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Quenching of a Brownian oscillator

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An asymptotic analysis of a classical Brownian oscillator in a fluid with diverging viscosity (glass-forming melt) is presented. For a quench-heating cycle, which is slow on the scale of the oscillator frequency, an explicit expression for the temperature-dependent specific heat, $c(T)$, is derived. In appropriate variables the shape of the $c(T)$ curve is universal, being insensitive to the details of the temperature dependence of the viscosity. The values of quenched-in energy and entropy also are obtained. [S1063-651X(99)07404-8]

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Starting from the early days of condensed-matter physics, important insight into thermodynamic behavior was gained through the analysis of simple oscillators — see, e.g., Ref. [1]. Kinetics of a harmonic oscillator in a thermal bath, described in terms of Brownian motion, also received much attention [2,3] as models of various stochastic processes.

The intent of the present paper is the analysis of a classical Brownian oscillator (or an array of such oscillators) placed in a fluid with a viscosity which rapidly increases with the lowering of temperature. The latter is typical for a glass-forming melt [4,5]. At low temperatures the behavior of such oscillators is expected to become nonergodic, with dramatic thermodynamic consequences. For other models which exhibit aging, the importance of the oscillator descriptions was also recognized [6].

We distance ourselves from the attempts of a first-principles explanation of the complicated behavior of the viscosity in glass-forming fluids. Rather, we intend to show that once the viscosity is known, the specific heat and other thermodynamic properties of the Brownian oscillator can be obtained in a general form, bearing certain similarities to what is known as a ‘‘calorimetric glass transition (GT)’’ [4,5]. (The similarity, however, will not be pursued in the present work, except for the occasional use of terminology.) Remarkably, when cast in appropriate variables the specific heat curves turn out to be insensitive to the details of the temperature dependence of the viscosity, but only because this viscosity virtually diverges when the system is cooled sufficiently low.

Below we shall analyze the thermodynamic behavior of a Brownian oscillator via a detailed study of its kinetics in a cooled and reheated system with the viscosity of the aforementioned kind. The Fokker-Planck-type equation which describes a Brownian oscillator, at least formally, is an exactly solvable one [2,3,7]. This feature will be exploited in the present work, although it will be seen that much more important is the further possibility of an asymptotic treatment which allows one to establish certain universal features in the nonequilibrium thermodynamics of the oscillator.

A Langevin equation for the position, x, of a Brownian oscillator of a unit mass has the form

$$\ddot{x}+\gamma\dot{x}+\omega_0^2x=\xi(t). \tag{1}$$

Here ω_0 and γ are the frequency and damping, respectively, and $\xi(t)$ is the random force with intensity given by the Einstein relation (fluctuation-dissipation theorem) $\langle\xi(t)\xi(t')\rangle=2\gamma T\delta(t-t')$ with the temperature measured in units of the Boltzmann constant. At high temperatures, damping is assumed to have an approximately constant small value, $\gamma_0\ll\omega_0$, but with lowering of T the dimensionless function $\tilde{\gamma}=\gamma(T)/\gamma_0$ becomes large. In fact, during the course of a quench, damping (thus viscosity) acquires very large (effectively infinite) values in a finite time interval—a situation typical for a glass-forming fluid.

Equation (1) will be treated for a macroscopically slow quench with a rate $q\equiv-\dot{T}\ll\gamma_0T$, with subsequent reheating with the same rate q. With these specifications, the problem is fully stated, and can be solved both exactly and asymptotically, being of certain independent mathematical interest. In view of applications a note of caution should be added since the extent of applicability of the Langevin equation to a very viscous fluid is currently unclear. More general, non-Markovian pictures can be mentioned [8]. Nevertheless, the Langevin picture is expected at least to be reasonable in its general features; and the results potentially are of broader validity than the model, as will be discussed in the concluding part.

Equation (1) corresponds to a two-dimensional Fokker-Planck equation for the distribution function

$$\dot{f}(x,p,t)=\left\{-\frac{\partial}{\partial x}p+\frac{\partial}{\partial p}(\omega_0^2x+\gamma p)+\gamma T\frac{\partial^2}{\partial p^2}\right\}f, \tag{2}$$

where p is the momentum of a particle.

