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# Linear response theory for thermodynamic properties

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A fluctuation-dissipation theorem, connecting all thermodynamic response functions to equilibrium fluctuations in the microcanonical ensemble, is derived from classical mechanics. This particular problem is not included in the usual linear response scheme, since the relevant perturbations cannot be stated as additional terms in the Hamiltonian. In experiments where the only control parameter is the heat flow, dissipation is present in terms of an entropy flow from the system to the surroundings. As an example, the full frequency-dependent thermodynamic response matrix is extracted from simulations of a supercooled binary Lennard-Jones fluid. This fluid shows rather high relaxation strength of all response functions, except of the adiabatic compressibility. The low frequency limit of all thermodynamic susceptibilities increases as temperature is decreased along an isocore. [S1063-651X(99)10105-3]

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## I. INTRODUCTION

Properties such as specific heat, thermal expansivity, and compressibility become dynamic in systems with slow internal relaxation processes. If, for instance, an instant volume increase $\delta V$ is imposed on such a system, the resulting pressure response $\delta P(t)$ will depend on time in a certain way, reflecting the internal dynamical properties of the system. In fact there are 24 different thermodynamic response experiments of the type $\delta X(t)/\delta Y_0|_Z$—response of $X$ following an instant perturbation of $Y$ while $Z$ is kept constant, where $X$, $Y$, and $Z$ can refer to one of the variables volume $V$, pressure $P$, heat $Q$, or temperature $T$. In the case where $Z$ refers to $Q$, the experiment is carried out without any heat transfer. This type of experiment is increasingly used on various biological systems, including, for example, vesicles and cell membranes [1]. Moreover, measurements of the isobaric frequency-dependent specific heat $\tilde{c}_p(\omega)$ [2–5] and the frequency-dependent adiabatic bulk modulus $\tilde{\kappa}_s(\omega)$ [6] have become an experimental tool in investigation of supercooled liquids.

Theoretical treatment of thermodynamic response functions has mainly been given in the context of hydrodynamics [7–11] or specific models [11,12], and it is still an open question whether a connection can be made between the microscopical properties of a system, and the measured thermodynamic response, in the same spirit as was done for other response functions [13–15]. Recently the fluctuation-dissipation (FD) theorem for dynamic specific heat was derived for systems under isothermal conditions [16], expressing a theoretically based relation between dynamic specific heat and energy fluctuations. The derivation was done in the context of general stochastic processes, which includes the case of classical Newtonian dynamics [17]. The expression ‘‘FD theorem’’ refers to a relation between the equilibrium fluctuations of a system and the response of the system to an external perturbation. As an example, consider relaxation of the enthalpy $H=E+PV$ upon a small instantaneous isobaric temperature increase $\delta T_0$ at time zero. The time-dependent isobaric specific heat, defined by $\delta H(t)=c_p(t)\delta T_0$, is given by

$$c_p(t)=\frac{1}{k_B T^2}\{\langle[\Delta H(0)]^2\rangle_{T,P}-\langle\Delta H(0)\Delta H(t)\rangle_{T,P}\}, \tag{1}$$

where $\langle\cdots\rangle_{T,P}$ means averaging over the isothermal-isobaric ensemble and $\Delta H(t)=H(t)-\langle H\rangle_{T,P}$ [16]. $k_B$ is Boltzmanns constant, which in the rest of this paper is put equal to 1. Other expressions for thermodynamic response functions are found in Ref. [9], where the dynamic iso*coric* specific heat is related to fluctuations of the potential energy in the grand canonical ensemble. In general, of course, the FD theorem for some thermodynamic property depends on the choice of ensemble.

In this article the focus is on the connection between, on the one hand, dynamic pressure and temperature response in systems where the parameters energy $E$ and volume $V$ are varied in time, and on the other hand fluctuations of pressure and temperature in the corresponding constant energy and volume ensemble. The motivation for this view is that molecular dynamics (MD) simulations have become an increasingly used tool in investigation of supercooled liquids [18,19]. The microcanonical ensemble ($NEV\mathbf{P}$ ensemble), where the number of particles, energy, volume, and total momentum are fixed parameters, is usually employed for this purpose, because observations in this ensemble reflect the intrinsic dynamical behavior of the model system without disturbance from artificial devices.

Obviously, there must be a connection between, for instance, kinetic energy fluctuations in the microcanonical ensemble and dynamic specific heat. It was found by Lebowitz *et al.* [20] that the static isocoric specific heat per molecule has the form

$$c_v=\frac{1}{2/3-N\langle(\Delta T)^2\rangle_{E,V}/T^2}, \tag{2}$$

where $\Delta T=T-\langle T\rangle_{E,V}$ is the fluctuation away from equilibrium of the kinetic temperature in a microcanonical ensemble. The kinetic temperature is defined by the total kinetic energy of the system (see below). In continuation of this work similar expressions were derived for other static properties [21]. However, there is no treatment of the more general case of thermo*dynamic* response functions in literature, although in Ref. [22] the frequency-dependent isocoric specific heat has been extracted from equilibrium kinetic energy fluctuations in a computer simulation of a single component Lennard Jones fluid by using an *ad hoc* generalization of Eq. (2). The reason for the absence of a rigorous microscopic theory for thermodynamic response functions may be that they cannot be derived from the usual response theory. In usual response theory [13–15] a perturbation is imposed on a system through an additional term in the Hamiltonian $H=H_0-Af(t)$, where $A$ is some phase space variable and $f(t)$ is its externally controlled conjugated force. The response of the system is derived by tracing the time-dependent phase space probability distribution to first order in $f(t)$. However, this method is not possible if one of the controllable variables is accumulated heat in the system. As an illustration, consider a thermally isolated system which has an electrode in each end, with an electrical resistance $R$ between the two electrodes. At time $t=0$, a small heat pulse $\delta Q_0$ is imposed by applying a voltage $\mathsf{V}$ to the electrodes in a small time interval $\delta t=R\,\delta Q_0/\mathsf{V}^2$. The perturbation can certainly be explicitly included in the Hamiltonian

$$H=H_0-\sum_i \mathsf{q}_i x_i \mathsf{E}(t), \tag{3}$$

where $\mathsf{q}_i$ are the charges, $\mathsf{E}=-(d/dx)\mathsf{V}$ the electric field, and $x_i$ particle $i$'s position in the $x$-direction. But the heat perturbation $\delta Q_0$ is quadratic in the perturbing field, instead of linear, thus the temperature response which is linear in $\delta Q_0$ will also be quadratic in $\mathsf{E}$. In addition to this difficulty the derivation of ordinary linear response theory relies on equivalence between ensembles [13,23,24]. Equivalence between, e.g., the canonical and microcanonical ensemble is indeed true when dealing with the average of some phase space variable or with correlation functions in time and space, which only include a few particles. But the equivalence is clearly broken when the question is about fluctuations of properties which are correlated to the total energy of the system under consideration.

