Fluctuations and Linear Response in Supercooled Liquids

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Ph.D. Thesis by Johannes K. Nielsen

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Abstract

Fluctuation dissipation theorems are derived for thermodynamic properties like frequency dependent specific heat and compressibility. First the case where a systems dynamics are restricted by constant volume and energy is considered. The dynamic linear response to a heat pulse and a volume change at time zero is calculated, under assumption of energy conservation. Then the case of isothermal isobaric conditions are treated by a slight modification of ordinary linear response theory. In both cases the perturbation cannot be stated through the Hamiltonian, but has to be imposed by variation of the external thermodynamic system parameters. In thermodynamic response theory equivalence between ensembles is broken, but time correlation functions sampled in different ensembles are connected through the Maxwell relations of thermodynamics generalized to the frequency domain. Different applications of the theory in the field of supercooled liquids are showed. First the full frequency dependent thermodynamic response matrix is extracted from simulations of a binary Lennard Jones liquid. Secondly some simple stochastic models of supercooled liquids are analysed in the framework of linear thermodynamic response theory. In addition low temperature universality of the specific heat is discussed.

Analysis of hydrogen bond dynamics in supercooled SPC/E model water shows that there is a separation between a fast (local) time scale, and a slow (collective) time scale in the supercooled regime. Time temperature scaling of the hydrogen bond correlation function is discussed in terms of a diffusion model.

Preface

This Ph.D. thesis is mainly based on articles in different stages of publication which I have produced during my study. These are listed below, and labeled with Roman numbers, which are used as reference labels throughout the thesis.

[**I**] *Thermodynamic Response Functions from Computer Simulations*, J. K. Nielsen, J. Non-Cryst. Sol. **235 -237** 346 (1998). Section (7.1).

[**II**] *Linear Response Theory for Thermodynamic Properties*, J. K. Nielsen. Submitted to Phys. Rev E., August (1998). Section (7.2).

[**III**] *Master Equation Models of The Glass Transition* J. K. Nielsen, K. D. Jensen and J. C. Dyre, in *Non equilibrium phenomena in supercooled* *fluids, glasses and amorphous materials, edited by M. Giordano, D. Leporini and M. P. Tosi* World Scientific Singapore (Conference Proceedings), 371 (1996). Section (7.3).

[IV] *Fluctuation Dissipation Theorem for Frequency Dependent Specific Heat*, J. K. Nielsen and J. C. Dyre, Phys. Rev. B **54**, 15754 (1996). Section (7.4).

[V] *Fast and Slow Dynamics of Hydrogen Bonds in Liquid Water*, Francis W. Starr, Johannes K. Nielsen & H. Eugene Stanley, submitted to Phys. Rev. Lett. Section (7.5).

The articles are printed in the last chapter of the thesis.

In 1995 I mainly worked on modelling liquids near the glass transition by dynamic stochastic models. The main task was to find energy-landscape models which can reproduce the time or frequency dependence of the so-called α-relaxation for various susceptibilities, see introduction chapter (2). The following problems were raised:

- Can the shape of the α-peak be understood from energy controlled stochastic models?
- What are the fundamental relaxing entities (regions), how are they interacting locally and how can the energy landscape of a relaxing entity be described?
- Which kinds of local energy density of states reproduces linear response experiments, and how can these be justified theoretically?

It turned out that the frequency dependent specific heat is an indicator of the soundness of energy landscape models, simply because it is derivable from models which predicts time correlations of energy fluctuations, and measurable for liquids near the glass transition. However it also turned out that a prober microscopical understanding of frequency dependent specific heat was absent in literature. So some work on this problem was necessary, and it lead to publication [IV], which showed the connection between frequency dependent specific heat of a system and the corresponding natural energy fluctuations under isothermal conditions.

At this point I became interested in molecular dynamics (MD) simulations of supercooled liquids. On advise from Jeppe Dyre I decided to concentrate on the problems of interpretation of MD simulations in terms of specific heat, in order to make the concept of frequency dependent specific heat the turning point of the present thesis. It was clear at that point, that MD and stochastic energy landscape modelling is not directly comparable, since they are restricted to separate temperature regimes. But there is a general motivating question in much of the work I have done, which can be phrased in the following manner:

- What is the frequency dependent specific heat, how can it be derived from microscopic theory, and how is it connected to other response functions?

Simultaneously with starting the computer programming for MD simulations, which I wanted to do on my own, I started to work intensive on the pure theoretical problem:

- How are the thermodynamic response functions connected to the time dependent fluctuations in the isocoric-isoenergetic ensemble.

I derived a new fluctuation dissipation theorem for this particular problem, and within the framework of this theory it was natural to include the whole thermodynamic repose matrix. The main results were published in publication [I], and a more thoroughly presentation was published in publication [II] along with some simulations on a simple model system.

Within the "MD-period" I worked a half year at the Center of Polymer Studies at Boston University. H. E. Stanley advised me to concentrate on some of the problems in supercooled water. I decided to cooperate with a Ph.D. student Francis Starr, which turned out to be a good decision. We studied hydrogen bond dynamics of supercooled liquid water by MD simulations. This part of my Ph.D. study is not exactly connected to the rest, except that it deals with dynamic fluctuations of a supercooled liquid. The questions which was the motivation for the research was quite specific, and addressed a certain debate in literature.

- What is the nature of the hydrogen bond time correlations in supercooled water?
- What is the connection between the bond life time distribution, and the reactive flux derived from the autocorrelation function of the bond indicator.
- How does the apparent dynamical behavior depend on the choice of bond indicator.

Basically the work we did, was a clarification of some differences between methods of analysis and between model potentials, plus an extension of previous work into a deeper temperature regime. But we also found some new things which might be of significance. The conclusions will probably be published in [V].

Acknowledgments

Thanks to Stine, Asger and Troels for still being around, and to Jeppe C. Dyre, Niels B. Olsen, Tage E. Christensen, Thomas B. Schrøder, Kenneth Geisshirt, Stine Korreman, Francis W. Starr and H. Eugene Stanley for stimulating interaction and cooperation. Special thanks to Niels B. Olsen for kindly permitting some of his unpublished measurements to be printed in the thesis.

Outline

In chapter (2) a brief general introduction to supercooled liquids is given. I have decided to break up the chronology, so chapter (3) deals with thermodynamic response theory in general. Section (3.1) is focused on publication [I] and [II]. In proceeding of this, section (3.2) deals with the general theory of, publication [IV]. Chapter (3) ends with general remarks on linear response theory, and a formal exercise, which establishes the foundation for discussion, in chapter (4), of energy controlled stochastic models and the quasi universality proposal of publication [III] and [IV]. Finally some comments are added to [V], in chapter (5).

The text summarizes very briefly the contents of the articles, but mostly it adds some further generalizations or application of theory, and discusses in greater detail some of the findings. Since the text does not include all the contents of the articles, these should be read as a substantial part of the thesis. Specially I recommend reading [II] and [IV].

Contents

Chapter 1

Thesis

I propose the view that frequency dependent specific heat $c(\omega)$ is a good indicator of the soundness of energy landscape models of supercooled liquids, since this property reflects the energy time correlations of a system.

a. c. specific heat spectroscopy will probably be increasingly used as an experimental tool, and its implications on theory needs to be investigated.

I demonstrate how $c_p(\omega)$, $c_v(\omega)$ and other response functions are derived from classical theory of liquids and from stochastic models, and show how they may be used to evaluate the validity of models in comparison with experiments.

Chapter 2

Introduction

This introduction is thought as a “initiation” of the topics which are in focus in the thesis. It is not intended to be a complete presentation of all the experimental and theoretical knowledge of supercooled liquids. The reader is advised to look at references [1, 2, 3, 4, 5, 6] and references therein for more detailed reviews.

2.1 Background

Relaxation in supercooled liquids has become a great and challenging topic, in physics and chemistry at the end of this century [7]. The area is expanding rapidly, which can be seen by the increasing number of publications on the topic, and on the increasing number of participants in conferences. New experimental methods and new attempts to model and understand supercooled liquids are constantly being developed. Besides that use of computer simulations has become an increasingly used tool in works on theory and models. Still there is not consensus on even the basic molecular mechanisms of relaxation and there is dispute about interpretation of almost all methods of measurement. The experimental methods applied on supercooled liquids are many, including amoung others specific heat measurements[8], dynamic enthalpy relaxation [9, 10, 11] viscosity measurements [12], frequency dependent shear modulus measurements [13, 14], dielectric measurements [15, 16] and dynamic compressibility [17]. Lately methods which probes the microscopic structure and dynamics more directly, such as various sorts of scattering experiments [18, 19, 20] and dynamic nuclear magnetic resonance spectroscopy [21], have also been added to the frequently employed tools.

