Fluctuation-dissipation theorem for frequency-dependent specific heat

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A derivation of the fluctuation-dissipation (FD) theorem for the frequency-dependent specific heat of a system described by a master equation is presented. The FD theorem is illustrated by a number of simple examples, including a system described by a linear Langevin equation, a two-level system, and a system described by the energy master equation. It is shown that for two quite different models with low-energy cutoffs—a collection of two-level systems and a system described by the energy master equation—the frequency-dependent specific heat in dimensionless units becomes universal at low temperatures, i.e., independent of both energy distribution and temperature. These two models give almost the same universal frequency-dependent specific heat, which compares favorably to experiments on supercooled alcohols.

I. INTRODUCTION

ac calorimetry was introduced in the 1960’s as an accurate method for measuring the ordinary dc specific heat.1,2 The use of ac calorimetry for measuring the frequency-dependent specific heat was pioneered in 1985 by Birge and Nagel3 and by Christensen.4 Frequency-dependence of the specific heat occurs, e.g., in liquids close to the glass transition,5 where structural relaxations take place on a time scale depending strongly on temperature.6 Other systems with slow enthalpy relaxations like unfolding proteins7 also exhibit frequency dependence of the specific heat. For measurements of the frequency-dependent specific heat, the accessible time scale typically involves times longer than one second.

Studies of enthalpy relaxation in supercooled liquids upon a large change of temperature had been carried out for several years before the introduction of “specific heat spectroscopy,”6,8–11 The study of enthalpy relaxation upon a small change of temperature, which is a linear phenomenon, is conceptually simpler but experimentally more difficult. This is probably why the first measurements of frequency-dependent specific heat appeared just 11 years ago. From a theoretical point of view, however, a linear response is much easier to model and understand than a nonlinear response. This may account for the recent increased interest in ac specific heat measurements.7,12–14

The main reason for the simplicity of a linear response is the fluctuation-dissipation (FD) theorem, which expresses the response of a system upon a slight time-dependent change of external parameters in terms of equilibrium fluctuations. In effect, a linear response probes the equilibrium dynamics (i.e., the dynamics in absence of any external disturbance). The standard proof of the FD theorem considers an external field that perturbs the Hamiltonian.15 Often, when dealing with the frequency-dependent specific heat, more or less explicit reference is made to the standard FD theorem.7,12,16–19 This, however, is inaccurate since the specific heat is not a response to an external field perturbing the Hamiltonian.

Shortly after the first appearance of publications reporting measurements of the frequency-dependent specific heat of supercooled liquids,3,4 a number of authors discussed theories for this quantity.20–24 The frequency-dependent specific heat was viewed in the context of generalized hydrodynamics for liquids with structural relaxation.20,21 It was suggested by Zwanzig that the frequency-dependent specific heat is directly related to the frequency-dependent longitudinal viscosity.23 Jäckle24 discussed heat conduction and frequency-dependent specific heat in one-component liquids near the glass transition and showed that a frequency dependence of the thermal conductivity is connected to a wave vector and frequency dependence of the specific heat. Despite these theoretical developments, a proof of the FD theorem for frequency-dependent specific heat does not seem to exist in the literature. This is ironic, since one of the very earliest indications of the existence of FD theorems is Einstein’s well-known result that the ordinary dc specific heat \( c_p \) is proportional to the mean-square enthalpy fluctuation in the canonical ensemble (here and henceforth the subscript 0 denotes an equilibrium average):

\[
c_p = \frac{\langle (\Delta H)^2 \rangle_0}{k_B T^2}.
\]

The outline of the paper is as follows. Section II briefly reviews the stochastic framework within which the FD theorem for frequency-dependent specific heat is derived in Sec. IV. This is done by analogy with the derivation of the ordinary FD theorem, which is reviewed in Sec. III. Section V illustrates the FD theorem for specific heat by working out a number of simple examples. In Sec. VI we discuss “quasi-universality” of the frequency-dependent specific heat in certain systems and compare the quasiuniversal frequency-dependent specific heat to data for six supercooled alcohols. Section VII contains the conclusion.

