

Modeling dynamically heterogeneous coupled relaxations

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A model describing dynamically heterogeneous relaxation in complex coupled systems is presented. The model predicts the splitting of a high-temperature single Debye relaxation to a low-temperature bimodal relaxation. The bimodal process shows a crossover from a Debye-type relaxation to an approximately stretched-exponential relaxation. Some general features of relaxation in complex systems emerge from the predictions of the model, and a comparison of the model with experiments is reported.

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I. INTRODUCTION

The relaxation dynamics of molecules and other mutually interacting densely packed embodies many challenging problems of current interest in many fields, including the glass transition, polymer viscoelasticity, and solid-state ionics [1,2]. These issues are difficult to treat because of the presence of several complicating factors. The foremost one is the many-body effect, sometimes loosely referred to as cooperativity, coupled dynamics, intermolecular constraints, or cage effect, that is very difficult to accurately describe. There are some models [3–5] that identify the cage effects or cooperative dynamics from the many-body molecular interaction as responsible for the nonexponential relaxation function [6,7] and the dynamically heterogeneous nature of the relaxation, i.e., the existence of fast and slow relaxing units [8]. Recent experiments employing nuclear-magnetic-resonance, dielectric, and optical techniques suggest the presence of dynamically distinguishable subensembles [9–12]. This important finding has recently been reviewed [13].

In principle, if the Hamiltonian that includes all interactions of the system is used, the nonexponentiality, dynamic heterogeneity, and other properties of the relaxation of the coupled units would emerge. Although such an approach is not possible at this time, molecular-dynamics simulations do indicate dynamical heterogeneity in a glass-forming system [14]. In this paper, we consider a model system of coupled fast and slow relaxing units. The purpose is to calculate the results of this paper, which has built in some features of dynamical heterogeneity. The model is also applicable to other problems that consider the slow down of the relaxation of a test molecular unit coupled to a nonrelaxing molecular environment.

II. MODEL

Under the influence of a small enough time-dependent external field $F(t)$, the linear response of all the units located at space point \vec{x} and at time t is described by a dynamic variable, $\xi(\vec{x}, t)$, such as polarization. The energy density associated with this response is $\xi(\vec{x}, t)^2/2\delta(\vec{x})$ [15], where $\delta(\vec{x})$ is the difference between the static and high-frequency limit susceptibilities, such as the dielectric susceptibility and

the compliance in dielectric and mechanical measurements, respectively. According to the Debye theory, the change of $\xi(\vec{x}, t)$ with time (i.e., relaxation) of the units is proportional to $\xi(\vec{x}, t)/\tau_D(\vec{x})$, and the energy dissipated per unit time is $\xi(\vec{x}, t)^2/\delta(\vec{x})\tau_D(\vec{x})$ [15], where $\tau_D(\vec{x})$ is the relaxation time.

Because of thermal agitation, the units move randomly in their interaction field and scattering processes will occur that give rise to the energy exchange between them. Thus, there is a spatial energy flux, $\vec{i}_E(\vec{x}, t)$, between different units. Although there is an energy exchange between two units for any single-scattering process at the equilibrium state, it is expected that the net energy exchange is zero, [$\vec{i}_E(\vec{x}, t) = 0$], for relatively long times compared with the time interval between two successive scattering processes. If the energy difference between the units is $\Delta(\xi(\vec{x}, t)^2/2\delta(\vec{x}))$, there will be a net energy exchange between the units so that $\vec{i}_E(\vec{x}, t)$ will be proportional to both the number of scattering processes per unit time, $v_S(\vec{x})$, and $\Delta(\xi(\vec{x}, t)^2/2\delta(\vec{x}))$, i.e., $\vec{i}_E(\vec{x}, t) \propto v_S(\vec{x})\Delta(\xi(\vec{x}, t)^2/2\delta(\vec{x}))$. The approximate replacement of the energy difference by the spatial differential form, $\nabla(\xi(\vec{x}, t)^2/2\delta(\vec{x}))$, leads to,

$$\vec{i}_E(\vec{x}, t) = -D_E(\vec{x})\nabla\left(\frac{\xi(\vec{x}, t)^2}{2\delta(\vec{x})}\right), \quad (1)$$

where $D_E(\vec{x})$ is the coupling constant whose sign is always positive. The negative sign in Eq. (1) indicates that the direction of the energy flux points from the units with higher energy to those with lower energy. As the temperature increases, the random motions of the units become stronger, so that v_S and consequently $D_E(\vec{x})$ will increase.