2.2 Linear Thermodynamic Response Experiments

Linear thermo*dynamic* response experiments are performed in laboratory by imposing a time dependent perturbation of some thermodynamical variable (pressure P, volume V, temperature T or heat Q^1), and monitoring the time dependent response of some other thermodynamical variable. Suppose that we perform an instant shift of some external parameter e.g. the temperature, at time $t = 0$, and watch the proceeding time dependent equilibration of another parameter, e.g. volume V. The normalized relaxation function $\Phi(t)$ is then defined in the following way

$$\Phi(t) = \frac{V(t) - V(\infty)}{V(0) - V(\infty)} \tag{2.1}$$

Of course temperature is not exactly constant in this experiment, but one can still think of the initial temperature T_0 as a external parameter which remains fixed while the system is perturbed by a small shift of temperature δT. Basically two sorts of information are obtained from such experiments. First, by performing the experiment at a given set of external parameters, i.e. constant values of temperature T_0 and pressure P_0, the time dependence of $\Phi(t)$ is achieved for the fixed set of parameters. As it is the case in other linear response experiments, one observes a non-exponential (or "non-Debye") decay of $\Phi(t)$ in supercooled liquids. The choice of temperature as input parameter and volume as response variable is just an example. In general the relaxation function $\Phi(t)$ is different if another set of variables are chosen.

Secondly, by varying the constant values of pressure and temperature, the temperature and pressure dependence of the shape and time scale of $\Phi(t)$, is obtained. τ_α, the primary relaxation time, may be defined as the inverse loss peak frequency. The loss peak frequency is defined by the first extremum of the imaginary part of the frequency dependent susceptibility $\chi(\omega) = -\int_0^\infty dt\ e^{-i\omega t}\frac{d}{dt}\Phi(t)$. $\chi(\omega)$ is called a frequency dependent response function.

Thermodynamic response experiments have not yet been carried out in really great detail. This is because thermodynamic response experiments in general are more complicated to perform than e.g. dielectric response experiments [10, 11, 17, 22]. For example in dynamic specific heat measurements one has to either make sure that the sample is thermally and mechanically

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[1] Since Q is not a state variable, a heat perturbation just refers to an experiment where the heat flow into the system is controlled.

equilibrated on a shorter time than the internal relaxation time τ_α, or to take the internal stress and temperature inhomogeneities in to account. In fact this circumstance is currently a matter of discussion among experimentalists [22].

2.3 General Linear Response Scenario

In dielectric or shear mechanical linear response experiments, the following scenario is often seen. The temperature dependence of the characteristic relaxation time τ_α deviates from the Arrhenius law $\tau = \tau_0 \exp(A/T)$. The Maxwell relaxation time $\tau_M = \frac{\eta}{G_\infty}$ is usually a good estimate of τ_α. η is the shear viscosity and G_∞ is the shear modulus at ∞ frequency, i.e. the shear modulus observed if one tries to impose a shear strain on the liquid faster than its internal degrees of freedom is able to relax. Since G_∞ is almost constant compared to η, the latter is often used as an indication of τ_α. In the very high temperature regime, τ_α obeys an Arrhenius law. This Arrhenius law is broken deeper in the supercooled regime, where τ_α graduately starts to increase rapidly, see figure (2.1), and exceed the extrapolated Arrhenius law. Eventually the liquid reaches the glass transition temperature T_g, which is defined as the temperature where the viscosity η reaches 10^{12} Pa·s. Generally τ_α is around 10^3 s at T_g. Note that neither the temperature T_g nor the time 10^3 s have any physical significance. The definition of T_g is simply chosen so that if a liquid is cooled below T_g, its internal relaxation time τ_α exceeds the time scale of human patience. The melting temperature T_m, which usually is located above T_g, is of course a physically defined property. But it has no implications on a liquid whether it is above or below T_m, as long as it does not crystallize. As a liquid is supercooled, the liquid passes T_m smoothly in all respects.

How pronounced the non-Arrhenius behavior is, varies from liquid to liquid, and liquids where it is very pronounced are referred to as “fragile” liquids, in opposition to “strong” network forming liquids [3], see figure (2.1). Below the temperature interval where τ_α is non-Arrhenius, another phenomenon occurs, namely the Johari Goldstein (JG)-β relaxation [16], which is seen as a maximum in the imaginary part of the susceptibility, at higher frequency than the α-relaxation peak. At high temperatures JG-β relaxation is not observed, but as the liquid is cooled the JG-β peak separates from the α-peak at a certain *merging* temperature. JG-β relaxation is characterized by a a broader peak in the imaginary part of the susceptibility than the α-relaxation, and a weak temperature dependence of its characteristic time scale $\tau_{\mathrm{JG}-\beta}$ [23], see the schematic illustration in Fig. (2.2). Unlike α relaxation, JG-β relaxation

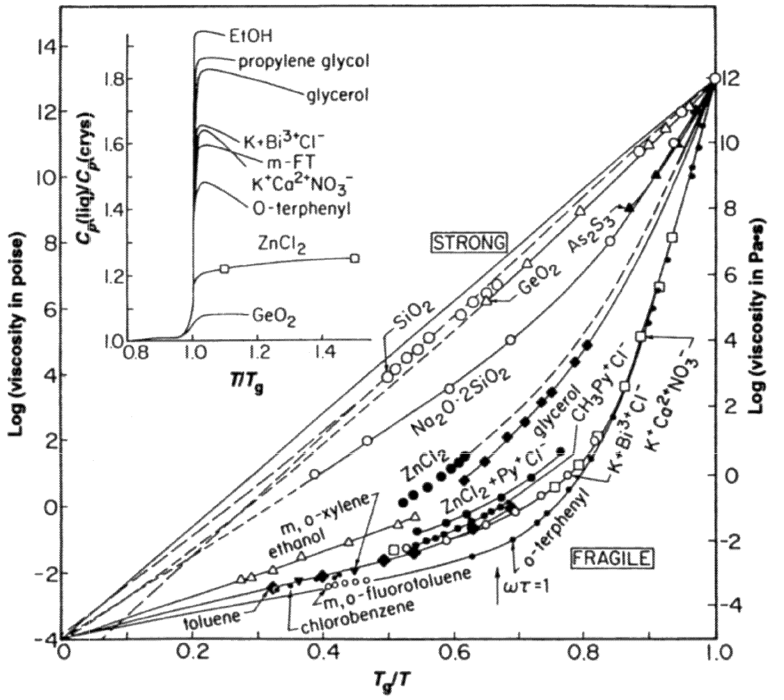

Fig. 4. Arrhenius plots of the viscosity data scaled by values of T_g from Fig. 3 and other sources showing the "strong-fragile" pattern of liquid behavior on which the liquid's classification of the same name is based. As shown in the insert, the jump in C_p at T_g is generally large for the fragile liquids and small for strong liquids, although there are a number of exceptions, particularly when hydrogen bonding is present. [From (36)]

Figure 2.1: C. A. Angell, Science **267**, 1927 (1995). The concept of "strong" versus "fragile" liquids were introduced by C. A. Angell in 1985. As indicated in the original figure caption the fragile liquids are those with the most pronounced deviation from the Arrhenius law (straight line). Strong liquids are believed to be those where a relatively strong type of chemical bond of some sort is present in the liquid phase, resulting in a more distinct activation energy, and a structure which do not depend so much on temperature. Fragile liquids are associated with a structure which is not so stable against change of temperature, and a more smeared distribution of activation energies.

is a individual phenomenon for each liquid, in the sense that JG-β relaxation varies in amplitude and temperature dependence from liquid to liquid, while α relaxation is more similar in different substances. JG-β relaxation must not be confused with the so called "mode-coupling β-relaxation", which occurs at much shorter time scale than the JG-β relaxation,i.e below the nano second scale. In fact the temperature interval where MCT breaks down, is where the JG-β-relaxation separates from the α-relaxation in some liquids. Another thing which is remarkable is that the "stretching" of the α relaxation is usually increasing as the intermediate temperature regime is crossed. "Stretching" refers to the phenomenon, that the decay rate of $\Phi_\alpha(t)$ seems to decrease as t approaches infinity. This is *not* a non-linear phenomenon. The stretching is conveniently expressed by the phenomenological Kohlrauch Williams Watts (KWW) fitting form:

$$\Phi_{\mathrm{KWW}}(t) = \Phi_0 e^{-\left(\frac{t}{\tau}\right)^{\beta_{\mathrm{KWW}}}}. \tag{2.2}$$

while no models of supercooled liquids predicts exactly the KWW form, it is usually a fairly good approximation of $\Phi(t)$. The parameter β_{KWW} measures the sharpness of the relaxation time distribution. Low values of β_{KWW} corresponds to broad spectra, which is also monitored as a broad peak of the imaginary part of the susceptibility. In a typical liquid the "stretching" goes from almost exponential relaxation $\beta_{\mathrm{KWW}} = 1$ at high temperature, to $\beta_{\mathrm{KWW}} = 0.4 - 0.6$ in the low temperature regime around T_g.

2.4 Time Temperature Scaling

In liquids where α and JG-β relaxation *are well separated* the α-peak of dielectric and shear mechanical response functions stays invariant [25], when the temperature is changed, except for a change in amplitude and in loss peak frequency, see figure (2.3). This phenomenon is referred to as "time temperature super position" or "time temperature scaling", (TTS). It is seen to really good accuracy well below the merging temperature where α and JG-β-relaxation separates. Traditionally TTS is only considered as an approximation in the low temperature regime, but the suggestion here is actually that TTS is exact well below the merging temperature, see also section (4.2.1).