II. STOCHASTIC MODEL

The system is described by probabilities to be in some “states” and the dynamics is given by a master equation. If \( P_i \) is the probability to be in state \( i \) and \( W_{ij} \) is the probability...
per unit time for a transition from state \( j \) to state \( i \), the master equation\(^{25} \) is the following first order differential equation:

\[
\frac{\partial P_i(t)}{\partial t} = -\sum_{j \neq i} W_{ji}P_i + \sum_{j \neq i} W_{ij}P_j. \tag{2}
\]

The first term on the right-hand side represents the probability per unit time of leaving state \( i \) while the second term represents the probability per unit time of jumping into state \( i \). Equation (2) is linear. The Green’s function \( G_{0}(i,t|j,t') \) is the probability to be in state \( i \) at time \( t \) given that the system is in state \( j \) at time \( t' < t \); in terms of the Green’s function the linearity of Eq. (2) implies\(^{25} \)

\[
P_j(t) = \sum_j G_{0}(i,t|j,t')P_j(t') \quad (t > t'). \tag{3}
\]

The equilibrium probability \( P_{\text{eq},i} \) is time independent and thus

\[
P_{\text{eq},i} = \sum_j G_{0}(i,t|j,t')P_{\text{eq},j} \quad (t > t'). \tag{4}
\]

### III. THE ORDINARY FLUCTUATION-DISSIPATION THEOREM

Consider a system which is in thermal equilibrium at time \( t = -\infty \). Applying a time-dependent external field \( f(t) \), the average deviation from equilibrium of some physical quantity, \( \delta B \), depends linearly on \( f(t) \) if the field is sufficiently small. The general linear expression for \( \delta B(t) \) reflecting causality and time homogeneity is

\[
\delta B(t) = \int_{0}^{\infty} \mu(t')f(t-t')dt'. \tag{5}
\]

In the frequency domain, one considers a small oscillating perturbation, \( f(t) = \text{Re}\{f_0 e^{i\omega t}\} \), where \( \omega \) is the imaginary frequency \( (\omega = i\omega) \) and \( \text{Re} \) denotes the real part. Inserting this into Eq. (5) gives

\[
\delta B(t) = \text{Re}\{f_0 \mu(s)e^{i\omega t}\}, \tag{6}
\]

where the frequency-dependent response function \( \mu(s) \) is the Laplace transform of \( \mu(t) \),

\[
\mu(s) = \int_{0}^{\infty} \mu(t)e^{-st}dt. \tag{7}
\]

If \( \Delta B_i = B_i - \langle B \rangle_0 \) is the deviation from equilibrium of the variable \( B \) in state \( i \) and \( \Delta A_i \) is the deviation from equilibrium of the variable conjugate to the external field \( f(t) \) [i.e., \( H(t) = H_0 - f(t)A \) where \( H_0 \) is the unperturbed Hamiltonian], the ordinary FD theorem\(^{15,26} \) states that

\[
\mu(t) = -\frac{1}{k_B T} \frac{d}{dt} \langle \Delta A(0) \Delta B(t) \rangle_0. \tag{8}
\]

Combining Eqs. (7) and (8) leads to

\[
\mu(s) = -\frac{1}{k_B T} \int_{0}^{\infty} \left( \frac{d}{dt} \langle \Delta A(0) \Delta B(t) \rangle_0 \right) e^{-st}dt. \tag{9}
\]

In terms of the Green’s function the correlation function is given by

\[
\langle \Delta A(0) \Delta B(t) \rangle_0 = \sum_{i,j} G_{0}(i,t|j,0)P_{\text{eq},j}\Delta A_j \Delta B_i. \tag{10}
\]

Equation (10) comes from considering the actual “path” of the system in state space due to equilibrium thermal fluctuations. The probability to be in state \( j \) at \( t = 0 \) is \( P_{\text{eq},j} \) and the probability of subsequently being in state \( i \) at time \( t \) is given by the Green’s function. Note that the correlation function refers to equilibrium fluctuations; the point of the FD theorem is precisely that the linear response to an external field is determined by fluctuations in thermal equilibrium with no external field.