## II. THERMODYNAMIC RESPONSE EXPERIMENTS ON COMPUTERS

In MD simulations the positions $r=\{\mathbf{r}_i(t)\}$ and momenta $p=\{\mathbf{p}_i(t)\}$ of $N$ particles are followed in phase space by numerical integration of the equations of motion derived from the Hamiltonian $H=U(r)+K(p)$. Conventionally, instantaneous kinetic temperature and pressure are defined [25] as

$$T(t)=\frac{2K(t)}{3N-n}, \quad P(t)=\frac{(2/3)K(t)+W(t)}{V}, \tag{4}$$

where the kinetic energy and the virial is

$$K=\sum_i \frac{\mathbf{p}_i^2}{2m_i}, \quad \text{and} \quad W=-\frac{1}{3}\sum_{i\neq j}\frac{\partial v_{ij}}{\partial r_{ij}}r_{ij}. \tag{5}$$

$v_{ij}$ and $r_{ij}$ are the pair potential and the pair distance, respectively. $n$ is a small number, counting how many kinetic degrees of freedom are removed by the external constraints on the system. If the momentum $\mathbf{P}$ and angular momentum $\mathbf{L}$ are conserved, the $3N$ kinetic degrees of freedom are reduced by 6 [26]. For large systems, $n=0$ is a good approximation. A more general concept of dynamic temperature in the microcanonical ensemble has recently been developed by Rugh [27]. It is shown that several choices of dynamic variables are possible, each on average equaling the microcanonic temperature $1/T=\partial S/\partial E$, where $S=\ln(\Omega)$ is the entropy. One of these choices, the kinetic temperature, defined in Eq. (4), specifically measures the temperature of the kinetic degrees of freedom. One could as well choose a certain part of the kinetic degrees of freedom for determination of the temperature, a ''thermometer'' if you will. Apart from tradition, a motivation for the choice of the kinetic temperature is that it is easy to calculate and easy to understand intuitively. However, the basic results in the following does not rely on this specific choice of temperature definition, because the response of any phase variable can be found from the basic FD theorem [Eq. (32)], and thereby the response of any defined temperature one might want to use.

The object is now to calculate how the system reacts to a small heat perturbation $\delta Q(t)$ combined with a volume perturbation $\delta V(t)$. Only linear perturbations are considered, which means that the perturbation has to be sufficiently small to ensure that the response depends linearly on the perturbation. For example in the case of the temperature response to a heat perturbation, a linear dependence of $\delta T(t)$ on the history of $\delta Q(t)$

$$\delta T(t)=\int_{-\infty}^{t}\mu(t-t')\,\delta Q(t')\,dt' \tag{6}$$

is assumed. The memory kernel $\mu(t)$ is specific for the system. *If* linearity is fulfilled, the frequency-dependent response function $\tilde{G}_{TQ}(\omega)$ is given by

$$\tilde{G}_{TQ}(\omega)=\int_0^{\infty}e^{-i\omega t}\mu(t)\,dt. \tag{7}$$

If the system is driven by an oscillating heat perturbation $\delta Q(\omega,t)=\delta Q_0 e^{i\omega t}$, then $\tilde{G}_{TQ}(\omega)$ is the time-independent complex ratio $\delta\tilde{T}(\omega,t)/\delta\tilde{Q}(\omega,t)$. For later reference consider also the response to an instantaneous forced heat perturbation $\delta Q_0$ at time $t=0$,

$$\delta T(t)=\int_0^{t}\mu(t-t')\,dt'\,\delta Q_0=\int_0^{t}\mu(t')\,dt'\,\delta Q_0. \tag{8}$$

The memory kernel $\mu(t)$ can be found from this specific experiment as

$$\mu(t)=\left(\frac{1}{\delta Q_0}\right)\frac{\partial}{\partial t}\delta T(t). \tag{9}$$

To avoid misunderstandings, please note that the slowing down observed in supercooled liquids is due to slowing down of fluctuations in potential degrees of freedom—not kinetic degrees of freedom. However, because of energy conservation, fluctuations of the potential energy $U(r)$ are balanced with opposite directed fluctuations of the kinetic energy $K(p)$, resulting in a slow relaxation of the kinetic temperature $T$ in the microcanonical ensemble.

### A. Perturbations

In a real laboratory, it is only possible to measure instantaneous temperature within a certain accuracy and time resolution, depending essentially on diffusivity and sample size. So following the temperature as a function of time on microscopic time scale in a microcanonical ensemble is only possible in computer simulations. In a laboratory one can use different means of imposing a heat perturbation $\delta Q(t)$ on a sample. For example, heating with a resistor or an oscillating electric field directly applied to the sample may be used. The actual perturbation of the phase space coordinates will in general depend on the method, the geometry, and also the initial phase space coordinates of the system. On the other hand, the temperature response is not expected to depend on the choice of perturbation in a laboratory experiment. To operate with the concept of thermodynamic response functions at all one has to *assume* that the average response of temperature and pressure on a long time scale is independent of how exactly the perturbation $\delta Q(t)$ is imposed. This allows one to freely choose ways of putting heat into a computer simulation. The only requirement is that the system must not be pushed far from equilibrium locally in real space by the perturbation. If there is some slow relaxation in the system, the long time linear response is independent of how one actually heats up the system.

#### *1. Heat perturbation*

As heat perturbation in the present study an instant scaling of all momenta is chosen,

$$\mathbf{p}_i \rightarrow \mathbf{p}_i' = (1+\varepsilon)\mathbf{p}_i \tag{10}$$

where $1+\varepsilon$ is close to 1. In agreement with laboratory experiments the energy change $\delta Q$ is controlled. As a result of this, $\varepsilon$ becomes a phase variable because it depends on the initial momenta. Expansion of $\varepsilon$ to first order in $\delta Q$ gives

$$\varepsilon = \frac{1}{2K}\delta Q. \tag{11}$$

Of course this choice gives rise to an instant overshoot of the temperature $\delta T_0 = 2\delta Q/(3N-n)$. However, the heat is immediately transfered into the configurational degrees of freedom, and within a few vibration times, the heat $\delta Q$ is distributed between configurational and kinetic energy in the same way as in a corresponding laboratory sample where the heat is spatially equilibrated upon a heating procedure, but where the slow structural degrees of freedom are still not relaxed. This may seem odd, but in fact the employment of specific heat spectroscopy in the laboratory as well as in computer experiments relies on a separation of relaxation times, which makes it possible to drive the system to a state where it is thermally equilibrated, but still needs to undergo a slow relaxation to reach equilibrium.

#### *2. Volume perturbation*

Let $H_V$ denote the isocoric Hamiltonian. If, for instance, the system is evolving in a cubic cell under periodic boundary conditions, then $H_V$ can be constructed by inserting a modified pair distance matrix $d_{V(L)}(r)=\{L|\,\mathrm{mod}(\mathbf{r}_i-\mathbf{r}_j,L)|\}$ in the potential,

$$H_V(r,p) = U(d_V(r)) + K(p). \tag{12}$$

An isotropic volume scaling is imposed by a scaling of all molecule positions, and a simultaneous scaling of the side length $L$,

$$\mathbf{r}_i \rightarrow \mathbf{r}_i' = \mathbf{r}_i(1+\delta), L \rightarrow L' = L(1+\delta), \tag{13}$$

implying that $V \rightarrow V' = V + \delta V = V + 3V\delta$. Since

$$d_{V'}(r') = (1+\delta)d_V(r), \tag{14}$$

one observes that

$$U_{V'}(r') = U(d_{V'}(r')) = U((1+\delta)d_V(r)) = U(d_V(r)) + \sum_{i=1}^{N} \frac{\partial U(d_V(r))}{\partial \mathbf{r}_i} \cdot \mathbf{r}_i \delta = U_V(r) + \delta U(r) \tag{15}$$

to first order in $\delta$. As in the previous example, the perturbation shifts the system to a new subset of phase space on which it relaxes, but the change in energy turns out to depend on the initial state $\Gamma$, which causes a problem in evaluation of the response function. To prevent this difficulty, the following perturbation experiment is constructed: Simultaneously with the volume chance, a scaling of all the momenta by $(1+\varepsilon)$ is imposed, which reduces the energy by an amount corresponding to the increase in energy due to the change of volume

$$\delta K = K(1+\varepsilon)^2 - K = -\delta U, \tag{16}$$

ensuring that $\delta H = 0$. Note the correspondence to the previous example, where the volume was fixed and the energy changed. Here the opposite situation is considered: Fixed energy and perturbation of volume. The idea is that if the linear response to any variation in energy and volume is known, then the linear response to an adiabatic volume perturbation can be reconstructed by a suitable superposition of energy or volume response functions. As the volume is the actual control parameter, the quantities $\delta$ and $\varepsilon$ is better expressed in terms of $\delta V$,

$$\delta = \frac{1}{3}\frac{\delta V}{V},$$

$$\varepsilon = -\frac{1}{2K}\sum_{i=1}^{N} \frac{\partial H_V}{\partial \mathbf{r}_i}\mathbf{r}_i \frac{1}{3}\frac{\delta V}{V} = \frac{W}{2K}\frac{\delta V}{V}. \tag{17}$$

In the following derivations, only perturbations which are linear combinations of the two perturbations defined above are considered. This simplifies the calculations, which can now be done under isocoric and isoenergetic conditions.