In molecular dynamics computer simulations (see below) of relatively simple liquids [34, 75], evidence of a temperature region has been found where β_{KWW} appears to be constant. This temperature interval is located where the relaxation time τ_α starts to deviate from Arrhenius behavior, and above the merging temperature (if there is such a thing as JG-β-relaxation in clas-

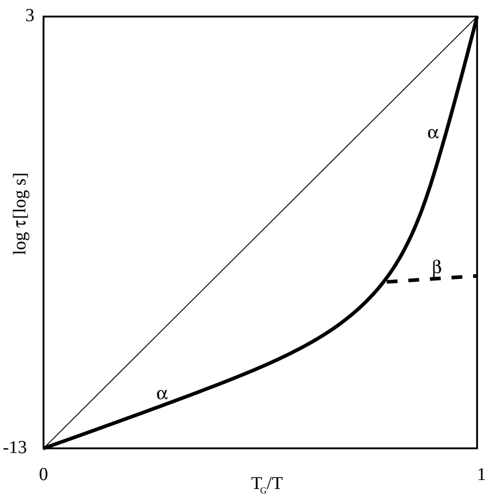

Figure 2.2: Schematic drawing showing how the α and JG-β relaxation time departs in an Arrhenius plot. Exactly where the JG-β relaxation breaks of depends on the substance. The nature of JG-β relaxation remains to be understood. It occurs with different strength in different liquids. Generally the temperature dependence of the $\tau_{\mathrm{JG}-\beta}$ is very weak, if not absent.

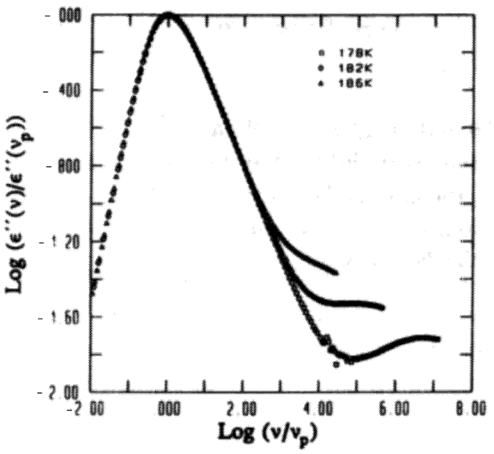

Figure 2.3: From Behrens et al. [26]. Imaginary part of dielectric susceptibility $\varepsilon(\omega)$ at three different temperatures. of Dibutylphthalate (DBP). The frequency axis is divided with the loss peak frequency ω_l for each temperature, and the response functions are divided with their value at ω_l. The increase of the susceptibility at high frequency is JG-β relaxation. This is an example of a liquid where the α and the JG-β process are separated at low temperatures, thus time temperature scaling of the α-relaxation is perfect.

sical liquids), thus this TTS phenomenon may origin from a different type of process in this case.

Turning now again to linear thermodynamic response functions, it is not obvious that the same pattern, with JG-β-relaxation and α-relaxation is seen, as it is in for example dielectric and shear mechanical relaxation. However, there *is* reason to belive that the overall pattern is the same, since variations of the polarisation, is likely to be connected with variations of energy in a disordered material. In fact JG-β-relaxation has been observed calorimetrically *below* T_g, in the fragile glass-former o-therpenyl [27], as an additional glass transition far below the α-transition. So all sorts of relaxation is expected to be seen in thermodynamical response functions, and the time scales of the various sorts of relaxation is expected to be roughly the same as it is in dielectric and shear mechanical relaxation.

2.5 Modeling

Roughly, the supercooled temperature region may be separated into a low and a high temperature interval with different dynamical behavior. The high temperature regime is characteristic by a relatively low apparent activation energy (inclination of Arrhenius plot), and a weak stretching of the relaxation function (β_{KWW} ranging from 0.7 to 1), while in low temperature regime higher activation energies and more pronounced stretching is typical. The two regimes graduately takes over from each other in the intermediate temperature interval, where the curvature of the Arrhenius plot is largest, and where JG-β and α separates from each other in some liquids. It is possible, that two different theories are needed to explain the behavior of supercooled liquids; one for the low temperature region and one for the high temperature region, since the two temperature regimes after all are different in phenomenology. In spite of this I shall use the term α-process to denote the basic relaxation mechanism.

Modeling of linear response of supercooled liquids can be categorized into explanation of the non-Arrhenius behavior [28], and explanation of the shape of the response functions (e.g. ref. [29]). One model which seeks to in-cooperate both aspects is the so called mode coupling theory (MCT) [30] which has taken a major role in the last decade. It describes some important features of supercooled liquids in a fairly high temperature regime, but it fails to include the lower temperature regime. MCT in its present form deals with density correlations, and recently it has also been extended to include rotational dynamics and current fluctuations [31, 32].

The basic variable of the theory, a correlator $\phi_k(t)$, is the k- component of the intermediate scattering function [33]. MCT makes quantitative predictions of $\phi_k(t)$, with the static structure factor as model input, but does not give any statements about e.g. thermodynamic response functions, and relations between these. MCT can partially reproduce $\phi_k(t)$ in the high temperature scenario, where τ_α begins to exceed the time scale of vibrational modes. This has been confirmed by molecular dynamics simulations [34, 35]. But the model breaks down in the low temperature regime, where it predicts a divergence of τ_α at a certain finite temperature T_c. This divergence is absent in real liquids. In the MCT picture non-Arrhenius behavior of fragile liquids is associated with this divergence, which is never completed because "hopping" processes.

It is generally believed that thermal activated processes, or "hopping" processes plays an increasingly dominating role as T is lowered into the low temperature region[6, 24].

Molecular Dynamics (MD) has showed very useful in tests of MCT, since MCT is based on classical mechanics, and therefore may be examined on its own premises by means of MD. In brief MD is simply stepwise integration of the classical equations of motion, derived from a molecular model, performed on computers. MD is a powerful tool for investigating supercooled liquids somewhat above the glass transition in the nano-second regime, because it enables one to sample particle correlations in time and space on a molecular level. This is within the limitations of the molecular model of course. MD represents a way of modeling which is closer to first principles than stochastic modeling (see below). But while stochastic modeling is reasonable starting point, if not the only one possible, for modeling dynamics at low temperatures, MD is restricted to high temperatures where the equilibration time is short.

Stochastic models which deals directly with the "jump processes" have been tried as a way of understanding both the time and temperature dependence of relaxation at low temperatures [45, 47, 53]. Of special interest are the so called energy controlled models, which has been used to give quantitatively good fits to the temperature dependence of relaxation times, and in some cases all so the stretching of dielectric susceptibility [49]. The energy controlled models assumes a temperature independent potential energy-landscape, and a certain energy dependence of the transition rate between two states of a local "region" of space, including an unspecified number of molecules. The slow α-relaxation is assumed to origin from a process where the local configuration has to pass an energy barrier or transition state, referred to as "transition state dynamics". Thus the probability of a region to escape a state i, γ_i, is assumed to be

$$\gamma_i = \gamma_0 \exp^{-\frac{E_t - E_i}{k_B T}}\ , \tag{2.3}$$

where γ_0 is a free parameter, referred to as the attempt frequency, E_t is the energy of the transition state and k_B is Boltzmanns constant. However, this type of models is only weakly founded in microscopic theory, which is one of the problems which will be discussed in the present thesis. I want to keep the possibility open, that maybe the non-Arrhenius behavior cannot be explained from an energy landscape point of view, unless the absolute energy of the barriers changes with temperature. This view is a necessarily consequence of the findings in publication [IV] (sec. 7.4), and it is partly motivated by a new finding of by Olsen, Dyre and Christensen [51, 50], namely that the activation temperature of the α-relaxation is proportional to the shear modulus G_∞.

The focus in this thesis will mainly be on the shape of the relaxation function for the α-process, rather than the temperature dependence of τ_α. This naturally includes use of linear response theory. Linear response theory, or to be more specific, the Fluctuation Dissipation (FD)-theorem, provides a connection between microscopic models and measurements of linear response functions. The FD-theorem establishes a connection between the measurable relaxation phenomena, which could be provoked by external stimulation of a system, and the fluctuations of the unperturbed system. In a way the FD-theorem simply says: A physical system which is in a state slightly displaced from equilibrium, does not know whether it came to that state because of an internal fluctuation, or because some external [52] force pushed it there, thus in both cases it relaxes towards equilibrium in the same way, governed by the physical laws of the unperturbed system. Exactly how the physical laws influence the relaxation has to be considered of course, and in fact this is one of the main issues in the present thesis.

Chapter 3

Thermodynamic Response Theory

One of the important points of thermodynamic response theory is the question about how the response functions are related to correlation functions sampled in different ensembles.

In usual linear response theory [71, 72, 33], the dynamical response is related to fluctuations of certain system variables, calculated under the assumption that the system is evolving according to its own Hamiltonian. I.e. iso-energetic conditions are assumed. The response under isothermal conditions is then obtained by an averaging performed over an ensemble of individual isolated systems, with different energies, weighted with a Boltzmann distribution. This may be thought of as an ensemble-equivalence assumption in the sense that the fluctuations of a phase variable is considered to be independent on whether there is some global constraint, e.g. a requirement of constant energy, acting on the system or not.

The usual linear response procedure procedure is to naive to be employed in calculation of thermodynamic response functions. For instance, frequency dependent specific heat is related to the energy auto correlation function in the canonic ensemble, a property which is exactly 0 in the microcanonical ensemble.

The following chapter shows how thermodynamic response functions can by derived from both microcanonical and isothermal conditions.