Following Doi and Edwards\(^{26} \) the derivation of the ordinary FD theorem proceeds in the following way. Suppose the system is equilibrated at a small constant time-independent external field \( f_0 \), which is turned off at time \( t = 0 \). For \( t > 0 \) the system relaxes towards equilibrium corresponding to the zero field situation. The approach of the variable \( B \) towards equilibrium is via Eq. (5) given by

\[
\delta B(t) = \int_{0}^{\infty} \mu(t')f_0 dt' = \alpha(t)f_0, \tag{11}
\]

where \( \alpha(t) \) is related to \( \mu(t) \) by

\[
\mu = -\frac{d\alpha}{dt}. \tag{12}
\]

If the unperturbed energy of state \( j \) is \( E_j \) and the value of \( A \) is \( A_j \), the initial state probability at \( t = 0 \), \( P_j(t=0) \), is the equilibrium probability in the external field \( f_0 \) \( [H = H_0 - f_0 A \) implies that the energy of state \( j \) is \( E_j - f_0 A_j] \),

\[
P_j(t=0) = \frac{e^{-\beta(E_j - f_0 A_j)}}{Z}, \tag{13}
\]

where \( \beta = 1/(k_B T) \) and \( Z = \sum e^{-\beta(E_j - f_0 A_j)} \). It is straightforward to show that Eq. (13) implies

\[
\left. \frac{\partial P_j(t=0)}{\partial f_0} \right|_{f_0 = 0} = \frac{1}{k_B T} P_{\text{eq},j}\Delta A_j. \tag{14}
\]

To first order in \( f_0 \) one therefore has

\[
P_j(t=0) = P_{\text{eq},j} \left( 1 + \frac{1}{k_B T} f_0 \Delta A_j \right). \tag{15}
\]

Using Eqs. (3), (4), (10), (15), and the fact that \( \langle \Delta B \rangle_0 = 0 \), to first order in the external field \( f_0 \).
\[ \delta B(t) = \sum_i P_i(t) \Delta B_i = \sum_{i,j} G_0(i,t|j,0)P_j(t=0) \Delta B_i \]

\[ = \sum_{i,j} G_0(i,t|j,0) P_{eq,i}(1 + \frac{f_0}{k_B T} \Delta A_j) \Delta B_i \]

\[ = \frac{f_0}{k_B T} \langle \Delta A(0) \Delta B(t) \rangle_0. \quad (16) \]

Thus

\[ \alpha(t) = \frac{1}{k_B T} \langle \Delta A(0) \Delta B(t) \rangle_0. \quad (17) \]

Via Eq. (12) one now arrives at the ordinary FD theorem Eq. (8).

IV. FLUCTUATION-DISSIPATION THEOREM FOR SPECIFIC HEAT

In measurements of the specific heat two different experimental situations may be realized. The most common is keeping the pressure constant (isobaric conditions); alternatively the volume may be kept constant (isochoric conditions). For both corresponding canonical ensembles, the equilibrium distribution is Boltzmann-like with an appropriate quantity \( Y_j \) in the exponential:

\[ P_{eq,i} = \frac{e^{-\beta Y_j}}{Z} \quad \Delta \beta \]

where \( Z = \sum_i e^{-\beta Y_j} \). In the canonical isobaric ensemble \( Y_j \) is the enthalpy \( Y_j = E_j + pV_j \), in the canonical isochoric ensemble \( Y_j \) is the energy.27

Consider now a system exposed to a temperature ‘field’ \( T(t) \) given by

\[ T(t) = \begin{cases} T + \delta T, & t < 0 \\ T, & t > 0 \end{cases} \quad (19) \]

Equation (18) implies

\[ \frac{\partial P_{eq,i}}{\partial T}(T) = \frac{1}{k_B T^2} P_{eq,i}(T) \Delta Y_j. \quad (20) \]

To first order in \( \delta T \), the distribution \( P_j(t=0) = P_{eq,i}(T + \delta T) \) may via Eq. (20) be expressed in terms of the equilibrium distribution at \( T \):

\[ P_j(t=0) = P_{eq,i}(T) \left(1 + \frac{\delta T}{k_B T^2} \Delta Y_j \right). \quad (21) \]

The time dependence of the average deviation of a physical quantity \( B \) from equilibrium is for \( t > 0 \) via Eqs. (3), (4), and (21) given by

\[ \delta B(t) = \sum_i P_i(t) \Delta B_i = \sum_{i,j} G_0(i,t|j,0)P_j(t=0) \Delta B_i \]

\[ = \sum_{i,j} G_0(i,t|j,0) P_{eq,i}(T) \left(1 + \frac{\delta T}{k_B T^2} \Delta Y_j \right) \Delta B_i \]

\[ = \frac{\delta T}{k_B T^2} \langle \Delta Y(0) \Delta B(t) \rangle_0. \quad (22) \]