It is well known that equations of the above type have solutions which are Gaussian with respect to x and p but which can have an arbitrarily complicated time dependence of the coefficients. Assuming an equilibrium distribution at $t=0$, we will seek an even solution in the form

$$f=(\sqrt{D}/2\pi)\exp\{-\alpha(t)x^2-\beta(t)p^2-\delta(t)xp\}, \tag{3}$$

where D denotes $4\alpha\beta-\delta^2$ and the coefficients α,β, and δ obey a nonlinear system of ordinary differential equations

$$\dot{\alpha}=\omega_0^2\delta-\gamma T\delta^2,\quad \dot{\beta}=2\gamma\beta(1-2\beta T)-\delta, \tag{4}$$

$$\dot{\delta}=2(\omega_0^2\beta-\alpha)-\gamma\delta+2\gamma\delta(1-2\beta T). \tag{5}$$

Once the values of α, β, and δ are obtained, one can compute all relevant thermodynamic quantities, namely the average kinetic and configurational energies,

$$\overline{K}=\alpha/D, \quad \overline{U}=\beta\omega_0^2/D, \tag{6}$$

as well as the entropy, S, and the specific heat, $C=d/dT(\overline{K}+\overline{U})$:

$$S=-\int\int dxdpf\ln(f/e)=2+\ln\{2\pi/\sqrt{D}\}, \tag{7}$$

$$C=(\dot{T})^{-1}\gamma T(1-2\alpha/DT). \tag{8}$$

In the static case, $\dot{T}=0$, Eqs. (4) and (5) have three negative eigenvalues for strong damping $\gamma>2\sqrt{2}\omega_0$, or one negative and two complex eigenvalues otherwise. One can show that for an arbitrary quench $(\dot{T}<0)$ the value of $D(t)$ remains positive, so that the even solution under consideration is reasonable; for more complicated thermal schedules, however, the situation is less clear and lies outside the scope of the present work [9].

For infinitely slow processes, Eqs. (4) and (5) predict standard equipartition with $\alpha=\omega_0^2/2T$, $\beta=1/2T$, $\delta=0$, and $C=1$. For finite $\dot{T}$ we still assume that the quench is slow on a ''molecular scale'' (i.e., compared to ω_0). Violation of equipartition is possible due to large values of γ at low temperatures. Indeed, the system (4) and (5) has a small eigenvalue $-\omega_0^2/\gamma$, implying a diverging relaxation time in the strongly overdamped case.

In the limit $\gamma\rightarrow\infty$, Eqs. (4) and (5) lead to near-equilibrium values of β and δ; deviation of β from $1/2T$ is still important, however, for correct evaluation of specific heat from Eq. (8). The value of D remains positive for both quench and heating stages. The equation for α results in a known form of the relaxation equation for the structural energy

$$d\overline{U}/dt=(T/2-\overline{U})2\omega_0^2/\gamma. \tag{9}$$

For $\overline{U}$ to be close to its equilibrium values, relaxation must keep up with the changing temperature. Equations of type (9) with different phenomenological relaxation times received much attention in the past [10,11]. What was not expected, however, was that a closed-form solution of such equations is possible at low T, which is asymptotically insensitive to the details of the relaxation temperature dependence and which describes both the quench and the heating stages.

Let us switch to a dimensionless ''time,'' τ, defined as $d\tau=dt2\omega_0^2/\gamma$ with a zero value at $T=0$ and negative values in the quench stage. Due to a rapid increase of damping at low temperatures, one has

$$\tau\approx\mp\{\tilde{q}\tilde{\gamma}(-\ln\tilde{\gamma})_T'\}^{-1}. \tag{10}$$

The upper and lower sign correspond to quench and reheating, respectively, and $\tilde{q}=q\gamma_0/2\omega_0^2$ is the dimensionless quench or heating rate.

The values of $\overline{U}$ are insensitive to conditions at $\tau\rightarrow-\infty$ where equilibration is fast, and one obtains for the quenched-in structural energy

$$\overline{U}(0)=\frac{1}{2}\int_0^\infty d\tau T(-\tau)\exp(-\tau). \tag{11}$$

In the limit of small $\tilde{q}$ the temperature T is a slow (logarithmic-type) function of τ which follows from Eq. (10). Let T_* determine the temperature for which $\tau=-1$. Expanding T in powers of $\ln\tau$ and performing the integration, one obtains

$$\overline{U}(0)\simeq\frac{1}{2}\{T_*-0.5772\ldots/(-\ln\tilde{\gamma})_T'\}\equiv\frac{1}{2}T_f, \tag{12}$$

where the logarithmic derivative is evaluated at $T=T_*$. Primarily, the quenched-in structural energy is determined by $T_*/2$; the correction term — the one with Euler's constant in Eq. (12) — is useful for estimations of accuracy of the leading expression. T_f is similar to what is known as ''fictive temperature'' in glass transformation literature [4,12]. Spatial fluctuations are frozen-in with a distribution which corresponds to equilibrium at $T=T_f$ (although a strictly equilibrium shape, most likely, is due to harmonicity of the oscillator).