### B. Perturbation of the microcanonical ensemble

Consider an $N$-particle system which is initially fixed on an energy surface defined by $H_V(\Gamma)=H_V(r,p)=E$. The system is assumed to be in equilibrium, so that the distribution in phase space is a uniform distribution on the energy surface

$$f_{E,V}(\Gamma)=\frac{1}{\Omega_{E,V}}\delta\{H_V(\Gamma)-E\}, \tag{18}$$

where the phase space volume $\Omega_{E,V}$ is defined by

$$\Omega_{E,V}=\int d\Gamma\,\delta\{H_V(\Gamma)-E\}. \tag{19}$$

At $t=0$ the system is displaced slightly in phase space by $\delta\Gamma(\Gamma)$, simultaneously with a change of the Hamiltonian $H_V\rightarrow H_{V+\delta V}$. This perturbation will in general change the energy of the system by

$$\delta E(\Gamma)=\sum_{i=1}^{6N}\frac{\partial H_V}{\partial \Gamma_i}\delta\Gamma_i(\Gamma). \tag{20}$$

In accordance with the preceding section, perturbations are constructed so that $\delta E$ does not depend on the initial state $\Gamma$, i.e., the system is shifted to another energy surface in phase space defined by $H_{V+\delta V}(\Gamma')=E+\delta E$.

Now the distribution immediately after the perturbation $f_0(\Gamma)$ can be constructed by ''picking out the points'' in phase space which were on the energy surface $H_V(\Gamma)=E$ before the perturbation. $f_0$ is formally written

$$f_0(\Gamma')=f_{E,V}[\Gamma'-\delta\Gamma(\Gamma')]\left|\frac{\partial[\Gamma'-\delta\Gamma(\Gamma')]}{\partial\Gamma'}\right| \tag{21}$$

and it is expected to be a nonuniform distribution on the energy surface $H_{V+\delta V}(\Gamma')=E+\delta E$. The Jacobian $|\partial[\Gamma'-\delta\Gamma(\Gamma')]/\partial\Gamma'|$ ensures proper normalization of $f_0$. It compensates for the immediate phase space expansion following the disturbance. Note that the determinant depends on $\Gamma'$. $f_0(\Gamma')$ is explicitly written as

$$f_0(\Gamma')=\frac{1}{\Omega_{E,V}}\delta\{U_V(r'-\delta r)+K(p'-\delta p)-E\}\times\left|\frac{\partial[\Gamma'-\delta\Gamma(\Gamma')]}{\partial\Gamma'}\right|, \tag{22}$$

which by use of Eq. (15) is reformulated in terms of the perturbed Hamiltonian

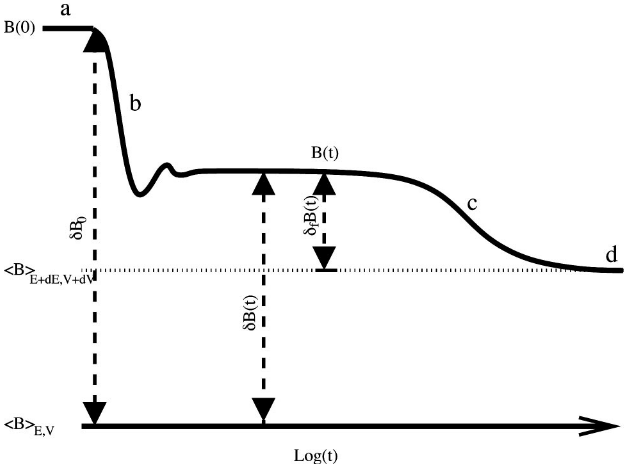

FIG. 1. Schematic illustration of a response experiment. The instant response $\delta B_0$ (a) is followed by a fast decay (b) to a state where the fast degrees of freedom are equilibrated. The slow decay (c) follows, and the system finally reaches equilibrium under the new constraint $(E+\delta E,V+\delta V)$ (d). It does not matter which value of $B$ is chosen as zero point in evaluation of the time dependence, since the value of $B(0)$ is subtracted anyway. For computational reasons $\delta_f B=B-\langle B\rangle_{E+\delta E,V+\delta V}$ is chosen.

$$\begin{aligned}f_0(\Gamma')&=\frac{1}{\Omega_{E,V}}\delta\{U_{V+\delta V}(r')-\delta U(r')\\&\quad+K(p')-\delta K(p')-E\}\left|\frac{\partial[\Gamma'-\delta\Gamma(\Gamma')]}{\partial\Gamma'}\right|\\&=\frac{1}{\Omega_{E,V}}\delta\{H_{V+\delta V}(\Gamma')\\&\quad-(E+\delta E)\}\left|\frac{\partial[\Gamma'-\delta\Gamma(\Gamma')]}{\partial\Gamma'}\right|.\end{aligned} \tag{23}$$

### C. Calculation of response in the microcanonical ensemble

The dynamical behavior is assumed to be described by a conditional probability distribution $G(\Gamma,t|\Gamma',t')$, which includes quite general types of systems. For instance, in classical mechanics, the conditional probability looks similar to

$$G(\Gamma,t|\Gamma',0)=\delta\{\Gamma-e^{itL}\Gamma'\}, \tag{24}$$

where $L=-i\{H,\cdot\}$ is the Liouville operator.

The response of a phase variable $B$ may be separated into two terms as illustrated in Fig. 1,

$$\delta B(t)=\delta B_0+[B(t)-B(0)], \tag{25}$$

that is, an instantaneous response $\delta B_0=\langle(\partial B/\partial\Gamma)\delta\Gamma\rangle_{E,V}$ plus a time-dependent response $[B(t)-B(0)]$, where $B(0)$ is the value of $B$ right after the perturbation. The first one is straightforward to calculate and the latter is calculated by averaging the deviation of $B(t)$ from its mean value in the *final* state: $\delta_f B(t)=B(t)-\langle B\rangle_{E+\delta E,V+\delta V}$, since $B(t)-B(0)=\delta_f B(t)-\delta_f B(0)$. By use of the initial distribution

(23) and the conditional probability $G(\Gamma,t|\Gamma',0)$, the development of the phase variable $\delta_f B(\Gamma)$ can be traced in time after the perturbation as

$$\delta_f B(t)=\int d\Gamma\int d\Gamma'\,\delta_f B(\Gamma)\times G_{V+\delta V}(\Gamma,t|\Gamma',0)\frac{1}{\Omega_{E,V}}\,\delta\{H_{V+\delta V}(\Gamma')-(E+\delta E)\}\left|\frac{\partial[\Gamma'-\delta\Gamma(\Gamma')]}{\partial\Gamma'}\right|. \tag{26}$$

Expansion of $1/\Omega_{E+\delta E,V+\delta V}$ in $\delta E$ and $\delta V$ yields

$$\frac{1}{\Omega_{E,V}}=\frac{1}{\Omega_{E+\delta E,V+\delta V}}\left(1+\frac{\partial\ln\Omega_{E,V}}{\partial E}\delta E+\frac{\partial\ln\Omega_{E,V}}{\partial V}\delta V\right) \tag{27}$$

and by inserting $1/\Omega_{E,V}$ in Eq. (26) one gets

$$\delta_f B(t)=\int d\Gamma\int d\Gamma'\,\delta_f B(\Gamma)G_{V+\delta V}(\Gamma,t|\Gamma',0)\times\frac{1}{\Omega_{E+\delta E,V+\delta V}}\left(1+\frac{\partial\ln\Omega_{E,V}}{\partial E}\delta E+\frac{\partial\ln\Omega_{E,V}}{\partial V}\delta V\right)\delta\{H_{V+\delta V}(\Gamma')-(E+\delta E)\}\times\left|\frac{\partial[\Gamma'-\delta\Gamma(\Gamma')]}{\partial\Gamma'}\right|, \tag{28}$$

which allows identification of the equilibrium distribution

$$f_{E+\delta E,V+\delta V}(\Gamma)=\frac{1}{\Omega_{E+\delta E,V+\delta V}}\,\delta\{H_{V+\delta V}(\Gamma)-(E+\delta E)\}. \tag{29}$$