We can now extract the function \( \alpha(t) \) defined by \( \delta B(t) = \alpha(t) \delta T \):

\[ \alpha(t) = \frac{1}{k_B T} \langle \Delta Y(0) \Delta B(t) \rangle_0. \quad (23) \]

The frequency-dependent response function is given by Eqs. (7) and (12), leading to

\[ \mu(s) = -\frac{1}{k_B T^2} \int_0^\infty \left\langle \frac{d}{dt}(\Delta Y(0)\Delta B(t))_0 \right\rangle e^{-st} dt. \quad (24) \]

In particular, the case where \( B \) is the energy (in the constant volume case) or the enthalpy (in the constant pressure case) gives the FD theorem for frequency-dependent specific heat.

V. FREQUENCY-DEPENDENT SPECIFIC HEAT IN SOME SIMPLE MODELS

In the isobaric case \( Y \) is the enthalpy \( H \) and the frequency-dependent specific heat is given by

\[ c(s) = -\frac{1}{k_B T^2} \int_0^\infty \left\langle \frac{d}{dt}(\Delta H(0)\Delta H(t))_0 \right\rangle e^{-st} dt. \quad (25) \]

After a partial integration this becomes

\[ c(s) = \frac{\langle (\Delta H)^2 \rangle_0}{k_B T^2} - \frac{s}{k_B T} \int_0^\infty \langle \Delta H(0)\Delta H(t) \rangle_0 \right\rangle e^{-st} dt. \quad (26) \]

For \( s = 0 \) we recover the standard expression for the dc specific heat Eq. (1). It is sometimes convenient to rewrite the FD theorem by substituting the identity \( \langle \Delta H(0)\Delta H(t) \rangle_0 = \langle H(0)H(t) \rangle - \langle H \rangle_0^2 \) into Eq. (26), leading to

\[ c(s) = \frac{\langle H^2 \rangle_0}{k_B T^2} - \frac{s}{k_B T} \int_0^\infty \langle H(0)H(t) \rangle_0 \right\rangle e^{-st} dt. \quad (27) \]

If the pressure is zero, the enthalpy is equal to the energy. In this case, one calculates the frequency-dependent isobaric specific heat by considering equilibrium energy fluctuations, as done below for some simple models. Note that \( c_p \neq c_v \) even when \( p = 0 \), although both quantities are given by formally identical expressions involving energy autocorrelation functions. This is because the dynamics in the two situations are different (when the pressure is constant the volume fluctuates and more states are allowed than in the constant volume case).
A. Langevin equation in harmonic potential

Consider first a system described by a variable $x$ which fluctuates in a harmonic potential, $E(x) = \frac{1}{2}kx^2$. We assume that $x$ obeys the Langevin equation

$$\dot{x} = -\mu \frac{\partial E}{\partial x} + \xi(t) = -\mu kx + \xi(t),$$  

(28)

where $\xi(t)$ is a Gaussian white noise term with variance given by $\langle \xi(t)\xi(t') \rangle = 2\mu kT \delta(t-t')$. The Langevin equation ensures the correct canonical probability proportional to $\exp[-\beta E(x)]$. Since $x(0)$ is uncorrelated with the noise at later times, $\langle x(0)\xi(t) \rangle = 0$ for $t>0$, Eq. (28) leads to

$$\langle d/dt \langle x(0)x(t) \rangle \rangle = -\mu k \langle x(0)x(t) \rangle,$$

implying that

$$\langle x(0)x(t) \rangle_0 = \langle x^2 \rangle_0 e^{-\mu kt}. \tag{29}$$

For the energy autocorrelation function one finds

$$\langle \Delta E(0)\Delta E(t) \rangle_0 = \langle E(0)E(t) \rangle_0 - \langle E \rangle_0^2$$

$$= \frac{k^2}{4} \langle x^2(x(t)) \rangle_0 - \frac{k^2}{4} \langle x^2 \rangle_0^2. \tag{30}$$