3.1 Isoenergetic-Isocoric Constrained Dynamics

3.1.1 Brief summary of I and II

Two main questions are raised in publication [I] and publication [II] (sec. 7.1 and sec. 7.2). The first question is how the thermodynamic response functions are to be derived from MD simulations of supercooled liquids. The second question is how these functions actually look.

Formulated in a more general way, the first question is how thermodynamic response functions are connected to equilibrium fluctuations in the isocoric-isoenergetic ensemble. The answer is stated without any proof in [I] as an FD theorem relating time correlations in the $NEV\mathbf{P}$ ensemble to thermodynamic response functions. The proof of the FD-theorem is showed in details in [II]. The basic assumption, which allows a convenient choice of perturbation, is that the long time macroscopic response does not depend on microscopic details of the heat or volume changes imposed on the system, as long as it is done sufficiently smooth. The assumption is based on the common sense argument, saying that in a laboratory experiment we would not expect e.g. $c(\omega)$ to depend on whether the system is heated by means of an electrical resistor or by an laser, as long as the heating is spatially homogeneous on time scale shorter than the Maxwell relaxation time τ_M.

Answering the second question involves simulations of different models at different temperatures, thus it is only partially answered by the presented simulations in [II], which is thought as an example. However, it has a unique content, since it is the first complete set of frequency dependent thermodynamic response functions in literature, obtained computationally as well as experimentally.

In addition the characterization of the response functions of the binary Lennard Jones fluid gave some new insight which, might be of significance. For example the finding that the equilibrium specific heat seems to be increasing with decreasing temperature calls for an explanation. It actually contradicts simulation results in reference [44], which indicates a constant c_p for all temperatures. I did not try to see if the different response functions can be scaled on a master-curve, since the data are to poor to make such a discrimination. A comment on the quality of the data was also made in [II]. The problem is that in order to calculate $c_v(\omega)$, only one variable namely the kinetic energy $K(t)$ is sampled. This leads to very poor precision of the correlation function $\langle \Delta K(0)\Delta K(t)\rangle_{E,V}$. It was concluded that it is not possible to decompose the system into smaller parts, calculate the local correlations, and add these in order to get better statistics. The reason, namely that even distant particles are correlated in the microcanonical ensemble shows how careful one should be when assuming equivalence between ensembles. For example it can be seen from figure (3.1) that $\langle \Delta K(0)\Delta K(t)\rangle_{E,V} \neq \langle \Delta K(0)\Delta K(t)\rangle_{T,V}$, by simply noting that for $t = 0$, $\langle \Delta K(0)\Delta K(t)\rangle$ is the variance of the kinetic energy distribution which clearly is different in the two cases. Since $\langle \Delta K(0)\Delta K(t)\rangle = \sum_{ij}\langle \Delta k_i(0)\Delta k_j(t)\rangle$ in both ensembles, some of the terms in this sum must be ensemble dependent, even for $N \rightarrow \infty$. Since $\langle \Delta k_i(0)\Delta k_i(t)\rangle$ cannot depend on the whether temperature or energy are fixed, at least to 0'th order in $\frac{1}{N}$, it must be the sum of cross correlation terms $\langle \Delta k_i(0)\Delta k_j(t)\rangle$, which causes the ensemble dependence. $\langle \Delta k_i(0)\Delta k_j(t)\rangle$ consists of two contributions; correlations origining from interaction of close particles, and correlations origining from a possible global constant energy constraint in the microcanonical ensemble. The first contribution is ensemble independent, and of order $\frac{1}{N}$, since locally the liquid can not feel whether the global energy is fixed or not. But the second contribution is 0 in the canonical ensemble, while it is of order $\frac{1}{N}$ in the microcanonical ensemble; if particle i has kinetic energy deviating from its mean by Δk_i, all other degrees of freedom has energy deviating from their mean energy by $-\frac{\Delta k_i}{\#\text{degees of freedom}}$ on average, and so their kinetic energy are also generally reduced by an amount proportional to $\frac{1}{N}$. Both contributions are significant, since the number of cross correlation terms scales as N^2. In conclusion $\langle \Delta k_i(0)\Delta k_j(t)\rangle_{i\neq j}$ is of order $\frac{1}{N}$ in both ensembles, but substantially different. I also mention this to emphasize, that the effects of isoenergetic as well as isocoric constraints on the system has nothing to do with finite size effects, but are present even in the macroscopic limit.

3.1.2 Further comments

Returning to the first question, a few comments on the chosen point of view is appropriate. One might ask why I do not simply perform the experiments defined in section A of publication [II] as simulations, instead of going through all the calculations to obtain the FD-theorem. First of all there would be no computer time saved by this procedure, since one would have to either perform a lot of experiments or to simulate an enormous sample to get good statistics. The reason for this is that the fluctuations of T and P exceeds the limit of linear response in a small sample. In figure (3.1) the size of the temperature fluctuations are illustrated by two histograms, sampled from the canonical ensemble in one case, and from the microcanonical ensemble in the other case. The relative temperature fluctuation in the microcanonical

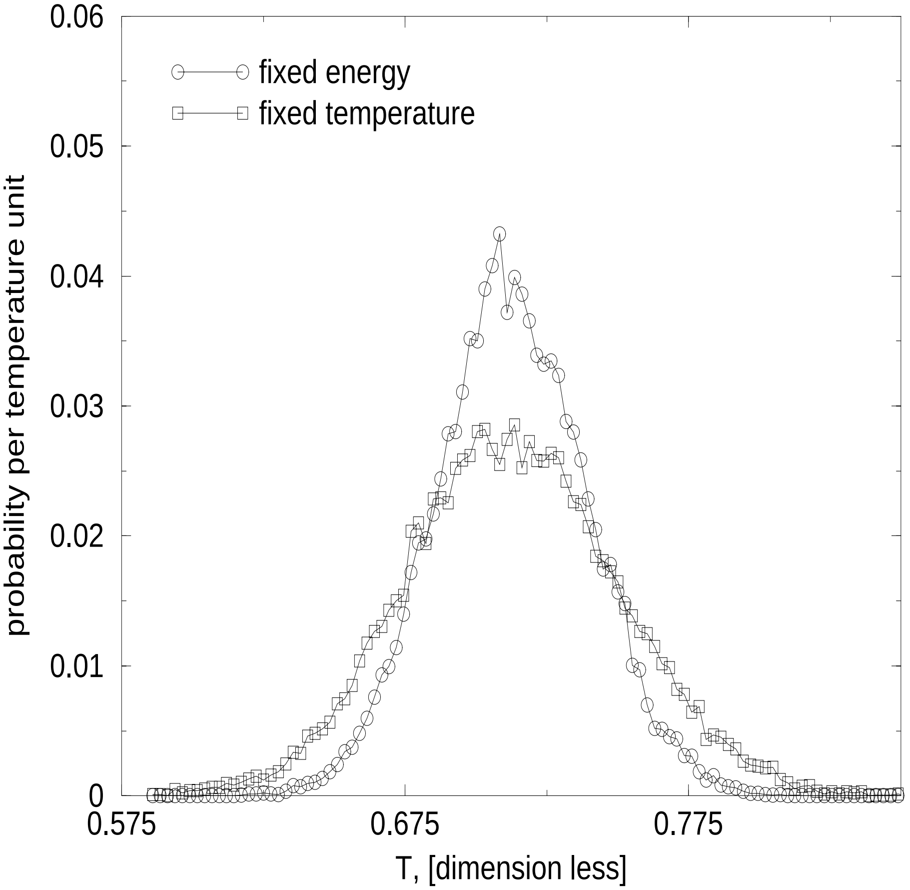

Figure 3.1: The kinetic temperature distribution in the $NEV\mathbf{P}$ ensemble and in the $NTV\mathbf{P}$ ensemble at $T = 0.71$, $N = 256$. The distribution in the first ensemble is clearly sharper ($\sqrt{\langle(\Delta T)^2\rangle} = 2.7 \times 10^{-2}$) than the distribution in the latter($\sqrt{\langle(\Delta T)^2\rangle} = 3.8 \times 10^{-2}$). The temperature distribution in the $NTV\mathbf{P}$ ensemble is found from the Maxwell velocity distribution as $\langle(\Delta T)^2\rangle = \frac{2}{3N}T^2$. In both cases $\langle(\Delta T)^2\rangle$ scales as $\frac{1}{N}$. The figure is just for illustration, and based on only 20000 samples.

ensemble is $\sqrt{\frac{\langle(\Delta T)^2\rangle}{T^2}} = 0.038$, at the given temperature and system size. $\sqrt{\frac{\langle(\Delta T)^2\rangle}{T^2}}$ scales as $\frac{1}{\sqrt{N}}$, both if we improve statistics by simulating one big system, or by simulating a lot of small systems. Suppose we want to make a perturbation which results in a temperature chance at 1 % of the absolute temperature which is a rather big temperature shift for a linear response experiment. To get an error of the response function at less than 10 %, the fluctuations has to be less than 1/1000 of the absolute temperature, i.e. 38 times better accuracy than the present. This would provide a sample size at $N = 38 \times 38 \times 256 = 369664$ molecules. So performing computer experiments directly its not a trivial thing to do.

Note that the fact that fluctuations of T exceeds the linear response amplitude δT, does not mean that linear response theory is not valid, since linear response theory deals with the mean value of the variables T and P, which may perfectly well depend linearly on a perturbation even though the response of a single trajectory does not [43].