When the averaging in Eq. (28) is carried out, it is noteworthy that the Jacobian determinant has no fluctuating terms of zeroth order, which means that the correction terms $[(\partial\ln\Omega_{E,V}/\partial E)\delta E+(\partial\ln\Omega_{E,V}/\partial V)\delta V]$ to the density of states do not influence the first order result. Therefore, $\delta_f B(t)$ turns out to be given by the equilibrium autocorrelation function

$$\delta_f B(t)=\left\langle\left|\frac{\partial(\Gamma-\delta\Gamma)}{\partial\Gamma}\right|(0)\Delta_f B(t)\right\rangle_{E+\delta E,V+\delta V}, \tag{30}$$

where $\Delta_f B=B-\langle B\rangle_{E+\delta E,V+\delta V}$ is the equilibrium fluctuation of the variable $B$ with respect to its average in the final state. $\langle\ \rangle_{E+\delta E,V+\delta V}$ means isoenergetic-isocoric average with the specified parameters $E+\delta E,V+\delta V$. The full response can be constructed as

$$\delta B(t)=\delta B_0+\left\langle\left|\frac{\partial(\Gamma-\delta\Gamma)}{\partial\Gamma}\right|(0)\Delta_f B(t)\right\rangle_{E+\delta E,V+\delta V}-\left\langle\left|\frac{\partial(\Gamma-\delta\Gamma)}{\partial\Gamma}\right|\Delta_f B\right\rangle_{E+\delta E,V+\delta V}, \tag{31}$$

which equals

$$\delta B(t)=\delta B_0+\left\langle\left|\frac{\partial(\Gamma-\delta\Gamma)}{\partial\Gamma}\right|(0)\Delta B(t)\right\rangle_{E,V}-\left\langle\left|\frac{\partial(\Gamma-\delta\Gamma)}{\partial\Gamma}\right|\Delta B\right\rangle_{E,V}, \tag{32}$$

in the linear limit. Below the notation $\langle\cdots\rangle$ is used for $\langle\cdots\rangle_{E,V}$.

Now the specific perturbations proposed in Sec. II A are considered. First the heat perturbation defined in Eqs. (10) and (11) is inserted in Eq. (32). The Jacobian is expanded to first order

$$\left|\frac{\partial(\Gamma-\delta\Gamma)}{\partial\Gamma}\right|=\prod_{i=1}^{3N}\left(1-\frac{1}{2K}\delta E\right)\approx 1-3N\frac{1}{2K}\delta E, \tag{33}$$

leading to the response

$$\delta B(t)=\delta B_0+\frac{3N}{3N-n}\left\langle\Delta\frac{-1}{T}(0)\Delta B(t)\right\rangle\delta E-\left\langle\Delta\frac{-1}{T}(0)\Delta B(0)\right\rangle\delta E. \tag{34}$$

The frequency-dependent response function $\tilde{G}_{BE}|_V(\omega)$ is found directly from Eq. (34) by use of Eqs. (7) and (9),

$$G_{BE|V}(\omega)=\int_0^\infty dt e^{-i\omega t}\frac{d}{dt}\theta(t)\left\{\left.\frac{\delta B_0}{\delta E}\right|_V+\frac{3N}{3N-n}\left\langle\Delta\frac{1}{T}\Delta B\right\rangle-\frac{3N}{3N-n}\left\langle\Delta\frac{1}{T}(0)\Delta B(t)\right\rangle\right\}, \tag{35}$$

where $\theta(t)$ is the Heaviside step function. Equation (35) can be written as

$$G_{BE|V}(\omega)=\left.\frac{\delta B_0}{\delta E}\right|_V+\frac{3N}{3N-n}\left\{\left\langle\Delta\frac{1}{T}\Delta B\right\rangle-i\omega\int_0^\infty dt e^{-i\omega t}\left\langle\Delta\frac{1}{T}(0)\Delta B(t)\right\rangle\right\}. \tag{36}$$

The temperature and pressure response may be found from Eq. (34) by substituting $B$ with $T$ and $P$, respectively.

The volume perturbation is now considered. The Jacobian is to first order

$$\left|\frac{\partial(\Gamma-\delta\Gamma)}{\partial\Gamma}\right|=\prod_{i=1}^{3N}(1-\delta)(1-\varepsilon)\approx 1-3N(\delta+\varepsilon). \tag{37}$$

Inserting the expression for the Jacobian from Eq. (37) in Eq. (32), with $\varepsilon$ and $\delta$ taken from Eq. (17) one arrives at

$$\delta B(t)=\delta B_0+\frac{1}{V}\frac{3N}{3N-n}\left\{\left\langle\Delta\frac{W}{T}\Delta B\right\rangle-\left\langle\Delta\frac{W}{T}(0)\Delta B(t)\right\rangle\right\}\delta V \tag{38}$$

and in the frequency domain the response function is

$$\tilde{G}_{BV|E}(\omega)=\frac{\delta B_0}{\delta V}\bigg|_E+\frac{3N}{V(3N-n)}\left\{\left\langle \Delta\frac{W}{T}\Delta B\right\rangle -i\omega\int_0^\infty dte^{-i\omega t}\left\langle \Delta\frac{W}{T}(0)\Delta B(t)\right\rangle\right\}. \quad (39)$$

The temperature and pressure response may now be found directly from Eq. (38). In each case the instantaneous term $\delta B_0/\delta V|_E$ must of course be evaluated by considering the actual perturbation. As an example the immediate *isoenergetic* pressure response is found to be

$$\frac{\delta P}{\delta V}\bigg|_E=\langle \delta P(\delta\Gamma)\rangle=\frac{-1}{V}\left\langle \frac{2K}{3}+\frac{1}{9V}\sum_{i\neq j}\frac{\partial^2 v(r_{ij})}{\partial r_{ij}^2}r_{ij}^2\right\rangle. \quad (40)$$

### D. Laboratory response functions

The results above can be contracted in the following matrix equation:

$$\begin{pmatrix}\delta\tilde{T}\\ \delta\tilde{P}\end{pmatrix}=\begin{pmatrix}\tilde{G}_{TE|V} & \tilde{G}_{TV|E}\\ \tilde{G}_{PE|V} & \tilde{G}_{PV|E}\end{pmatrix}(\omega)\begin{pmatrix}\delta\tilde{E}\\ \delta\tilde{V}\end{pmatrix}. \quad (41)$$

The object is now to construct the response functions for an adiabatic volume perturbation. This means an experiment carried out without energy exchange, *except* work done by the immediate volume expansion $\delta E=-\langle P\rangle$. Note the difference from an isoenergetic experiment, where $\delta E=0$. To derive the adiabatic response, one can use linearity and calculate the response as a superposition of two experiments: one experiment with energy fixed $\delta E=0$, while volume is changed instantaneously, and one with volume fixed $\delta V=0$, but $\delta E=-\langle P\rangle\delta V$, the (mean) change of energy produced by the change of volume $\delta V$ in an adiabatic experiment.