As is well known, the linear Langevin equation Eq. (28) has the property that $x(t)$ is distributed according to a Gaussian. Since $\langle x^2(0) \rangle_0 = \langle x^2(t) \rangle_0 = \langle x^2 \rangle_0$, this implies that $\langle x^2(0)x^2(t) \rangle_0 = \langle x^2 \rangle_0 + \frac{\mu kT}{2} \langle x^2 \rangle_0 t$. When this is substituted into Eq. (30) the following expression for the equilibrium energy autocorrelation function is obtained (using the fact that in a harmonic potential $\langle E \rangle_0 = \frac{1}{2}k_BT$)

$$\langle \Delta E(0)\Delta E(t) \rangle_0 = \frac{k^2}{2} \langle x(0)x(t) \rangle_0 - \frac{k^2}{2} \langle x^2 \rangle_0 e^{-\mu kt}$$

$$= 2\langle E \rangle_0^2 e^{-\mu kt} + \frac{1}{2} \frac{k_BT^2}{\mu k} e^{-\mu kt}. \tag{31}$$

For the frequency-dependent specific heat one finally obtains from Eq. (25)

$$c(s) = k_B s \left( \frac{\mu k}{s + 2\mu k} \right). \tag{32}$$

This is the Debye expression for a linear response function, first derived for dielectric relaxation (remember that $s = i\omega$). At high frequencies the specific heat goes to zero. This is because for a fast small periodic temperature variation the average energy only has time to change insignificantly.

B. Two-level system

Consider next a system which can be in two different states $|i \rangle = 0,1$ with energies $E_i$. It is assumed that there is an energy maximum $E_{\text{max}}$ which the system has to pass to go from one state to the other. In thermal equilibrium the probability flow between the two states is zero (principle of detailed balance), implying that

$$\gamma_0 P_{\text{eq},0} = \gamma_1 P_{\text{eq},1}, \tag{33}$$

where $\gamma_i$ is the rate of jumps out of state $i$. This is fulfilled if the rates are given by those of transition state theory (where $\tau_0$ is the inverse of the “attempt frequency”):

$$\gamma_i = \frac{1}{\tau_0} = e^{-\beta (E_{\text{max}} - E_i)}. \tag{34}$$

The differential equation for the probability of being in state number 1 is (utilizing the fact that $P_0 + P_1 = 1$)

$$\frac{dP_1}{dt} = -\gamma_1 P_1 + \gamma_0 P_0 = -\gamma_0 P_0 - \gamma_1 P_1 + \gamma_0. \tag{35}$$

The solution is

$$P_1(t) = \frac{P_1(0)}{\gamma_0 + \gamma_1} e^{-(\gamma_0 + \gamma_1)t} + \frac{\gamma_0}{\gamma_0 + \gamma_1}. \tag{36}$$

The energy autocorrelation function is given by

$$\langle \Delta E(0)\Delta E(t) \rangle_0 = \langle E(0)E(t) \rangle_0 - \langle E \rangle_0^2$$

$$= \sum_{i,j=0} G_0(i,t|j,0)E_iE_jP_{\text{eq},j} - \langle E \rangle_0^2. \tag{37}$$

It straightforward to evaluate this sum using Eq. (36) from which all four conditional probabilities $G_0(i,t|j,0)$ may be found. However, it is easier to note that, since Eq. (36) implies that each of the conditional probabilities is a linear function of $e^{-(\gamma_0 + \gamma_1)t}$, the entire energy autocorrelation function also depends linearly on this quantity. Thus, for some constants $A$ and $B$ we have

$$\langle \Delta E(0)\Delta E(t) \rangle_0 = A e^{-(\gamma_0 + \gamma_1)t} + B. \tag{38}$$

Letting $t$ go to zero we find $A + B = \langle (\Delta E)^2 \rangle_0$, letting $t$ go to infinity gives $B = 0$. Therefore, Eq. (38) becomes

$$\langle \Delta E(0)\Delta E(t) \rangle_0 = \langle (\Delta E)^2 \rangle_0 e^{-(\gamma_0 + \gamma_1)t}. \tag{39}$$

When substituted into the FD theorem Eq. (25) we thus find

$$c(s) = \frac{\langle (\Delta E)^2 \rangle_0}{\frac{k_BT^2}{\mu k} + \frac{\mu k}{s + 2\mu k}} \left( \frac{\gamma_0 + \gamma_1}{s + \gamma_1} \right). \tag{40}$$

For $s = 0$ Eq. (40) reduces to Eq. (1).