A second reason for the derivation in [II] is that it has to be seen in connection to the FD-theorems derived for the isobaric-isoenergetic ensemble. The general approach presented contributes to the completion of the exploration of an previous unsolved problem, namely how to compare measurements of thermodynamic response functions to any model which is able to predict time correlations of thermodynamic variables in a specified ensemble.

3.2 Isothermal Conditions

In Publication [IV] (7.4) the general fluctuation dissipation (FD)-theorem for the response of a phase variable B to a temperature perturbation is derived for a system in an arbitrary isothermal ensemble from the assumption, that the dynamical behavior of the system in interaction with a heat reservoir is described by an unspecified stochastic process. The response function referring to an experiment where the temperature is oscillated with some frequency ω is defined by the frequency dependent ratio $\delta\tilde{B}/\delta T$ and found to be

$$\frac{\delta\tilde{B}}{\delta T}(\omega) = \frac{-1}{k_B T^2}\int_0^\infty e^{-i\omega t}\frac{d}{dt}\langle\Delta Y(0)\Delta B(t)\rangle_{T,\,\cdot}\, dt, \tag{3.1}$$

where k_B is Boltzmanns constant and $Y = H = E + PV$, the enthalpy, if the pressure is fixed, and $Y = E$, the energy, if the volume is fixed, and $\langle\cdot\rangle_{T,\,\cdot}$ means averaging over the appropriate (isothermal) ensemble.

The isobaric specific heat is found to be

$$c_P(\omega) = \frac{-1}{k_B T^2}\int_0^\infty e^{-i\omega t}\frac{d}{dt}\langle\Delta H(0)\Delta H(t)\rangle_{T,P} dt. \tag{3.2}$$

and the expansivity is found to

$$\alpha_P(\omega) = \frac{-1}{k_B T^2} \int_0^\infty e^{-i\omega t} \frac{d}{dt} \langle \Delta H(0) \Delta V(t) \rangle_{T,P} dt. \tag{3.3}$$

In the following I want to make a comment about completion of these results to also include a FD-theorem for the compressibility. This was left out of [IV] because we felt that it was to trivial for publication.

3.2.1 Completion of the thermodynamic FD-theorems

Equation (3.1) is derived by considering the response of B upon a temperature perturbation. Also a perturbation of pressure may be considered in the same manner: First expand the initial distribution in the perturbing field, next turn of the field and calculate the relaxation of an arbitrary phase variable B as a function of time after the field has been turned of. This approach is inspired by Doi an Edwards [42]. In ([IV], equation 18) a general expression is given for the probability distribution in a isothermal ensemble. If one considers the isothermal isobaric case, the equilibrium distribution reads

$$P_{\mathrm{eq},j} = \frac{e^{-\beta(E_j + PV_j)}}{Z} \tag{3.4}$$

where $\beta = \frac{1}{k_B T}$. By expansion of equation (3.4) in a given arbitrary pressure perturbation δP, one finds to first order

$$P_{\mathrm{eq},j}(T, P + \delta P) = P_{\mathrm{eq},j}(T, P) \left(1 + \frac{\delta P}{k_B T} \Delta V_j\right), \tag{3.5}$$

where $\Delta V_j = V_j - \langle V_j \rangle$ by assuming that the dynamics are given by a conditional probability density $G_0(i, t|j, 0)$, the relaxation of a phase variable B, after the perturbation has been turned of at $t = 0$, is found to be

$$\begin{aligned} \delta B(t) &= \sum_{i,j} G_0(i, t|j, 0) P_{\mathrm{eq},j}(T, P) \left(1 + \frac{\delta P}{k_B T} \Delta V_j\right) \Delta B_i \\ &= \frac{\delta P}{k_B T} \langle \Delta V(0) \Delta B(t) \rangle_{T,P} \ . \end{aligned} \tag{3.6}$$

One can now identify the frequency dependent isothermal compressibility $\kappa_T(\omega)$, as

$$\kappa_T(\omega) = \frac{-1}{k_B T} \int_0^\infty e^{-i\omega t} \frac{d}{dt} \langle \Delta V(0) \Delta V(t) \rangle_{T,P} dt. \tag{3.7}$$

This completes the derivation of thermodynamic FD-theorems, since we now posses explicit formulas for three independent response functions e.g.

$c_P(\omega)$,$\alpha_P(\omega)$ and $\kappa_T(\omega)$ in terms of fluctuations in both the isoenergetic-isocoric ensemble, and the isothermal-isobaric ensemble. In both cases the derivation does not rely on any specific underlying dynamics, but only energy conservation in the first case and "conservation of the canonical distribution" in the second case; the dynamics just has to assure that a state i on average is visited so often that the probability of finding the system in state i at a certain time is proportional to the Boltzmanns factor $e^{\frac{-E_i}{k_B T}}$.

3.3 Comments to Linear Response Theory

It appears that the frequency dependent linear response functions are identical to the static response functions, except that the static correlations of the type $\langle \Delta A \Delta B \rangle$ are exchanged with correlation terms of the type $-\int_0^\infty e^{-i\omega t} dt \frac{d}{dt} \langle \Delta A(0) \Delta B(t) \rangle$. Of course this makes the theorems trivial in a sense. But on the other hand how should one trust this simple relation without deriving it from reasonable assumptions? The fluctuation-dissipation theorems of the specific heat was in fact anticipated by other authors [37, 38, 39, 40, 41, 76] before there was any theoretical derivation of these.

An examination of the derivation in [II] shows that besides the already mentioned assumption of the response being independent on the microscopic details of the perturbation, it includes only an assumption of the dynamics being driven by a stochastic process and on conservation of energy. This means that the FD-theorems are general laws which does not rely on a specific model, but rather relations which will always hold in any model. As an example consider the FD- theorem for specific heat in [II]. In the derivation it is mentioned that Newtonian dynamics are included as a special stochastic process, thus justifying the use of the theorem in MD. But if we change the dynamics to randomized jumps, which are constructed in a energy conserving way, the fluctuation dissipation theorem is still valid, since we would still be able to describe the dynamics by a conditional probability $G(\Gamma, t|\Gamma', t')$. Thus the FD-theorem is a law that is more general than Newtons second law in the sense that it does not rely on a specific sort of dynamics, but on the other hand it is not of any significance unless we have specified the dynamics. So a derivation of an FD-theorem is to start at a sufficient general level and derive the connection between response and fluctuations of a category of systems.

The framework of stochastic processes is a way of stating the dynamics which is quite general, but it is not sufficient to include quantum mechanics. Looking from a theoretical point of view it would be nice to use a framework sufficient general include also quantum mechanics. However there are some difficulties in derivation of a fluctuation dissipation theorem for frequency dependent specific heat of a quantum mechanical system in an isoenergetic/isocoric ensemble, which I have not been able to overcome [36].

I also feel like adding a comment regarding the "van Kampen objection to linear response theory" [43]. N. G. van Kampen noted correctly already in 1971, that the whole idea of linear expansion of the single phase space trajectories in an external perturbing field, as it is done in ordinary linear response theory, is pure nonsense. Essentially the point is that the chaotic nature of all realistic systems quickly moves the perturbed trajectory so far from the unperturbed trajectory, that linearization is impossible.

In publication [II] an initial perturbation $\delta\Gamma$ of the phase space coordinates Γ, of a system in equilibrium at $t = 0$ is considered. The way linearization is introduced is not by expansion of the single trajectories, but by expansion of the distribution right after the perturbation, $f_0(\Gamma)$, in terms of the equilibrium distribution $f_{E+\delta E,V+\delta V}(\Gamma)$, to first order in the perturbation $\delta\Gamma$. The calculation of the response is performed in [II], by preparing an ensemble, which is slightly off equilibrium, according to $f_0(\Gamma)$ at $t = 0$ and then monitor the decay of the distribution towards equilibrium, led by only the systems internal dynamics. In this way the van Kampen Objection is avoided. The linearity assumption used here is, that the uncertainty in $f_0(\Gamma)$, which is of second order in $\delta\Gamma$, is not developing into response terms of first order in $\delta\Gamma$ at any time during the decay towards equilibrium.

The response functions are expected to be the same no matter which ensemble they are calculated in. I mean, in the macroscopic limit we can perform an a.c. specific heat measurement by controlling temperature and measure the heat flow, or control heat flow and measure temperature, but $c_p(\omega)$ is expected to be the same in each case. Thus the complete set of response functions may also be interpreted as relations between time dependent fluctuations in different ensembles. As an example, comparison of $c_v(\omega)$ calculated in the microcanonical ensemble [II, equation (45)] an $c_v(\omega)$ calculated in the canonical ensemble:

$$\begin{aligned} & \frac{k_B N}{\frac{2}{3} + \frac{N}{\langle K\rangle^2}\int_0^\infty dt e^{-i\omega t}\frac{d}{dt}\langle \Delta K(0)\Delta K(t)\rangle_{E,V}} \\ = & \frac{-1}{k_B T^2}\int_0^\infty e^{-i\omega t}\frac{d}{dt}\langle \Delta E(0)\Delta E(t)\rangle_{T,V} dt \ . \end{aligned} \tag{3.8}$$

This relation is of course only valid in the low frequency regime (long time), to which the isoenergetic FD-derivation was restricted. But in this regime it provides a rigid relation between the fluctuations of kinetic energy under isoenergetic conditions, and fluctuations of the total energy at isothermal conditions.