Since γ increases at low T faster than an exponential, the value of T_* changes with the quench rate slower than a logarithm. For example, for the empirical dependence $\tilde{\gamma}=\exp\{\kappa/(T-T_0)\}$ (with κ and T_0 known as the Vogel-Fulcher parameters), one has

$$T_*=T_0+\kappa/[\ln(\kappa/\tilde{q})-2\ \ln\ln(\kappa/\tilde{q})] \tag{13}$$

so that the fictive temperature increases approximately inversely proportional to the absolute value of the logarithm of the quench rate, approaching T_0 in the strict limit $\tilde{q}=0$.

In the same approximation one gets the entropy, Eq. (7), as

$$S(T)=(1/2)\ln(\overline{U}T)+\ln(e^2 2\pi\sqrt{2}/\omega_0). \tag{14}$$

At $T\rightarrow0$ its structural part acquires a quenched-in value of $(1/2)\ln(T_f/2)$.

The τ dependence of the specific heat is given by

$$C(\tau)=\frac{1}{2}+\frac{1}{2}(dT/d\tau)^{-1}\int_0^\infty\frac{d}{d\tau}T(\tau-\tau')\exp(-\tau')d\tau'. \tag{15}$$

The value of $dT/d\tau$ in the above expression is determined by $1/\tau(-\ln\gamma)_T'$. In the limit $\tilde{q}\rightarrow0$ the logarithmic term varies slowly compared to $1/\tau$, and the second term in Eq. (15) can be evaluated asymptotically as $-(1/2)\tau\exp(-\tau)E_1(-\tau)$, where E_1 is the first exponential integral [13]. Reheating with an identical rate q can be described as an analytical continuation of the above expression to positive τ. This leads to an exponential integral, $\mathrm{Ei}(\tau)=-E_1(-\tau)$, and gives for $C=(1/2)(1+\delta C)$ the following expression:

$$\delta C=1+\tau\exp(-\tau)\mathrm{Ei}(\tau). \tag{16}$$

This variable part of the specific heat which is a universal function of the scaling parameter τ is shown in Fig. 1. Specifics of a particular system enters through relation of τ to the quench rate and the dissipation via Eq. (10). During a quench one gets $\delta C\approx1/2$ at $\tau=-0.614\ldots$, which can be associated with the calorimetric GT. The temperature of this

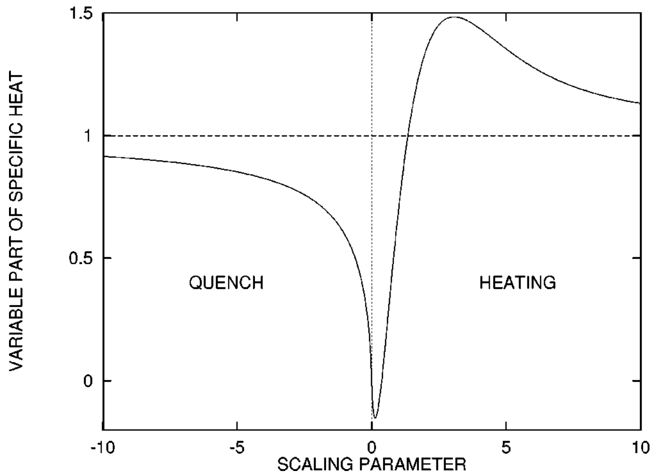

FIG. 1. δC Eq. (16) as a function of the scaling parameter, τ, for the quench ($\tau < 0$) and reheating ($\tau > 0$) stages.

GT can be estimated as $T_g \approx T_* - 0.49/(-\ln\tilde{\gamma})'_T$ (with logarithmic derivative evaluated at $T = T_*$), and is rather close to T_f.