Equation (40) is formally indistinguishable from the frequency-dependent specific heat of the Langevin equation for a harmonic potential Eq. (32), since for a suitable choice of $\Gamma$ Eqs. (32) and (40) may both be written $c(s) = c(0)\Gamma/(s + \Gamma)$. Thus the frequency-dependent specific heat is not able to distinguish between the continuous Langevin model and a discrete two-level system.

It is straightforward to show that for a two-level system

$$\langle (\Delta E)^2 \rangle_0 = \frac{(E_1 - E_0)^2 e^{-\beta E_0 + E_1}}{(e^{-\beta E_0} + e^{-\beta E_1})^2}. \tag{41}$$

Combining Eqs. (34), (40), and (41) and introducing the dimensionless imaginary frequency

$$\tilde{s} = s \tau_0 e^{\beta E_{\text{max}}}, \tag{42}$$
the following expression is arrived at

\[ c(\tilde{s}) = \frac{(E_1 - E_0)^2}{k_B T^2} \int_{E_0}^{E_{\text{max}}} \frac{(E_1 - E_0)^2 f(E_1) dE_1}{[e^{-\beta E_0} + e^{-\beta E_1}] [\tilde{s} + (e^{\beta E_0} + e^{\beta E_1})]} \]  \( \text{(43)} \)

C. Collection of two-level systems

Consider a collection of two-level systems, each with the same \( E_0 \) and \( E_{\text{max}} \), but with a distribution \( f(E_1) \), where \( E_0 < E_1 < E_{\text{max}} \). The frequency-dependent specific heat of this system is just the sum of all the single two-level system specific heats given by Eq. (43); thus

\[ c(\tilde{s}) = \frac{1}{k_B T^2} \int_{E_0}^{E_{\text{max}}} \frac{(E_1 - E_0)^2 f(E_1) dE_1}{[e^{-\beta E_0} + e^{-\beta E_1}] [\tilde{s} + (e^{\beta E_0} + e^{\beta E_1})]} \]  \( \text{(44)} \)

A discussion of the low-temperature limit of this expression is given in Sec. VI.

D. Energy master equation

This and related equations have been discussed as models for enthalpy relaxation in supercooled liquids.\(^{10,29-32} \) The idea is the following. The supercooled liquid is thought of as temporarily trapped in some configuration. To jump into another configuration, a number of molecules (a “region”) collectively have to pass an energy barrier given by \( \Delta E = E_{\text{max}} - E \), where \( E \) is the energy of the initial state. The maximum to be overcome, \( E_{\text{max}} \), is assumed to be independent of the initial state. A further assumption is that, once excited into the transition state, the region has forgotten which state it came from and ends up in a randomly chosen state. If \( n(E) \) is the normalized density of states and one defines

\[ \Gamma(E) = \Gamma_0 e^{-\beta(E_{\text{max}} - E)}, \]  \( \text{(45)} \)

the above assumptions lead to the energy master equation \(^{31,32} \) (EME) for the energy probability distribution \( P(E,t) \):

\[ \frac{\partial P(E,t)}{\partial t} = -\Gamma(E) P(E,t) + n(E) \int_{-\infty}^{\infty} \Gamma(E') P(E',t) dE'. \]  \( \text{(46)} \)

The first term on the right-hand side represents the probability per unit time for jumping away from a state of energy \( E \), the second term is the probability per unit time for having a region changing its energy into \( E \). To make sense physically, the energy integration in Eq. (46) should only extend up to \( E_{\text{max}} \); however, at not too high temperatures the integration may be extended to infinity without changing the relaxation properties of the equation around the main parts of the relaxation spectrum.

If \( G_0(E|E')(s) \) is the Laplace transform of the Green's function, Eq. (27) implies

\[ c(s) = \frac{(E_1 - E_0)^2}{k_B T^2} \int_{E_0}^{E_{\text{max}}} \frac{(E_1 - E_0)^2 f(E_1) dE_1}{[e^{-\beta E_0} + e^{-\beta E_1}] [\tilde{s} + (e^{\beta E_0} + e^{\beta E_1})]} \times P_{\tilde{c}}(E'|E') EE'dEdE'. \]  \( \text{(47)} \)