The response is then given as a superposition of the response to the volume perturbation and the energy perturbation, implying that the response function looks similar to

$$\tilde{G}_{BV|Q}(\omega)=[\tilde{G}_{BV|E}(\omega)-\langle P\rangle\tilde{G}_{BE|V}(\omega)]=\frac{\delta B_0}{\delta V}\bigg|_E-\langle P\rangle\frac{\delta B_0}{\delta E}\bigg|_V+\frac{1}{V}\frac{3N}{3N-n}\left\{\left\langle \Delta\frac{W-\langle P\rangle V}{T}\Delta B\right\rangle -i\omega\int_0^\infty dte^{-i\omega t}\left\langle \Delta\frac{W-\langle P\rangle V}{T}(0)\Delta B(t)\right\rangle\right\}. \quad (42)$$

In large systems, for instance,

$$G_{PV|Q}(t)=\frac{\delta P_0}{\delta V}\bigg|_E-\langle P\rangle\frac{\delta P_0}{\delta E}\bigg|_V+\frac{1}{\langle T\rangle}\left\{\langle \Delta P\Delta P\rangle -i\omega\int_0^\infty dte^{-i\omega t}\langle \Delta P(0)\Delta P(t)\rangle\right\}. \quad (43)$$

Now the response matrix for the situation where volume and heat are the controllable parameters may be written. Defining $q=Q/N$ and $v=V/N$, and defining the frequency-dependent response matrix by

$$\begin{pmatrix}\delta\tilde{T}\\ \delta\tilde{P}\end{pmatrix}=\begin{pmatrix}\tilde{G}_{Tq|v}(\omega) & \tilde{G}_{Tv|q}(\omega)\\ \tilde{G}_{Pq|v}(\omega) & \tilde{G}_{Pv|q}(\omega)\end{pmatrix}\begin{pmatrix}\delta\tilde{q}\\ \delta\tilde{v}\end{pmatrix}, \quad (44)$$

one finds in the $N\to\infty$ limit, that the matrix elements are given by

$$\tilde{G}_{Tq|v}(\omega)=\tilde{c}_v(\omega)^{-1}=\frac{2}{3}+N\left\{\left\langle \Delta\frac{1}{T}\Delta T\right\rangle -i\omega\int_0^\infty dte^{-i\omega t}\left\langle \Delta\frac{1}{T}(0)\Delta T(t)\right\rangle\right\}, \quad (45)$$

$$\tilde{G}_{Tv|q}(\omega)=-T\tilde{G}_{Pq|v}(\omega),$$

$$\tilde{G}_{Pq|v}(\omega)=\frac{2}{3}\rho+N\left\{\left\langle \Delta\frac{1}{T}\Delta P\right\rangle -i\omega\int_0^\infty dte^{-i\omega t}\left\langle \Delta\frac{1}{T}(0)\Delta P(t)\right\rangle\right\}, \quad (46)$$

$$\tilde{G}_{Pv|q}(\omega)=\rho\left\{\frac{\langle W\rangle}{V}-\frac{5}{3}\langle P\rangle-\frac{1}{9V}\left\langle\sum_{i\neq j}\frac{\partial^2 v_{ij}}{\partial r_{ij}^2}r_{ij}^2\right\rangle\right\}+\frac{N}{\langle T\rangle}\left\{\langle \Delta P\Delta P\rangle-i\omega\int_0^\infty dte^{-i\omega t}\times\langle\Delta P(0)\Delta P(t)\rangle\right\}. \quad (47)$$

This constitutes the FD theorem for thermodynamic response functions. Equation (45) is in agreement with the expression used by Grest and Nagel [22], while $\lim_{\omega\to 0}\tilde{c}_v(\omega)$ is in accordance with Eq. (2), taken from Lebowitz *et al.* (Ref. [20]). Also, the frequency-dependent bulk modulus $G_{Pv}|_q(\omega)$ approaches the well known expression for the static adiabatic bulk modulus [21,25] in the $\omega\to 0$ limit.

Consider the situation, where $T$ and $P$ are controllable parameters, while $q$ and $v$ are fluctuating freely. By inversion of Eq. (44),

$$\begin{pmatrix}\delta\tilde{q}\\ \delta\tilde{v}\end{pmatrix}=\begin{pmatrix}\tilde{c}_P(\omega) & -T\tilde{\alpha}_P(\omega)\\ \tilde{\alpha}_P(\omega) & -\tilde{\kappa}_T(\omega)\end{pmatrix}\begin{pmatrix}\delta\tilde{T}\\ \delta\tilde{P}\end{pmatrix}=\frac{1}{\tilde{D}(\omega)}\begin{pmatrix}\tilde{G}_{Pv|q}(\omega) & -\tilde{G}_{Tv|q}(\omega)\\ -\tilde{G}_{Pq|v}(\omega) & \tilde{G}_{Tq|v}(\omega)\end{pmatrix}\begin{pmatrix}\delta\tilde{T}\\ \delta\tilde{P}\end{pmatrix}, \quad (48)$$

$$\tilde{D}(\omega)=\tilde{G}_{Tq|v}(\omega)\tilde{G}_{Pv|q}(\omega)-\tilde{G}_{Pq|v}(\omega)\tilde{G}_{Tv|q}(\omega).$$

Note that the properties $\tilde{c}_P(\omega)$, $\tilde{\kappa}_T(\omega)$, and $\tilde{\alpha}_P(\omega)$ are calculated ‘‘per particle.’’

### E. Dissipation

A few remarks about dissipation are appropriate at this point. In any linear response experiment there is a dissipation which is of second order in the perturbing variable, usually characterized by a positive net heat production. For example, if an adiabatic volume perturbation $\delta V(t)=\mathrm{Re}\{V_0 e^{i\omega t}\}$ is forced on the system, the work done on the system during one cycle is given by the integral

$$\begin{aligned}\delta E &= \int_0^{T_{\text{cycle}}} -P(t)\dot{V}dt = \int_0^{T_{\text{cycle}}} -[P_0+\delta P(t)]\dot{V}dt \\ &= \int_0^{T_{\text{cycle}}} -[P_0+\mathrm{Re}\{\delta V_0 \tilde{G}_{Pv}|_q(\omega)e^{i\omega t}\}]\mathrm{Re}\{i\omega\delta V_0 e^{i\omega t}\} \\ &= \frac{\delta V_0^2\pi}{N}\mathrm{Im}\{\tilde{G}_{Pv|q}(\omega)\} = \frac{\delta V_0^2\pi}{N}\mathrm{Im}\left\{\frac{1}{\tilde{\kappa}_S(\omega)}\right\}. \end{aligned} \tag{49}$$

Since $\mathrm{Im}\{\tilde{G}_{Pv|q}(\omega)\}$ is non-negative, this means that if there is an imaginary part of $\tilde{G}_{Pv|q}$ at all, the system is slightly heated by the adiabatic oscillating compression, and the temperature will eventually increase so much that the linearity is broken.

Of course, if one considers an isocoric specific heat experiment where the heat is controlled by the function $\delta Q(t)=\mathrm{Re}\{\delta Q_0 e^{-i\omega t}\}$, there is no energy absorbed during a cycle of the experiment, since the system returns to exactly the same thermodynamic state after each cycle. However, there is an *entropy* production during a cycle, as noted by Birge and Nagel [3]. This entropy production is a general feature, which, like the linear response, does not depend on the choice of heat perturbation. However, the entropy increase resulting from a perturbation of the sort specified in Eqs. (10) and (11) may be calculated directly. Consider an arbitrary ensemble spread out in phase space by some distribution $f(r,p)$. The entropy is given by $S[f]=-\int drdp f(r,p)\ln h^{3N}f(r,p)$, where $h$ is some constant with the same dimension as $r\times p$. The actual size of $h$ has no significance, since a change of $h$ will only shift the zero point of the entropy axis. When all momenta are scaled simultaneously by $\mathbf{p}_i\to\mathbf{p}_i'=\mathbf{p}_i(1+\varepsilon)$, the new distribution is

$$f'(r,p')=f(r,p'(1-\varepsilon))\left|\frac{\partial p}{\partial p'}\right|, \tag{50}$$

and the new entropy is

$$\begin{aligned} S' &= -\int drdp f(r,p'(1-\epsilon))\left|\frac{\partial p}{\partial p'}\right| \\ &\quad \times \ln\left(f(r,p'(1-\epsilon))\left|\frac{\partial p}{\partial p'}\right|\right) \\ &= -\int drdp f(r,p)\left\{\ln(f(r,p))-3N\frac{\delta Q}{2K}+O(\delta Q^2)\right\}. \end{aligned} \tag{51}$$

Thus the first order entropy increase is found to be in accordance with the well known thermodynamic expression

$$\delta S=S'-S=\frac{3N}{3N-n}\left\langle\frac{\delta Q}{T}\right\rangle=\left\langle\frac{\delta Q}{T}\right\rangle+O\left(\frac{1}{N}\right), \tag{52}$$

as it should be for any choice of small heat perturbation.