To obtain δC as a function of temperature, the oscillator frequency ω_0 can be estimated as the speed of sound, v_s, over the intermolecular distance. Damping can be estimated from the Stokes relation, $\gamma = 6\pi a\eta/m$, with a and m being the molecular size and mass, respectively, and η the viscosity of the fluid. One thus obtains

$$\tau \approx \pm \frac{1}{q}\frac{v_s^2\rho}{\eta'_T} \qquad (17)$$

for the scaling parameter τ with $\rho \sim m/a^3$ being the density.

A typical shape of the $\delta C(T)$ curve is shown in Fig. 2 using parameters from *o*-terphenyl for the viscosity η [14]. Note the closeness of the GT to the experimentally observed value of 243 K [15]. The ''Fermi'' and ''Bose'' types of the specific heat curves during quench and heating also bear strong similarities to experimental observations, as well as to results of numerical simulations — see, e.g., [4,12,16]. Since the dimensionless parameter $\tilde{q}$ is smaller than 10^{-12}, the proposed asymptotic description is virtually exact for the example considered. Generalizations of the result for unequal quench-reheating rates will be discussed in Ref. [9]. It seems appropriate to remark that experimentally realistic shapes of the $\delta C(T)$ curves could signify not only the adequacy of the proposed Brownian oscillator picture, but also the archetypal nature of a single-time relaxation Eq. (9). For any relaxation time which rapidly increases at low temperatures, the relaxation equation will have the same form of the solution given by Eq. (16), regardless of the underlying model.

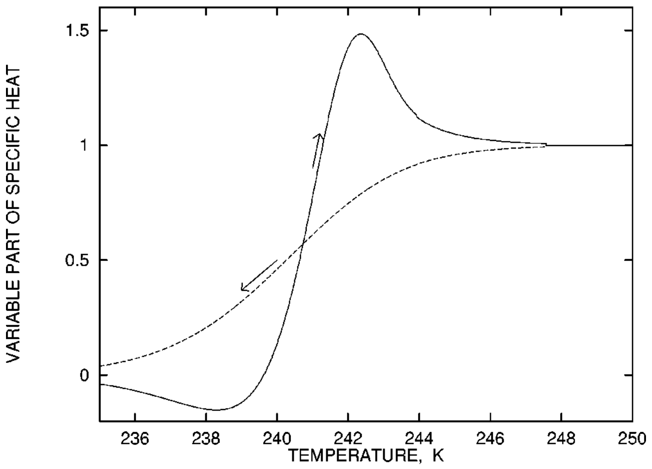

FIG. 2. Temperature dependence of the specific heat during quench and reheating with $q \simeq 10^{-2}$ K/s. Viscosity data for *o*-terphenyl by Laughlin and Uhlmann (1972) were used to evaluate τ in Eqs. (16) and (17). Changing q by a factor of 10 shifts the curves by about 4 K.

For an array of oscillators with a density $\nu(\omega)$ one needs to consider contributions of each mode. Assuming that the damping parameter for each mode is identical, one has from Eqs. (10) and (16) written in dimensional variables

$$\delta C \propto (|d\eta/dt|/v_s^2\rho)^{1/2}\left\{\int_0^{\tau_{\max}} \nu\, d\tau \sqrt{\tau}\exp(-\tau)\mathrm{Ei}(\tau)\right\} \qquad (18)$$

with $\tau_{\max} = 2\omega_{\max}^2/(d\gamma/dt)$. Note that the presence of slower oscillators does not have a dramatic effect on the location of the GT, although the shape of the $\delta C(T)$ curve can be modified. Specifics of this curve are determined by the explicit form of the spectral density, $\nu(\omega)$. For example, for a power-law spectrum $\delta C(T)$ will remain a universal function of $\tau_{\max}$. An interesting point is the dependence of the result on the rate of the viscosity change, but not on its absolute values. A detailed investigation of $\delta C(T)$ for typical spectra will be presented elsewhere [9].

To summarize, an asymptotic study of the nonequilibrium thermodynamics of a quenched Brownian oscillator in a fluid with diverging viscosity was performed. It was shown that the system exhibits certain qualitative features of a calorimetric glass transition, namely the abrupt drop in specific heat (and its overshoot during reheating), nonzero values of the quenched-in structural energy, and residual entropy. Analytically, the key result of the study is the expression for the variable part of the specific heat, Eq. (16), which is a universal function of a single scaling parameter, τ.

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