To find \( G_0(E|E')(s) \) one refers to the general solution of the EME [Eq. (A10) in Ref. 32], according to which the Laplace transform of \( P(E,t) \) is given by

\[ P(E,s) = \frac{n(E)}{s + \Gamma(E)} \int_{-\infty}^{\infty} \Gamma(E') P(E',t=0) \frac{dE'}{s + \Gamma(E')} + \frac{P(E,t=0)}{s + \Gamma(E)}. \]  \( \text{(48)} \)

\[ G_0(E|E')(s) \] is found by substituting \( P(E',t=0) = \delta(E'-E') \) into Eq. (48). After some elementary reductions utilizing the fact that \( P_{\tilde{c}}(E) \propto n(E)/\Gamma(E) \), one finally finds \(^3^3 \) from Eq. (47)

\[ c(s) = \frac{1}{k_B T^2} \left\{ \frac{\Gamma(E)E^2}{s + \Gamma(E)} - \frac{\left( \frac{\Gamma(E)E}{s + \Gamma(E)} \right)^2}{0} \right\}. \]  \( \text{(49)} \)

VI. QUASIUNIVERSALITY OF THE FREQUENCY-DEPENDENT SPECIFIC HEAT AT LOW TEMPERATURES

This section discusses quasiuniversality at low temperatures for two models. The one model is a collection of two-level systems (Sec. V C), the other is defined by the EME (Sec. V D). Each model has a common value of the energy maximum to be overcome in transitions between any two states. As shown below for both models, if the density of states has a sharp low-energy cutoff, the frequency-dependent specific heat at low temperatures in dimensionless units becomes independent of both temperature and density of states. It turns out that the two universal curves are very similar, justifying the term “quasiuniversality.”

Consider first a collection of two-level systems, each with ground state energy \( E_0 \). If the distribution of excited states, \( f(E_1) \), obeys \( f(E_0) \neq 0 \), this model results in a normalized specific heat which is universal. This is because, in the low-temperature limit, \( f(E_1) \) in the integral of Eq. (44) may be replaced by the constant \( f(E_0) \) and the integration may be extended to infinity. Doing this one finds that the normalized specific heat, \( \tilde{c}(\tilde{s}) = c(\tilde{s})/c(0) \), is given by

\[ \tilde{c}(\tilde{s}) = \frac{F(1 + \tilde{s}^2 + \tilde{s})}{F(1,2)}, \]  \( \text{(50)} \)

where \( \tilde{s} \) is given by Eq. (42) and

\[ F(a,b) = \int_0^\infty \frac{x^2}{e^x + ae^{-x} + b} dx. \]  \( \text{(51)} \)

Consider now the energy master equation. In this case, whenever there is a sharp low-energy cutoff at \( E = E_0 \) for the density of states [i.e., \( n(E) = 0 \) for \( E < E_0 \) and \( n(E_0) \neq 0 \)], \( n(E) \) may be replaced by \( n(E_0) \) at low temperatures. Thus, as shown in Appendix A, Eq. (49) implies [where \( \tilde{s} = s/\Gamma(E_0) \) and \( \text{Li}_m(z) \) is the \( m \)th polylogarithm, \(^{3^4} \) ]
We have derived the fluctuation-dissipation theorem for frequency-dependent specific heat. In this case the "external field" does not enter into the Hamiltonian but is the temperature—a statistical concept. Consequently, the suitable framework for discussing frequency-dependent specific heat is to consider systems described by a master equation.

The FD theorem was illustrated by simple examples, including a system described by a linear Langevin equation and a two-level system. These models both give rise to Debye frequency dependence of the specific heat, so specific heat spectroscopy cannot distinguish between these conceptually very different models (of course, the models can be distinguished by the temperature dependence of the loss peak frequency). This is analogous to what happens for dielectric relaxation described by the same two models; it reflects the fact that both models have a single relaxation time.

In the low-temperature limit, a distribution of two-level systems—each with the same energy difference between ground state and barrier to be overcome—gives rise to a frequency-dependent specific heat, that in dimensionless units is independent of the distribution of level spacings. Interestingly, almost the same universal frequency-dependent specific heat arises from a quite different approach, that of the energy master equation. In real units the frequency-dependent specific heat is usually strongly temperature dependent; the prediction of universality just means that the shape of the specific heat loss peak is temperature independent. Thus, universality implies that these systems at low temperatures have frequency-dependent specific heats obeying the time-temperature superposition principle. The two universal curves give a good fit to four of the six alcohols studied in Refs. 4 and 35. Whether this is a pure coincidence or a result of general significance remains to be seen. It is thus an open question whether or not supercooled liquids close to the laboratory glass transition (where the measurements of Fig. 1 were made) are at "low temperatures" in the sense of Sec. VI, meaning that the molecular configuration is close to the ground state (excitations of which give rise to the universal frequency-dependent specific heat). Further work is needed to clarify this point.