Following Christensen [28], the oscillatory heat pulse $\delta Q(t)$ is constructed from small successive steps of the type indicated by Eq. (11), so that the entropy flow into the system during one cycle of duration $T_{\text{cycle}}$ may be calculated as

$$\delta S_{\text{cycle}}=\left\langle\int_0^{T_{\text{cycle}}}dt\frac{\delta\dot{Q}(t)}{T(t)}\right\rangle. \tag{53}$$

If terms of second order in $\delta Q$ are included in Eq. (52), these will appear as products of sine and cosine, and integrate to 0 over one cycle. Thus the only second order term stems from expansion of the right-hand side of Eq. (53). Letting $T_0$ denote the mean temperature of the process, one may write

$$\delta S_{\text{cycle}}=\left\langle\int_0^{T_{\text{cycle}}}\frac{\delta\dot{Q}(t)}{T_0}-\frac{\delta\dot{Q}(t)\delta T(t)}{T_0^2}dt\right\rangle. \tag{54}$$

The first term in the time integral is just a cosine which integrates to 0. Since $\delta T(t)=\mathrm{Re}\{[\delta Q_0/N\tilde{c}_v(\omega)]e^{i\omega t}\}$, the entropy flow into the system to second order in $\delta Q_0$ is found to be

$$\delta S_{\text{cycle}}=-\pi\frac{\delta Q_0^2}{NT_0^2}\mathrm{Im}\left\{\frac{1}{\tilde{c}_v(\omega)}\right\}. \tag{55}$$

The entropy flow into the system is negative, meaning that entropy flows out of the system. There is a net entropy productions within each cycle inside the system, which is captured by the surroundings, and may be interpreted as a loss of free energy of the surroundings [28]. In the case of an oscillatory adiabatic volume perturbation, the system was heated up by work done on the system, causing a loss of energy in the surroundings. In both cases the dissipation is proportional to the imaginary part of the relevant response function.

## III. EXAMPLE: BINARY LENNARD-JONES LIQUID

### A. Simulations

To illustrate the use of the FD theorem, MD simulations of the well known Kob and Andersen model [18] were performed. The model consists of a mixture of two different kinds of particles, labeled *A* and *B*. Each sample consists of 80% *A* particles and 20% *B* particles. Interaction between two particles is governed by a Lennard-Jones potential $V_{\alpha\beta}(r)=4\epsilon_{\alpha\beta}[(\sigma_{\alpha\beta}/r)^{12}-(\sigma_{\alpha\beta}/r)^6]$, where $\alpha$ and $\beta$ refer to the labels *A* and *B*. The particles have identical mass $m$ and the parameters are chosen [29] as $\epsilon_{AA}=1.0$, $\epsilon_{AB}=1.5$, $\epsilon_{BB}=0.88$, $\sigma_{AA}=1.0$, $\sigma_{AB}=0.8$, and $\sigma_{BB}=0.88$.

Below, distances are in dimensionless units of $\sigma_{AA}$, energy in dimensionless units of $\epsilon_{AA}$, and time is given in dimensionless units of $(m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$. A characteristic vibration time is around 1/10 time units. The potential is truncated at the distance 2.5.

Simulations were carried out at the temperatures $T = 0.464, 0.527, 0.614, 0.711 \pm 0.002$ and pressures $P = 2.43, 3.20, 4.40, 5.61 \pm 0.02$. The density was kept fixed at $\rho = 1.18873$ in all cases by means of periodic boundary conditions, and the equations of motion was integrated by means of the Verlet velocity algorithm [30]. At each temperature four different samples with 256 particles in each were prepared by first quenching a random configuration, then equilibrating with a Nosé Hoover thermostat [31], and there upon tuning the energy to make sure that all four samples were at the same energy surface with a relative uncertainty of less than $10^{-3}$ of the total energy. Then the samples where equilibrated under constant energy in 400 time units in the cases $T = 0.614, 0.711$, 4000 time units in the case $T = 0.527$ and 8000 time units in the case $T = 0.464$, which in each case is more than the slow relaxation time. After this preparation the kinetic energy, the pressure and the property $\Sigma(\partial^2 v_{ij}/\partial r_{ij}^2) r_{ij}^2$ was sampled during runs at $1.6 \times 10^5$ time units ($4 \times 10^7$ time steps) for $T = 0.464$, $8 \times 10^4$ time units for $T = 0.527$, and $8 \times 10^3$ time units for $T = 0.614$ and 0.711. The autocorrelation function and Fourier transforms were calculated by use of the ESSL subroutines library [32]. In addition five samples of 800 particles each, and the same density as above were prepared at $T = 0.527$, and runned for $4 \times 10^4$ time units to check for finite size effects.

### B. Simulation results

In Fig. 2 the time correlation function

$$-N\langle (1/T)(0) T(t) \rangle$$

is plotted at different temperatures. The long tail of the correlation function is identified with the slow structural relaxation in the liquid. The slow relaxation increases in strength and duration with decreasing temperatures. The often used phenomenological stretched exponential (Kohlrausch-Williams-Watts [33] form) is used as a fitting formula. Relaxation times grow in a non-Arrhenius way [34], common to supercooled liquids, as shown in the inset of Fig. 2. The $\beta$ exponents change from approximately 1 at $T = 0.711$ down to 0.7 at $T = 0.464$. $\beta$ measures the sharpness of the relaxation time distribution. Lower values of $\beta$ correspond to broader spectra. In laboratory measurements on organic liquids [2–5,16,35] the specific heat spectra have in general been found to be broader, with $\beta$ lying in the range 0.50–0.65. However, these measurements were done much closer to the glass transition temperature $T_G$, and for molecular liquids. In general $\beta$ for other relaxation functions (for instance, the intermediate scattering function) is found to be in the interval $0.7 - 1$ in the high-temperature range accessible to computer simulations [18,19]. The relaxation strength is increasing with decreasing temperature, a feature which is qualitatively different from the behavior of the intermediate scattering function [18], which is found to have temperature-independent relaxation strength. However, there is no reason to believe that these two properties should behave exactly in the same manner, so there is no direct contradiction here. The low relaxation strength of

$$-N\langle (1/T)(0) T(t) \rangle$$

at high temperatures is consistent with an energy landscape picture, where the number of configurational traps is reduced as temperature is increased, and it is qualitatively consistent with the general behavior of $c_P$ found in real liquids [36].