It is worth noting that Eq. (1) has the same form as the well-known diffusion law [16]. However, while thermal energy is transported during a thermal diffusion process, Equation (1) describes the energy exchange between different interaction units. To know whether $D_E(\vec{x})$ has a definite relation with the thermal diffusion coefficient requires further study.

Without losing generality, let the external field

$$F(t) = \begin{cases} F_0, & t < 0 \\ 0, & t \geq 0. \end{cases}$$

For a closed interface S around a unit, the conservation of energy requires that,

$$E(0) = \int_V \frac{\xi(\vec{x}, t)^2}{2\delta(\vec{x})} dV + \int_0^t \left(\oint_S \vec{i}_E(\vec{x}, t') d\vec{s} \right) dt' + \int_V \left[\int_0^t \frac{\xi(\vec{x}, t')^2}{\delta(\vec{x}) \tau_D(\vec{x})} dt' \right] dV, \quad (2)$$

where $E(0)$ is the energy of the unit at $t=0$, V is the volume closed by S , and the positive direction of $d\vec{s}$ is along the out normal of the interface. By differentiating all terms in Eq. (2) with respect to t , and by using the Gaussian theorem [16], the following key equation of the model is obtained:

$$\frac{\partial}{\partial t} \left(\frac{\xi(\vec{x}, t)^2}{2\delta(\vec{x})} \right) + \frac{1}{\tau_D(\vec{x})} \frac{\xi(\vec{x}, t)^2}{\delta(\vec{x})} = D_E \nabla^2 \left(\frac{\xi(\vec{x}, t)^2}{2\delta(\vec{x})} \right). \quad (3)$$

This expression suggests two possible dissipation ways: (1) the dissipation depicted by the term $[\xi(\vec{x}, t)^2]/[\delta(\vec{x})\tau_D(\vec{x})]$, called self-dissipation; and (2) the energy of a unit first transferred by the term $D_E \nabla^2(\xi(\vec{x}, t)^2/2\delta(\vec{x}))$ to others and then dissipated by the term $[\xi(\vec{x}, t)^2]/[\delta(\vec{x})\tau_D(\vec{x})]$, called cooperative dissipation. This equation describes the coupling of the slow and the fast relaxation units. If the coupling is weak enough, i.e., $D_E(\vec{x}) \rightarrow 0$, then the coupled relaxation will reduce to individual relaxations, a case that will not be discussed in this paper.

For the field $F(t)$ indicated above, the normalized relaxation function of the whole system $\varphi(t)$ obtained by integrating $\xi(\vec{x}, t)$ over space, is given by

$$\varphi(t) = \frac{\int \xi(\vec{x}, t) d^3x}{\int \xi(\vec{x}, 0) d^3x}. \quad (4)$$

As mentioned above, there is an energy flux, \vec{i}_E , from the slow to the fast units because the relaxation rate of the slow units is slower than that of the fast ones. If the energy transported out from a slow unit is much larger than that dissipated by the unit itself, then the self dissipation of the slow unit may be neglected. In this paper, we will focus on this case, i.e., strong coupling between the fast and the slow units so that $D_E(\vec{x})$ has a relatively large value. In this situation, the following simplifications will be made in Eq. (3) to make it amenable for numerical calculations. $\tau_D(\vec{x})$ is taken to have the same value τ_D for all the fast units. The parameter $\delta(\vec{x})$ is equal to a constant value δ for both the fast and the slow units. The coupling coefficient, $D_E(\vec{x})$, is taken to be independent of \vec{x} . Then, Eq. (3) can be rewritten as

$$\frac{\partial \xi(\vec{x}, t)^2}{\partial t} + 2\theta \frac{\xi(\vec{x}, t)^2}{\tau_D} = D_E \nabla^2 [\xi(\vec{x}, t)^2], \quad (5)$$

$$\theta = \begin{cases} 1 & \text{for fast units,} \\ 0 & \text{for slow units.} \end{cases}$$

III. RESULTS AND DISCUSSIONS

In principle, Eq. (5) could be solved by numerical methods for the whole system. If the fast units are distributed uniformly in space, then the solution of $\xi(\vec{x}, t)$ is periodic in