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APPENDIX: DERIVATION OF UNIVERSAL LOW-TEMPERATURE FREQUENCY-DEPENDENT SPECIFIC HEAT IN THE EME WITH A LOW-ENERGY CUTOFF

We here derive Eq. (52), the universal low-temperature frequency-dependent specific heat for the EME with a low-energy cutoff in the density of states at \( E_0 \). Introducing the quantity

\[
A_m(s) = \left\langle \frac{\Gamma(E)E^m}{s + \Gamma(E)} \right\rangle_0 ,
\]

Eq. (49) becomes
The equilibrium energy probability distribution is given by
\[ P_{\text{eq}}(E) = n(E) e^{-\beta E}/Z \]
where \( Z = \int_{E_{\text{min}}}^{E_{\text{max}}} n(E) e^{-\beta E} dE \). At low temperatures the density of states \( n(E) \) may be replaced by the number \( n(E_0) \) and the equilibrium energy probability is simply \( P_{\text{eq}}(E) = \beta e^{-\beta(E-E_0)} \). Without loss of generality it may be assumed that \( E_0 = 0 \) and Eq. (A1) becomes
\[ A_m(s) = \beta \int_0^\infty \frac{e^{-\beta E} E^{m-1}}{1 + s e^{-\beta E}} dE. \]  
(A3)

Introducing the dimensionless imaginary frequency \( \tilde{s} = -s/\Gamma_0 e^{-\beta E_{\text{max}}} \). 
Eq. (A3) becomes \( A_m(s) = \beta^{-m} f_m(\tilde{s}) \) where
\[ f_m(\tilde{s}) = \int_0^\infty \frac{x^m}{s + e^x} dx. \]  
(A5)

In terms of \( f_m(\tilde{s}) \), Eq. (A2) implies for the normalized frequency-dependent specific heat \( c = c(s)/c(0) \) [because \( c(0) = k_B \) for the flat density of states]
\[ c(\tilde{s}) = f_2(\tilde{s}) \frac{\tilde{s}^2}{f_0(\tilde{s})}. \]  
(A6)

The function \( f_m(\tilde{s}) \) may be expressed in terms of the \( m \)th polylogarithm \( \text{Li}_m \) defined by
\[ \text{Li}_m(z) = \sum_{n=1}^\infty \frac{z^n}{n^m}. \]  
(A7)

This is done by expanding for \( |\tilde{s}| < 1 \):
\[ c(s) = \frac{1}{k_B T} \left[ A_2(s) \frac{A_2^2(s)}{A_0(s)} \right]. \]  
(A2)

For \( s \rightarrow 0 \), Eq. (A9) implies \( c = 1 - \tilde{s}^4 \). For \( s \rightarrow \infty \), Eq. (A9) implies for the real part of the frequency-dependent specific heat \( \text{Re} \{ c(\tilde{s}) \} = \pi \text{Li}_1(\tilde{s}/(8\tilde{s})) \) and for the imaginary part \( \text{Im} \{ c(\tilde{s}) \} = -\ln(8\tilde{s})/(12\tilde{s}) \). The loss peak frequency is given by \( \omega_m = 4.51 \) and the maximum of the negative imaginary part is given by \( c'' = -0.313 \).
28 P. Debye, Polar Molecules (Dover, New York, 1945).
35 T. Christensen, Description of a Method of Measuring the Shear Modulus of Supercooled Liquids and a Comparison of their Thermal and Mechanical Response Functions (IMFUA text no. 279, Roskilde, 1994).
36 Higher Transcendental Functions, edited by A. Erdelyi, W. Magnus, F. Oberhettinger, and F. G. Tricomi (McGraw-Hill, New York, 1953), Vol. 1, Eq. (1.11.18) [note that in this equation $2\pi i$ should be $(2\pi i)^m$].