Generally the FD-theorems were derived for macroscopic variables, so e.g. it is understood that the enthalpy occurring in equation (3.2) is the total enthalpy of the system. But if the system can be divided into microscopical subsystems labeled $\{i\}$, we may separate the expression for $c_v(\omega)$ into the sum:

$$c_v(\omega) = \sum_{ij} \frac{-1}{k_B T^2} \int_0^\infty dt \frac{d}{dt} \langle \Delta E_i(0) \Delta E_j(t) \rangle_{T,V}, \tag{3.9}$$

because the energy E is the sum of the energies E_i of the respective subsystems. $\langle \cdot \rangle_{T,V}$ means averaging over the isothermal isocoric ensemble of the macroscopic system. Even if there was such a thing as a well defined volume of a subsystem, this volume would of course not be conserved. On the other hand, even though locally system i and system j are experiencing a constant temperature and a constant pressure on average, the index T, V cannot be omitted or changed to T, P since the dynamics are influenced by the global constraint $V = 0$. Clearly a subsystem inside the bulk cannot feel whether the total volume of the sample are fixed or not, neither can two closely positioned subsystems, so the constraint results in an correction to the cross-correlations $\langle \Delta E_i(0) \Delta E_j(t)$, which is present also for infinitely distant subsystems i and j, and becomes significant when the $N^2 - N$ cross-terms are added up.

However, in the following chapters a more naive view is taken. The cross-correlations are assumed to be zero, meaning that there is no interaction between the subsystems, so the specific heat is the sum of the specific heat of all the subsystems:

$$c(\omega) = \sum_i c_i(\omega) = \sum_i \frac{-1}{k_B T^2} \int_0^\infty dt \frac{d}{dt} \langle \Delta E_i(0) \Delta E_i(t) \rangle. \tag{3.10}$$

Since the isocoric or isobaric constraint would have to be embedded in the cross correlation terms, this view is so primitive that it does not even have the ability to distinguish between $c_v(\omega)$ and $c_p(\omega)$, though since $c_p(\omega)$ includes no global correlations, it is conceptually closer to $c_p(\omega)$ than $c_v(\omega)$. For now I only want to note that this is *not* because I think it is a good approximation. The motivation for the view is just, that it the most primitive way of modelling, and to see how good it works, and how far it can be taken without breaking down seems like a natural thing to do for a start.

3.4 Specific Heat from General Master Equation

For later reference I shall finish this chapter by deriving the frequency dependent specific heat, in a system under isothermal conditions described by a general master equation.

$$\dot{P}_x = \sum_y W_{xy} P_y \tag{3.11}$$

x and y refers to different states of the system, which may be macroscopic as well as microscopic, and if one like E may be exchanged with H throughout the calculation. First an algebraic expression for the specific heat, which is not so well suited for computer calculations, is derived. The computability is improved by symmetrization of the W-matrix. A diagonalisation of W leads to a "spectral-form" of the specific heat, which is preferable in cases where one has to compute the specific heat for a lot of different frequencies, and useful for the analysis and comparison of different models.

Laplace transformation of equation (3.11) yields

$$s\tilde{P}_x - P(t=0)_x = \sum_y W_{xy} \tilde{P}_y \tag{3.12}$$

It is desirable to isolate $\tilde{P}_y$ in equation (3.12). This is possible if the matrix $s-W$ is invertible, which it actually is: The W-matrix spectrum has pure real non-positive eigenvalues, including one special (unique) eigenvector, namely the equilibrium distribution $P_{\mathrm{eq},x}$, which corresponds to the eigenvalue $\lambda_0 = 0$ [74]. If the Laplace frequency is assumed pure imaginary and non-zero, all the eigenvalues of $s - W$ are at the form $s - \lambda$ i.e non-zero, and $(s - W)^{-1}$ exists. Now $\tilde{P}_x$ may be isolated in equation (3.12):

$$\tilde{P}_x = \sum_y (s - W)^{-1}_{xy} P(t=0)_y, \tag{3.13}$$

and $\tilde{P}_x$ may be interpreted as the Laplace transform of a solution to equation (3.11) with the initial condition $P(t = 0)$. As in the case of the energy master equation it is of interest to evaluate the Laplace transformed transition probability $\tilde{G}(x, s|x', 0)$, which is the property that enters the expression for the specific heat. This is simply done by inserting $P(t = 0)_y = \delta(y - x')$ in equation (3.13).

$$\tilde{G}(x, s|x', 0) = (s - W)^{-1}_{xx'} \tag{3.14}$$

According to [IV] the frequency dependent specific heat for the system may be written on the form

$$c(\omega) = \frac{1}{k_B T^2} \left\{ \langle (\Delta E)^2 \rangle - \int_0^\infty e^{-st} dt \langle \Delta E(0) \Delta E(t) \rangle \right\} \tag{3.15}$$

By inserting (3.14) in equation (3.15), one arrives at an algebraic expression.

$$\begin{aligned} c(s) &= \frac{1}{k_B T^2}\sum_{xx'} \Delta E_x \Delta E'_x (W(W-s)^{-1})_{xx'} P_{\mathrm{eq},x'} &\quad (3.16)\\ &= \frac{1}{k_B T^2}\sum_{xx'} \Delta E_x \Delta E'_x (\delta_{xx'} - s(s-W)^{-1}_{xx'}) P_{\mathrm{eq},x'} &\quad (3.17)\end{aligned}$$

For large systems this expression is hard to evaluate. But a commonly used normalization of P_x makes W symmetric: According to principle of detailed balance we have:

$$W_{yx} P_{\mathrm{eq},x} = W_{xy} P_{\mathrm{eq},y} \tag{3.18}$$

or

$$P^{-\frac{1}{2}}_{\mathrm{eq},y} W_{yx} P^{\frac{1}{2}}_{\mathrm{eq},x} = P^{-\frac{1}{2}}_{\mathrm{eq},x} W_{xy} P^{\frac{1}{2}}_{\mathrm{eq},y} \tag{3.19}$$

This means that the matrix $\hat{W}$ defined by

$$\hat{W}_{xy} = P^{-\frac{1}{2}}_{\mathrm{eq},x} W_{xy} P^{\frac{1}{2}}_{\mathrm{eq},y} \tag{3.20}$$

is symmetric. By defining a coordinate transformation, by $\hat{P}_x = P^{-\frac{1}{2}}_{\mathrm{eq},x} P(x)$, we save some computational efforts by writing the specific heat as:

$$c(s) = \frac{1}{k_B T^2}\sum_{xx'} \Delta E_x \Delta E'_x P^{\frac{1}{2}}_{\mathrm{eq},x} (\hat{\delta} - \hat{s}(\hat{s}-\hat{W})^{-1})_{xx'} P^{\frac{1}{2}}_{\mathrm{eq},x'} \tag{3.21}$$

Note that the matrices s and δ transform into themselves: $\hat{s} = s$ and $\hat{\delta} = \delta$.

One may go a step further and expand the specific heat at the normalized eigenfunctions Φ^α_x of $\hat{W}$: Let us define the diagonal matrix $\bar{W} = S^{-1}\hat{W}S$, where S is a coordinate transformation defined by $S_{xy} = \Phi^y_x$, fulfilling $S^T S = 1$. The specific heat can now be expressed in the following way:

$$c(s) = \frac{1}{k_B T^2}\sum_{xx'} \Delta E_x \Delta E'_x P^{\frac{1}{2}}_{\mathrm{eq},x} (S\bar{W}(\bar{W}-\bar{s})^{-1}S^{-1})_{xx'} P^{\frac{1}{2}}_{\mathrm{eq},x'} \tag{3.22}$$

Using that $\bar{W}$ is diagonal we can evaluate the matrix product.

$$(\bar{W}(\bar{W}-\bar{s})^{-1})_{\alpha\beta} = \frac{\lambda_\alpha}{\lambda_\alpha - s}\delta_{\alpha\beta} \tag{3.23}$$

Inserting equation (3.23) in equation (3.22)we get

$$\begin{aligned} c(s) &= \frac{1}{k_B T^2}\sum_{xx'} \Delta E_x \Delta E'_x P^{\frac{1}{2}}_{\mathrm{eq},x} \sum_{\alpha\beta} S_{x\alpha}\frac{\lambda_\alpha}{\lambda_\alpha - s}\delta_{\alpha\beta} S^{-1}_{\beta x'} P^{\frac{1}{2}}_{\mathrm{eq},x'} &\quad (3.24)\\ &= \frac{1}{k_B T^2}\sum_{\alpha}(\sum_{x} \Delta E_x P_x^{\frac{1}{2}} \Phi^\alpha_x)^2 \frac{\lambda_\alpha}{\lambda_\alpha - s} &\quad (3.25)\end{aligned}$$

The last expression (3.25) will be named the spectral form of the frequency dependent specific heat. It is a very useful equation, as shall be seen in chapter (4.3), where it has been used for examination of different models. Note that $c(s) \to \frac{\langle(\Delta E)^2\rangle}{k_B T^2}$ in the limit $s \to 0$, - the equilibrium specific heat is recovered.

I have made a program, which can calculate the exact $c(s)$ for a given master equation, through a diagonalisation of the master equation. The program can deal with systems of about 2000 distinct states, and not much more.