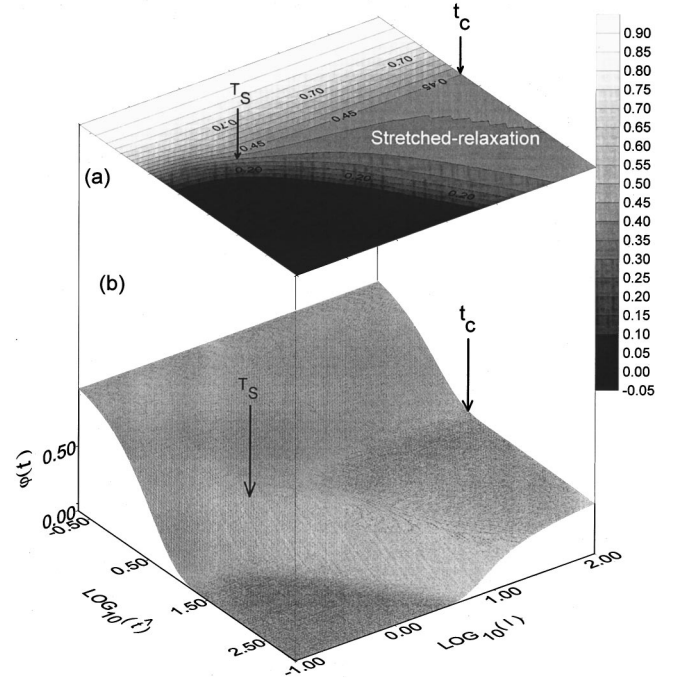


FIG. 1. Calculated relaxation function, $\phi(\hat{t})$, plotted as a contour plot (a) and a surface plot (b), respectively, as functions of normalized time $\hat{t} \equiv t/\tau_D$ and l for $c=0.6$.

space and symmetric about any fast unit. For the sake of simplicity, we only focus on this case and the calculations will be carried out in one dimension assuming that the smallest period between the fast units is L . With this approach, we only need to calculate $\xi(\vec{x}, t)$ within the range $0 \leq x \leq L/2$ for a fast unit with size, L_F , which is placed at the origin. The numerical method for solving Eq. (5) is the classical-differential method [17] (see Appendix for details).

The partial-differential Eq. (5) can be normalized to a dimensionless equation, $\partial \xi(\hat{x}, \hat{t})^2 / \partial \hat{t} + 2\theta \xi(\hat{x}, \hat{t})^2 = \nabla^2 [\xi(\hat{x}, \hat{t})^2]$, by expressing it in terms of the dimensionless quantities, $\hat{t} \equiv t/\tau_D$, $\hat{x} \equiv \vec{x}/\sqrt{D_E \tau_D}$, where $\nabla^2 = \partial^2 / \partial \hat{x}^2 + \partial^2 / \partial \hat{y}^2 + \partial^2 / \partial \hat{z}^2$. Thus, the solutions of Eq. (5) depend on two dimensionless parameters: $c \equiv L_F/L$, and $l \equiv L/\sqrt{D_E \tau_D}$, where c represents the ratio of the relaxation strengths of the fast and the slow relaxations, and l stands for the spatial coupling strength between the units. Here, we shall focus our attention on the dependence of the relaxation function, $\varphi(t)$, on l .

In Fig. 1, $\varphi(t)$ for $c=0.6$ is plotted as a function of $\log_{10}(t/\tau_D)$ and $\log_{10}(l)$ in two different ways. In this manner, contour and surface plots of the same data of $\varphi(t)$ are obtained. An important characteristic of $\varphi(t)$ is that it exhibits a crossover from a faster decay to a slower one occurring at t_c , i.e., a bimodal relaxation for large $l (> 10^{-0.5})$ corresponding to small D_E . The crossover time t_c is almost independent of l . However, when l is small enough ($< 10^{-0.5}$), the bimodal relaxation transforms to a single-mode relaxation. These results mean that there is a splitting from a high-temperature single relaxation into a low-temperature bimodal process at a certain temperature T_S since $l \sim D_E^{-1/2}$ and

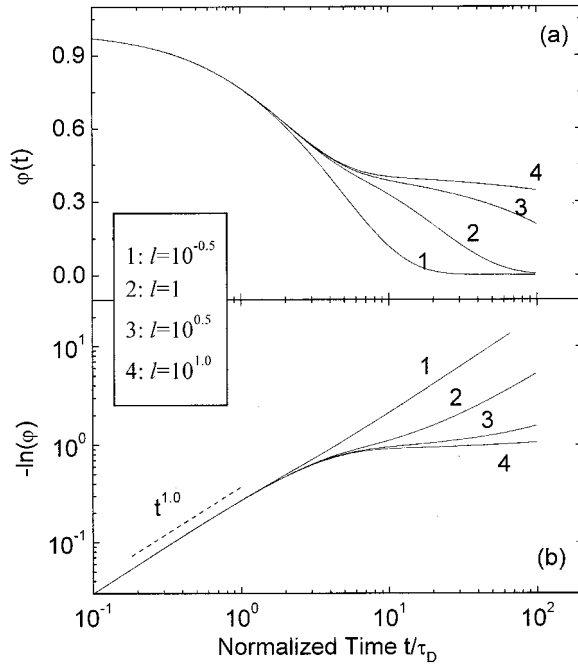


FIG. 2. Calculated relaxation function, $\phi(t)$, in (a) and $-\ln[\phi(t)]$ in (b) vs the normalized time, t/τ_D , for four discrete values of l with $c=0.6$.