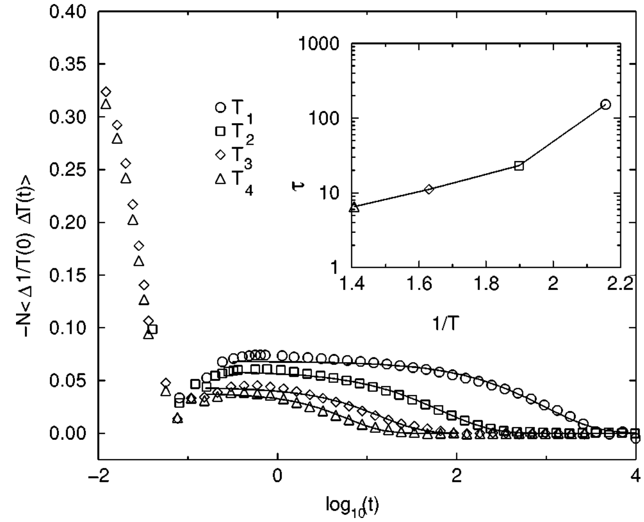

FIG. 2. The correlation functions $\langle -N\Delta(1/T)(0)\Delta T(t) \rangle$ for four different mean temperatures, on a logarithmic time axis. Each correlation function is based on eight different runs with $10^6$ sample points each. No smoothing has been employed. The data points have been logarithmically averaged, i.e., the data points on the graph are averaged over increasing time intervals with increasing time. The lines are fits to stretched exponentials, $f(t) = \exp[-(t/\tau)^\beta]$, with exponents $\beta = 0.73, 0.75, 0.92, 1.05$ for the temperatures $T_1 = 0.464 \pm 0.002$, $T_2 = 0.527 \pm 0.002$, $T_3 = 0.614 \pm 0.002$, and $T_4 = 0.711 \pm 0.002$, respectively. The insert shows the non-Arrhenius temperature dependence of the relaxation time $\tau$.

There is a small finite size effect for samples at 256 particles. In Fig. 3 real parts of specific heat and compressibility are compared for runs with both 800 and 256 particles with the same amount of total energy per particle. The specific heat was the same in the two cases as seen in Fig. 3, which was also the case for the mean temperature. On the other hand $\tilde{\kappa}_T$ is smaller by approximately 3%, and the pressure is systematically larger by 3% in an $N = 800$ sample. That is, there is a small finite size effect, which is most pronounced in properties related to the pressure, but which is small compared to the noise in the data.

Figures 4, 5, and 6 show the response functions $\tilde{c}_P(\omega)$, $\tilde{\alpha}_P(\omega)$, and $\tilde{\kappa}_T(\omega)$. The overall behavior is the same. The crossover frequency which reflects the slow ($\alpha$) decay is moving approximately two decades down, as the temperature is lowered. In general the configurational part is increasing with decreasing temperature, but while $\tilde{c}_P$ and $\tilde{\alpha}_P$ have a high configurational part relative to the vibrational part, $[c_P'(0) - c_P'(\infty)]/c_P'(\infty) \approx 0.4 - 0.6$, $[\alpha_P'(0) - \alpha_P'(\infty)]/\alpha_P'(\infty) \approx 0.5 - 0.8$, the same property calculated for $\tilde{\kappa}_T$ is somewhat lower, $[\kappa_T'(0) - \kappa_T'(\infty)]/\kappa_T'(\infty) \approx 0.15 - 0.3$.

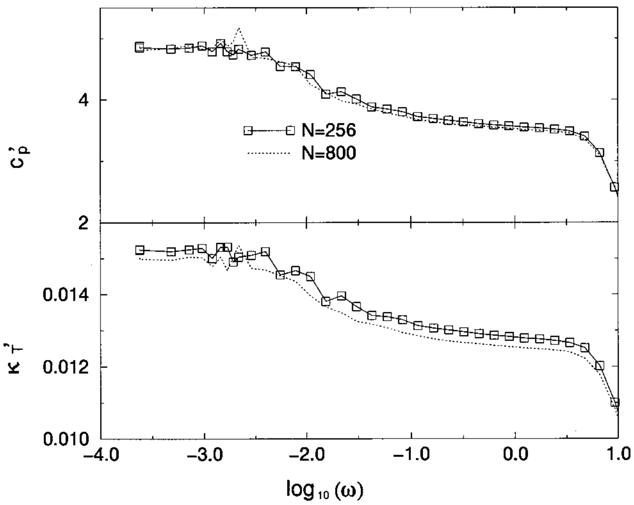

FIG. 3. Real part of isobaric specific heat, and real part of isothermal compressibility at $T_2 = 0.527$, for two different sample sizes. The samples were prepared so that the total energy per particle is the same in each case. The temperature appeared to be the same within an insignificant relative deviation of $2 \times 10^{-3}$, while the pressure showed a relative deviation of $3 \times 10^{-2}$ (largest in the $N = 800$ sample) which is interpreted as a small finite size effect.

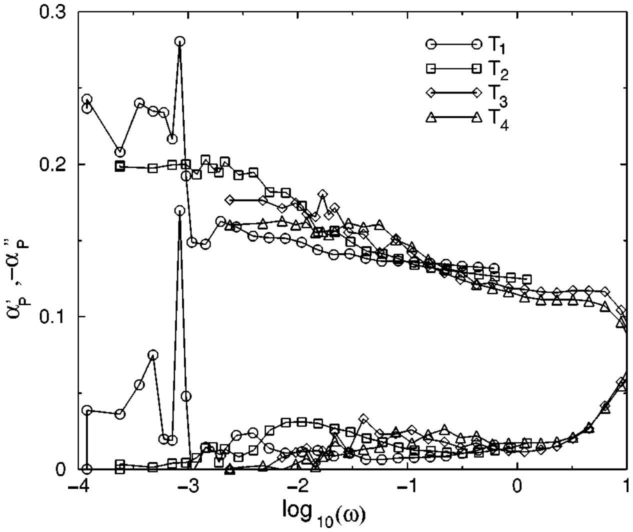

FIG. 5. Real part and negative imaginary part of isobaric expansivity per particle. Same temperatures as in Fig. 2. Logarithmically averaged data.

For comparison, real parts of the pairs $\tilde{c}_v(\omega)$, $\tilde{c}_P(\omega)$, and $\tilde{\kappa}_s(\omega)$, $\tilde{\kappa}_T(\omega)$ are also shown in Figs. 7 and 8. There is a significant difference between isocoric specific heat and isobaric specific heat, as it was also found by other methods [22]. The shapes of the relaxational parts of the response functions $[c'(\omega) - c'(\infty)]/[c'(0) - c'(\infty)]$ are very much alike each other, but $\tilde{c}_P(\infty)$ is 20% bigger than $\tilde{c}_v(\infty)$, and the ratio between configurational and vibrational parts in the case of $\tilde{c}_v(\omega)$, is only around 30–40 % of that of $\tilde{c}_P(\omega)$. Even more pronounced is the difference between $\tilde{\kappa}_s(\omega)$ and $\tilde{\kappa}_T(\omega)$. The ratio between configurational and vibrational parts of $\tilde{\kappa}_s(\omega)$ is only between 3 and 5%. Generally the ratio between configurational and vibrational parts of thermodynamic properties for this substance are small, compared to the same ratio of, e.g., the intermediate scattering function [18]. But considering the high temperature range, they are actually quite big when compared to experiments on various liquids [2–6].

It is found that the $\omega = 0$ value of all susceptibilities are increasing with decreasing temperature. Empirically it is known for several substances, that around $T_G$ the overall equilibrium specific heat $[c_P'(\omega = 0)]$ is decreasing with decreasing temperatures [36], while only the relaxational part is increasing. In addition to the fact that this is a Newtonian model, two things may have to be taken into account to rationalize this difference. First the model investigated here is far above its $T_G$. Second, the cooling is done along an isocore. So the fact that $\kappa_T(0)$ is increasing upon cooling (the substance is getting softer) may be due to the isocoric constraint. The increase is not inconsistent with the estimated structure factor at the low $q$ values reported in Ref. [18].