In the following discussions the program has been used to calculate $c(\omega)$ for different models, instead of going into a complicated analytical solution in each case. If one has to analyse a continuous model, e.g. a certain energy master equation, the procedure is simply to split up the continuous (energy) axis in a finite number of small pieces, each of which are identified with a state x in equation (3.11), and then analyse the discrete master equation numerically by means of equation (3.25).

Chapter 4

Stochastic Modelling

4.1 Canonical Ensemble and Stochastic modelling

In the past decade different models of dynamics supercooled liquids near the glass transition based on energy controlled stochastic models [45, 46, 47, 48, 49, 53, 54, 55, 29] has been suggested. Typically these works focuses on a local part (a "region") of the supercooled liquid, and assumes that the dynamics of such a region can be described by randomized jumps in configuration space. The jump rate between two states depends on the energy of the involved states. In the most simple cases it is assumed that energy is the only controlling variable, i.e. there is no topological or spatial dependence of the jump rates. Generally any model which predicts time correlation of energy fluctuations has an interesting aspect; it is directly falsificable by frequency dependent specific heat measurements. Frequency dependent specific heat measurements are increasingly used as an experimental tool in investigations of supercooled liquids near the glass transition [61, 57, 11, 59]. I find this particular experimental method interesting because it directly probes the time correlations of the energy fluctuations, and these may be of special significance since the local potential energy is likely to be strongly correlated to the local relaxation time.

4.2 Quasi universality

In the following I will discuss some applications of thermodynamic linear response theory by starting from the proposed universality in low temperature specific heat and then characterising the frequency dependent specific heat origining from different types of models. The universality will be discussed in connection to other experiments than those referred in [IV], and a few comments will be made on the use of transition state models in general. I shall now turn to the following questions:

- What is the significance of the proposed "quasi universality" of [IV],- can it be responsible for the nearly identical α-peak observed in different liquids?
- Can the proposed "cut-off models", of [IV] be justified from a microscopical point of view?

From experiments it is known that the imaginary part of various susceptibilities shows an α-peak which imaginary part is not symmetric on the logarithmic frequency axis, but instead shows a steep inclination at the low frequency side. and a more gradual declination at the high frequency side,

In specific heat measurements this asymmetric peak is also seen, and it has some consequences on the range of possible energy controlled models of the glass transition. In general the susceptibilities are different for different substances, but they are not *that* different though, and therefore it is tempting to look for some common explanation of the shape of the α-peak for all liquids.

Resent dielectric an shear mechanical results from the glass transition laboratory at IMFUFA indicates [26, 25] that in at least 6 organic liquids, where the alpha-peak is well separated from the JG-β-peak above the glass transition, the α-peak shows perfect time temperature scaling in a temperature range corresponding to a four decade shift of frequency in some cases.

In [III] and [IV], a rather radical proposal is presented, namely that the skew shape of the α-peak is due to essentially a local region density of potential energy states (DOS), with a low energy cut of. Two different models, the energy master equation (EME) and collection of two level systems, both with a single absolute barrier energy are proposed. (Sometimes EME with single barrier energy, and a DOS which is a Heaviside step-function is referred to as "EME with step DOS"). They both gives time temperature scaling, and the specific heat of these models matches experiments good. We named this observation "quasi universality" because the low temperature limit of the α-peak, printed in [IV, figure (1)], is the same of all models where the DOS has finite values down to a ground state with energy E_0, below which, it suddenly drops to zero, and where the absolute energy barrier is the same for all transitions. The word "quasi" refers to the fact, that $c(\omega)$ of a system where the states are only connected pairwise, is *almost* identical to $c(\omega)$ of a system where all states are are connected through the same barrier.

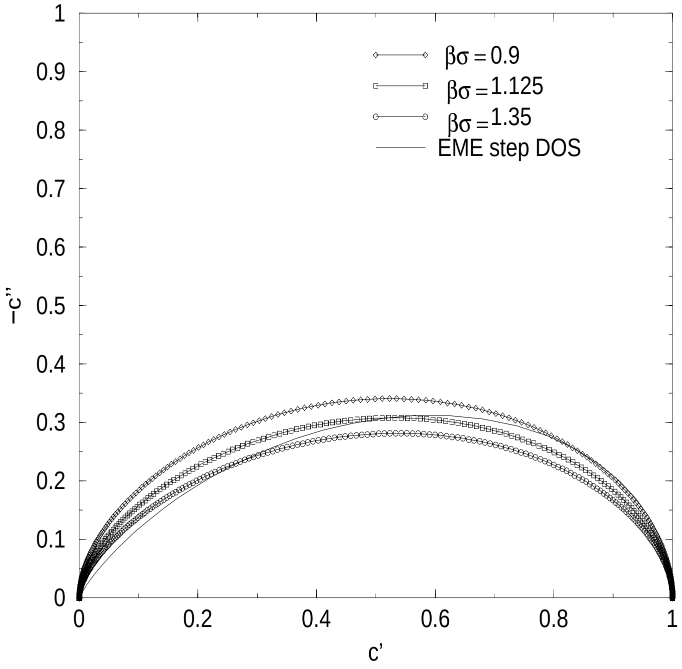

Figure 4.1: A transition state model with Gaussian DOS (variance = σ^2 is far to symmetric to be the right model of supercooled liquids. It also suffers from the flaw of not obeying TTS.

Even though the EME with constant barrier energy and step DOS, is a simple model the found universality is non-trivial in several ways.

It is a zero-parameter model which is quite close to the experimental specific heat. Moreover it obeys time temperature scaling which is not an inherent property of EME models. If for example a Gaussian DOS is assumed, TTS is not obeyed (see figure (4.1).

Besides pure Debye relaxation all EME models where DOS is of the form $n(E) = E^a$, $a \geq 0$ obeys TTS. EME with DOS may be considered as a limiting case $a = 0$ of the family of "power law DOS models" see figure (4.2).

4.2.1 Evidence of quasi universality

Besides the measurements of T.E. Christensen, reported in [IV], one finds $c_P(\omega)$ measurements of glycerol [61, 11, 58], propylene glycol [58], o-terpenyl /o-phenylphenol mixtures [59], salol [60] and $[(\mathrm{Ca(NO_3)})_2]_{0.4}(\mathrm{KNO_3})_{0.6}$ (CKN) [62] in literature. A fairly good way to represent the shape of the experimen-

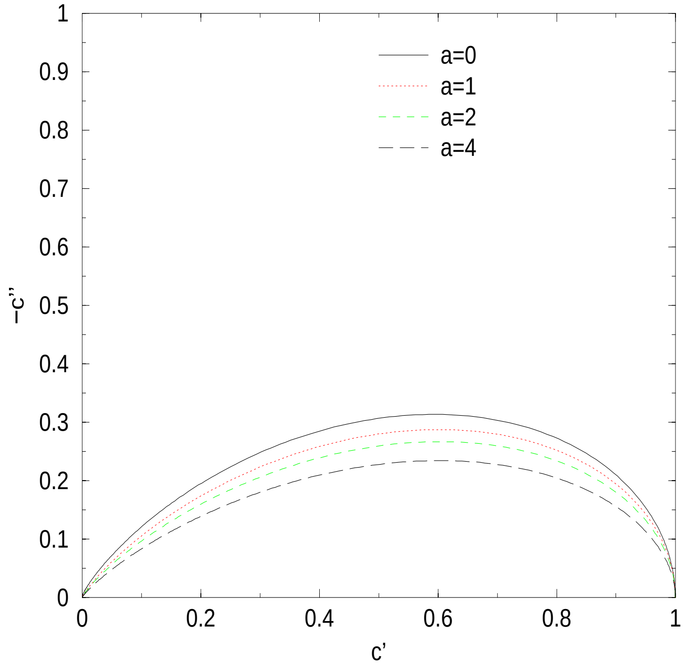

Figure 4.2: The EME with DOS may be considered as a limiting case of a family of models with power law DOS. ($n(E) \propto E^a$). However there is a qualitative difference between $a > 0$ and $a = 0$, namely that $n(E = 0)$ is non-vanishing for the latter.

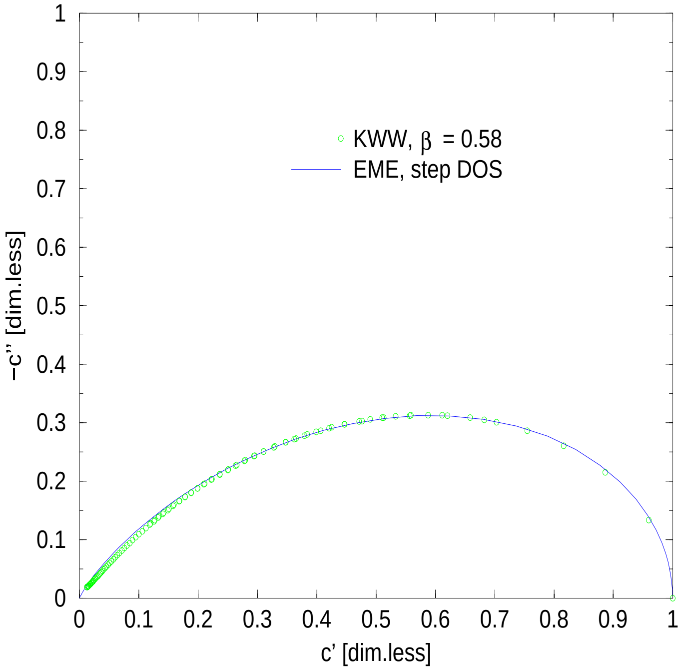

Figure 4.3: Comparison of the KWW form and the EME with cut-off in DOS.

tal data, is by the KWW form (2.2).