D_E increases with temperature, as shown in Fig. 1(a) and 1(b).

In Fig. 2, the decay function $\phi(t)$ is plotted against $\log_{10}(t/\tau_D)$ for four different values of l . We have plotted the same data in two ways, $\phi(t)$ vs $\log_{10}(t/\tau_D)$ [Fig. 2(a)] and $\log_{10}(-\ln \phi)$ vs $\log_{10}(t/\tau_D)$ [Fig. 2(b)]. If $\phi(t)$ is assumed to be a stretched-exponential function,

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right], \quad (6)$$

then the slope of $\log_{10}(-\ln \phi)$ vs $\log_{10}(t/\tau_D)$ is just equal to the stretched factor β .

Although a crossover can be seen in both Figs. 2(a) and 2(b), the latter figure shows better the crossover from a linear-exponential decay to an approximately stretched-exponential decay for large values of l , in a similar way as that observed in Fig. 1(a). Moreover, the value of β increases with either the decrease of l or increase of D_E , i.e., with temperature.

In this paper, we have assumed that the self dissipation of the slow units is so small, compared with the energy transported out from them, that it could be neglected. In this situation, the only dissipation of the whole system originates from the fast units. These units will relax first, and then the slow units will transport their energy to the fast units where it will be dissipated. Therefore, at short time, the fast units will relax independently. A Debye relaxation will occur because the energy difference between the fast and the slow units is very small and, consequently, the energy exchange between them is negligible. However, at long time, both the energy difference and the energy exchange become larger, so that the relaxation of the fast units will be modified by the

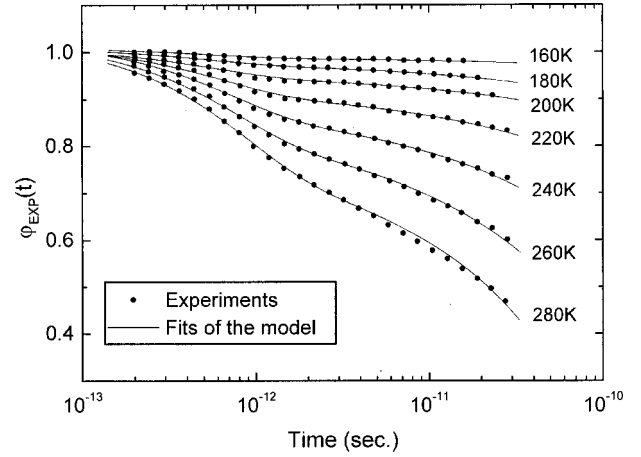


FIG. 3. Comparisons of the present model with the experimental data of polybutadiene (PB) from Ref. [19] at different temperatures.

energy transported to them from the slow units. Conversely, the modified relaxation of the fast units will affect the energy transport of the slow units and their relaxation dynamics. As a consequence, the stretched relaxation after \hat{t}_c is a coupled relaxation between the fast and the slow units. The crossover from the fast Debye-like mode of relaxation to the slow relaxation mode corresponds to a transformation from the independent relaxation of the fast units to a coupled relaxation involving both the fast and the slow units. For relatively weak coupling between the fast and the slow units, i.e., small D_E , there exists a crossover time \hat{t}_c after which the relaxation is slowed down in such a way that it is described by a stretched exponential decay that has a much larger relaxation time. Stretched exponential decay mean that the effective relaxation time, $\tau_{\text{eff}} = \tau^\beta t^{1-\beta}$ [1], increases with time. According to our paper, only the fast units intervene in the relaxation occurring at short time. With time, the slow units near the fast units first, and then more and more slow units located far away from the fast units will relax through the cooperative dissipation. This means that the spatial correlated region of relaxation increases and energy transport from the region to the fast units will need long time. As a result, τ_{eff} becomes larger with time so that the relaxation shows an approximately stretched-exponential feature.