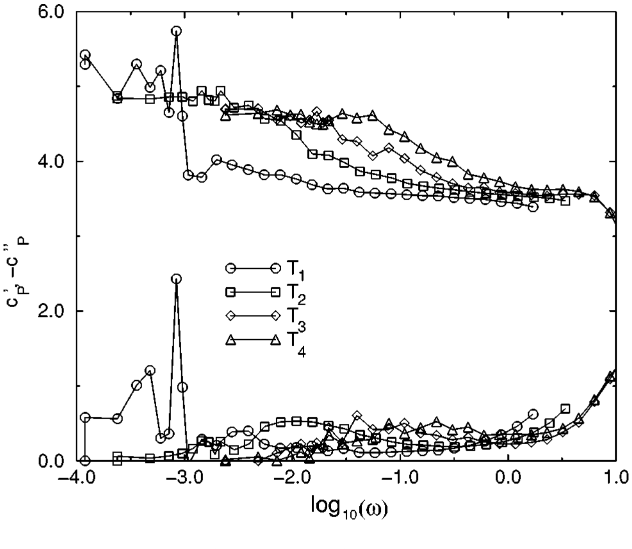

FIG. 4. Real part (upper curves) and negative imaginary part (lower curves) of isobaric specific heat per particle. The four temperatures are the same as in Fig. 2. Logarithmically averaged data.

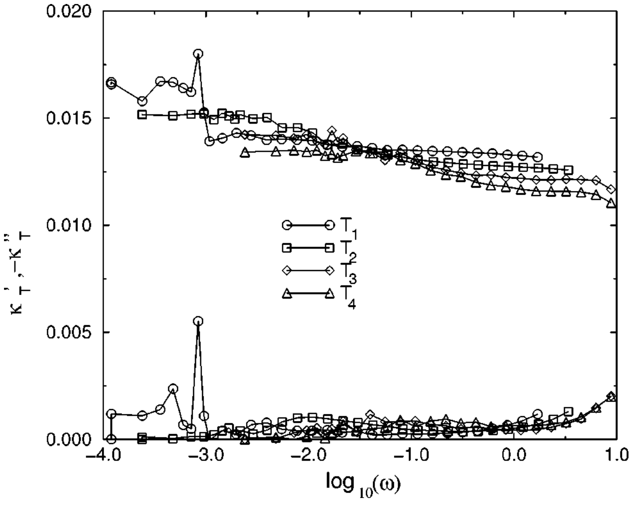

FIG. 6. Real part and negative imaginary part of isothermal compressibility per particle. Temperatures are the same as Fig. 2. Logarithmically averaged data.

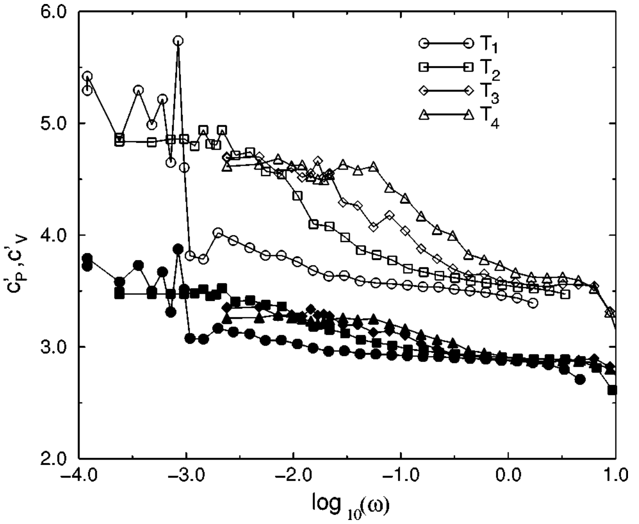

FIG. 7. Real part of isobaric (open symbols) and isocoric (filled symbols) specific heat. Same temperatures as in Fig. 2.

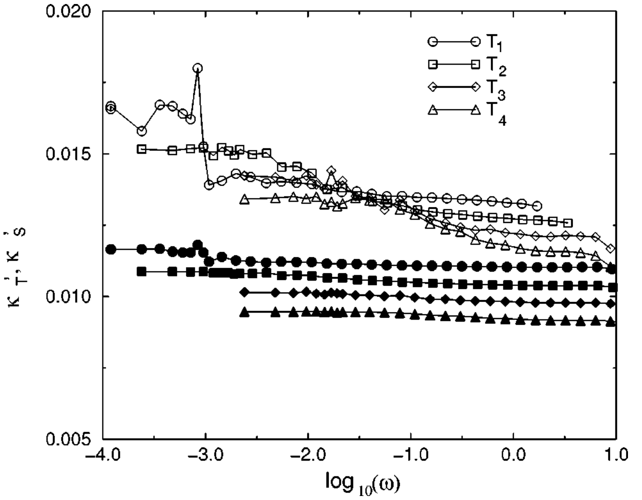

FIG. 8. Real part of isothermal compressibility (open symbols) and adiabatic compressibility (filled symbols). Temperatures as in Fig. 2.

However, recent computer simulations [37] of amorphous silica shows a specific heat which is first increasing with decreasing temperature, and then decreasing on further cooling, indicating that this feature may be model specific, or dependent on the temperature range investigated.

Finally a remark about the quality of the data: Clearly they are quite noisy. This is because the thermodynamic response functions are calculated from the fluctuations of a few correlated properties $K$ and $P$ in opposition to a property such as the intermediate scattering function [18], where the positions of each particle are sampled at different times and added up in the correlation function. This method gives much more statistical material with which to perform the averaging than the one presented here. It is not possible to decompose, for example, the correlation function $\langle \Delta K(0)\Delta K(t)\rangle$ into small parts, referring to different parts of the sample, evaluate them separately, and then add up these parts to give better statistics. This is simply because the kinetic energies of two particles in a system with constant energy are in general anticorrelated even if the particles are very far from each other. This anticorrelation contributes significantly to the correlation function. In fact, it reflects the nature of a system's response under isoenergetic/isocoric constraints. The response is determined by the restricted motion of the particles, and therefore actually a collective organized motion of the whole system. One might get the idea that it would be simpler to extract thermodynamic response functions from an isothermal simulation, employing the FD theorem derived from isothermal conditions in Ref. [16]. However, the problem is that there is no method by which to perform isothermal simulations [31] without influencing the energy fluctuations of the system in an artificial way, which clearly spoils the dynamic response functions.

## IV. SUMMARY AND CONCLUSIONS

In the first part of this paper the question of whether an FD theorem for thermodynamic properties can be derived from microscopic theory was raised. It was shown that this is indeed possible, though the derivation has to be performed in a way which is substantially different from regular linear response theory. (i) The perturbation of the system cannot be stated as an additional term in the Hamiltonian, as in usual response theory. It is introduced as a direct change of the phase space coordinates. In general it is not a phase space conserving perturbation, as in the case where the perturbation is introduced through the Hamiltonian. (ii) There is some freedom in the choice of perturbations (see Sec. II A). This is justified with analogy to laboratory experiments where one does not expect the actual choice of heating aggregate to influence the specific heat of the system. (iii) The derivation of the FD theorem is done under strictly isoenergetic and isocoric constraints, thus taking into account the fact that the presence of these constraints affects the dynamical fluctuations of $T$ and $P$. In ordinary response theory [13], equivalence of ensembles is assumed.

The FD theorem, essentially expressed in Eqs. (44)–(47), connects all thermodynamic response functions to equilibrium fluctuations of the isocoric/isoenergetic ensemble. The dissipation has to be be considered carefully when dealing with heat flow as a control parameter. It was demonstrated in Sec. II E, that even in the case where the system is heated and cooled in a cyclic process, and in this way returned to the same state after each cycle, there is a net entropy production in the surroundings of the system which is proportional to the imaginary part of the frequency-dependent response function $\tilde{G}_{Tq}|_v(\omega)$.

The response theory was applied on a binary Lennard-Jones model system. This model showed a rather high configurational part in all response functions, except that of $\tilde{\kappa}_S$. Generally both the configurational part of the susceptibilities, and the total amplitude of the susceptibilities at $\omega=0$ increased with declining temperature. The broadness of the relaxation spectrum was found to be in qualitative agreement with that of other response functions [18].

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