathbf{x}_0,$$

since $\Sigma_{\mathbf{a}}P(\mathbf{a},0)=1$.

[1] W. Götze, in *Freezing and the Glass Transition in Liquids*, edited by J. P. Hansen, D. Levesque, and J. Zinn-Just (North-Holland, Amsterdam, 1989), p. 287; W. Götze, J. Phys.: Condens. Matter **11**, A1 (1999).
[2] M. Mézard and G. Parisi, J. Chem. Phys. **111**, 1076 (1999).
[3] O. Yamamuro, I. Tsukushi, A. Lindqvist, S. Takahara, M. Ishikawa, and T. Matsuo, J. Phys. Chem. B **102**, 1605 (1998).
[4] A. Angell, Nature (London) **393**, 521 (1998).
[5] T. Odagaki and A. Yoshimori, J. Phys.: Condens. Matter **12**, 6509 (2000).
[6] T. Tao, A. Yoshimori, and T. Odagaki, Phys. Rev. E **64**, 046112 (2001).
[7] T. Odagaki and M. Lax, Phys. Rev. B **26**, 6480 (1982); **24**, 5284 (1981).
[8] R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).
[9] P. W. Anderson, B. I. Halperin, and C. M. Verma, Philos. Mag. **25**, 1 (1972).
[10] T. Tao, A. Yoshimori, and T. Odagaki, Phys. Rev. E **66**, 041103 (2002).
[11] T. Odagaki and Y. Hiwatari, Phys. Rev. A **41**, 929 (1990).
[12] T. Odagaki, Phys. Rev. Lett. **75**, 3701 (1995); T. Odagaki, Prog. Theor. Phys. Suppl. **126**, 9 (1997).
[13] L. Angelani, G. Parisi, G. Ruocco, and G. Viliani, Phys. Rev. E **61**, 1681 (2000).
[14] T. Odagaki, presented at International conference on ''Unifying Concepts in Glass Physics,'' ROMA 2002 (Rome, 2002).
[15] T. Tao, A. Yoshimori, and T. Odagaki (unpublished).