The results obtained from numerical calculations bear strong resemblance to those of the coupling model [3,4]. The key feature of the coupling model is the rather sharp crossover, at some time \hat{t}_c , from independent relaxation with an approximately linear-exponential time dependence, $\exp(-t/\tau_0)$, to a coupled or cooperative relaxation with a stretched-exponential relaxation function, $\exp[-(t/\tau_0)^{1-n}]$. There is support of this crossover from experimental data [18–22]. This feature is reproduced by the results of the model and other models based on nonlinear Hamiltonian dynamics [4]. In the present paper, the parameter D_E determines the coupling strength, and hence, the magnitude of the coupling parameter n ($\beta \equiv 1 - n$) of the coupling model [Fig. 2(b)]. The crossover at t_c gives rise to the relation, $\tau = [t_c^{-n} \tau_0]^{2/(1-n)}$, which has proven to be prolific in applications [23]. Thus, we think that the consequences of the

TABLE I. Fitting parameters of the present model for the fits of experimental data of polybutadiene (PB) from Ref. [19] at different temperatures.

Temperature (K)	τ_D (sec)	L^2/D_E (sec)	c	φ_{BAC}
280	4.5×10^{-13}	1.64×10^{-10}	0.334	0.025
260	4.1×10^{-13}	2.78×10^{-10}	0.263	0.025
240	3.8×10^{-13}	6.67×10^{-10}	0.185	0.025
220	3.5×10^{-13}	2.01×10^{-9}	0.121	0.017
200	3.3×10^{-13}	6.68×10^{-9}	0.071	0.001
180	3.0×10^{-13}	1.05×10^{-8}	0.042	0.009
160	3.1×10^{-13}	1.25×10^{-7}	0.024	0.008

present model are consistent with the physical picture proposed by the coupling model.

In Fig. 3, comparisons of the present paper with the experimental data reported for polybutadiene (PB) in Ref. [19] are given. $\varphi_{\text{EXP}}(t) = \varphi(t) + \varphi_{\text{BAC}}$, where $\varphi(t)$ is calculated from Eqs. (4) and (5) with the three fitting parameters, τ_D , L^2/D_E , and c . The values φ_{BAC} given in the last column of Table I represent a very small background that let the fits look better. In the fitting, we find that L and D_E are not independent-fitting parameters. Moreover, L^2/D_E and c determine the long-time stretched-exponential relaxation while τ_D and c control the short-time fast process. The four fitting parameters for the data of Ref. [19] at seven temperatures are shown in the Table I. The fits of the present paper to the experiments, shown in Fig. 3, look quite good.

The present paper predicts a transformation from the bimodal to the single-mode relaxation when the coupling between the fast and the slow units is strong enough, i.e., for large values of the coupling constant D_E . As mentioned above, when temperature goes up, D_E increase. Therefore, the calculated single-mode relaxation corresponds to higher temperature, and it split into a bimodal relaxation as temperature decreases. In other words, the heterogeneity will diminish with increasing temperature. This temperature dependence seems to be supported by experiments. For example, light scattering [24], dielectric relaxation [25–27],

nuclear-magnetic-resonance [28], and molecular-dynamics simulations [29] show that the Kohlrausch-Williams-Waff exponent, β for OTP (o-terphenyl) and other small molecule glass formers increases with temperature. One key point of the present paper is that there are two kinds of coupled relaxation units, one fast and the other slow. We would like to point out, with two relaxation times assumed, a recent work based upon the kinetic Ising model on an alternating isotopic chain [30] gives the Nagels' scaling law [25] for the susceptibility.

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APPENDIX

For one dimension, the zone between 0 and $L/2$ is divided into n small segments with length $\Delta x = L/2n$ (usually n is taken to be 1000), and we label the segments as $1, 2, \dots, i, \dots, n$ from the left end to the right end. Based on the classical-differential method [17], we obtain the following differential equations for the numerical calculation of the partial-differential Eq. (5):

$$\xi(i, t + \Delta t)^2 = \xi(i, t)^2 \left(1 - 2\theta \frac{\Delta t}{\tau_D} \right) + \frac{\Delta t}{\Delta x^2} D_E [\xi(i+1, t)^2 + \xi(i-1, t)^2 - 2\xi(i, t)^2], \quad i = 1, \dots, n,$$

where Δt is the calculation time step. The convergence conditions of the above equation are $\Delta t \leq 0.5 \Delta x^2 / D_E$ and $\Delta t \leq 0.1 \tau_D$. Moreover, the boundary condition is the symmetric condition, i.e., $\xi(0, t) = \xi(2, t)$ and $\xi(n+1, t) = \xi(n-1, t)$. The initial condition is $\xi(i, 0) = 1$, $i = 1, \dots, n$.

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