The KWW form looks like a power low in the high frequency limit, which is seen as an asymptotic straight line in the left bottom of a Cole-Cole plot. See figure (4.3). But the prediction of EME with the cut-off in DOS yields $c'' = \ln^3(\omega)/\omega$, where c'' is the imaginary part of the frequency dependent specific heat, i.e. no power law. Apparently the imaginary part of c in the model bends off a little too quick compared with the KWW form. But the KWW-form with $\beta_{\mathrm{KWW}} = 0.58$ seems to be roughly consistent with the model, thus it serves as a tool for comparison with experiments in the following. In table (4.1) β_{KWW} is showed for several liquids. β_{KWW} is only close to 0.58 in the first 4 liquids. In 1.2.6 hexanetriol β_{KWW} is totally off and in glycerol, di-n-buthyltalate and CKN it decreases from values above 0.58 to values below, as temperature is decreased. In the o-therpenyl mixture β_{KWW} also decreases with deceasing temperature, but fails to cross 0.58 in the measured temperature range.

Can these measured values be consistent with universality at all? The answer is yes, they *may* be consistent with universality *in the low temperature*

Substance	$\beta_{\mathbf{KWW}}$	**T-range**	**Reference**
1.2 propanediol (propylene glycol)	0.61	174.1 K	[14],[58]
2 methyl-2,4-pentanediol	0.58	191 K	[14]
1.2 butanediol	0.57	182 K	[14]
1.3 butanediol	0.55	180 K	[14]
glycerol *	0.53	183 K	[10]
glycerol	0.65	203-219 K	[11]
1.2.6-hexanetriol	≈ 0.2	206 K	[14]
o-therpenyl$_{0.91}$-o-tepenylphenol$_{0.09}$!	0.60-0.75	242-268 K	[59]
salol (phenylsalisylate)!	0.62-0.71	226-237 K	[60]
di-n-butylphtalate*!	0.53-0.58	177-194 K	[61]
$(Ca(NO_3)_2)_{0.4}(KNO_3)_{0.6}$!	0.53-0.67	344-358 K	[62]

Table 4.1: β_{KWW} of $c_p(\omega)$ for several liquids. In general $c_p(\omega)$ is determined with less acuracy than the electric susceptibility. Moreover there is still a dispute about the validity of the various methods of measuring $c_p(\omega$ [22]. !) The measured value of β_{KWW} is increasing with temperature, i.e. the α-peak is getting more narrow. *)β_{KWW} was estimated by comparing the ratio $\frac{c''(\omega)}{c'(\infty)}$ at the loss peak to the same property of the KWW form, with uncertainty on β_{KWW} at around 0.02. The lowest temperature meassured in reference [61] is remarkably narrow, with $\beta_{\mathrm{KWW}} = 0.58$.

limit, but to see that one has to adobt a certain view on JG-β relaxation: As discussed in the introduction (2), there exists some fluids, where the α-and JG-β relaxation is well separated at T_g. In these substances an observable low temperature regime exists, where time temperature scaling of the α peak is obeyed. What might be the case is that this actually true for all liquids, but not observable in most liquids, because α and β relaxation is not separated properly above the glass transition. Remember as it was discussed in the introduction, that T_g is not really a physical significant temperature, since it only sets a human timescale, thus it is coincidental whether α and JG-β relaxation is well separated at the glass transition for a given liquid.

As the two relaxation peaks are separating, the α-peak shrinks towards an assymtotic invariant shape. This is seen as a *decraese* of the α width, when temperature is decreased further below the region where the two peaks separates. In figure (4.4) this narrowing phenomenon is seen very clearly for some liquids. Note that in DBP the β-relaxation is so well separated from the α relaxation, that TTS works to excelent degree. It was also seen in figure (2.3), where the dielectric susceptibility of DBP was shown. In figure (4.5) specific heat measurements of DBP are shown. It is remarkable that in the specific heat measurements of DBP, the α-peak [61] is broadening down to the temperature range where TTS is observed in other response functions. This apparent broadening is consistent with the departure of a JG-β-relaxation in the right part of the spectrum, resulting in two separated peaks at $176.5K$. It is noteable that $c_p(\omega)$ is remarkably narrow ($\beta_{\mathrm{KWW}} = 0.58$) at $T = 176.5$ Returning to figure (4.4), it is noted that in salol the separation is only about to start at T_g, that is salol is still close the merging temperature (see introduction (2.3)). This is consistent with the very narrow loss peak in $c_p(\omega)$ measured at higher temperatures see table (4.1), since in general the α-peak is more narrow at temperatures above the merging temperature than below.

$\varepsilon(\omega)$ of 1.3-butanediol is measured just below the merging temperature, but the JG-β relaxation is rather weak, so the α-peak is showing TTS, except for a slight disturbanse of the high frequency tail. This is consistent with beeing in the universality regime in the specific heat measurement, refered in table (4.1).

1.2.6-hexanetriol is very atypical liquid. In this substance one actually sees an extra peak which is partly separated from the α-peak in the specific heat [IV]. This is consistent with the apparently very broad α-peak, which I interpret as the result of a very pronounsed JG-β relaxation merging with the α-peak just in the measured temperature interval.

Several meassurements have been preformed on glycerole, and they all seem to confirm that glycerole is somewhat atypical in the sence that the α-peak seems to be broader, than in other liquids. In the interpretation

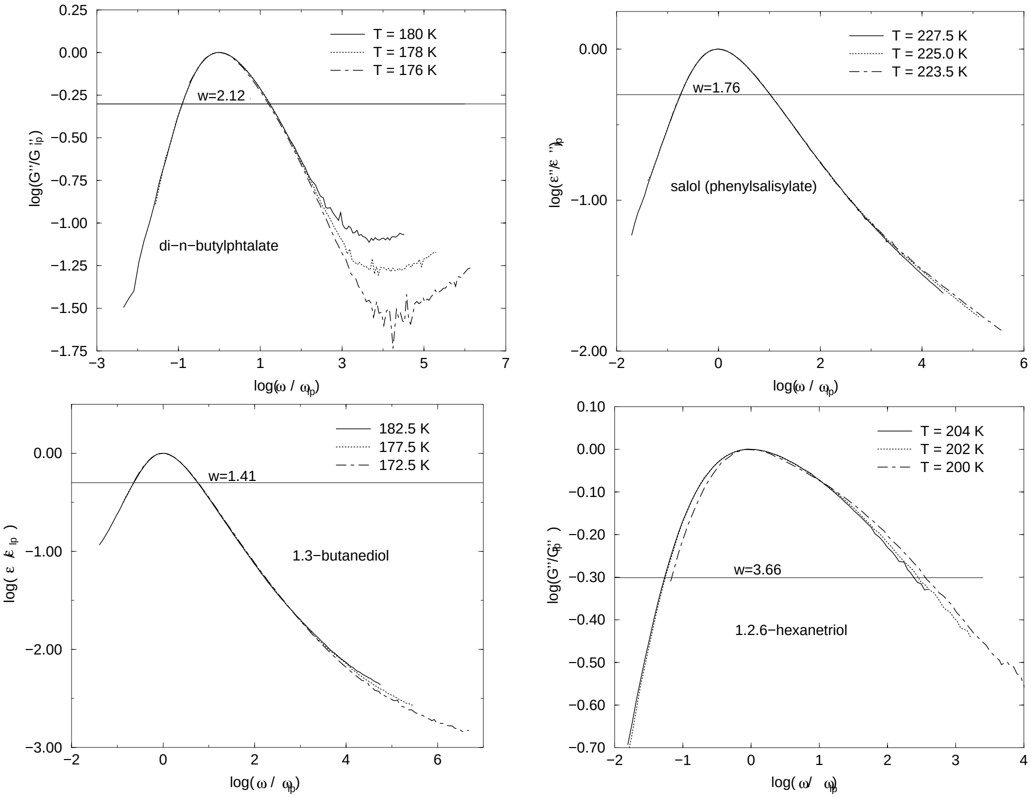

Figure 4.4: The imaginary part of the dieltric susceptibility $\varepsilon''(\omega)$ of 1.3-butanediol and salol, and the imaginary part of the shear modulus $G''(\omega)$ of 1.2.6-hexanetriol and di-n-butylphtalate (DPB) in a log-log plot. In all figures the response functions have been devided with their values at the loss peak (lp) frequency ω_{lp} and ω has been devided with ω_{lp} so that the top points of the α-peaks collapses. The separation of α and JG-β relaxation is therefore observed as a JG-β-peak that moves to the right as temperature is decreased. I must emphasize that these measurements, which I have no part in, are made by N. B. Olsen and Tage E. Christensen, who has kindly given permission [25] print them. In DBP TTS is seen very clearly, since the α and JG-β peaks are well separated. In 1.3-butanediol the peaks are separating at the measured temperatures, but the JG-β-relaxation is so weak that it does not spoil the shape of the alpha peak too much, and TTS is obeyed in the measured regime. In salol we are only in the begining of the separation, and what is observed is an α-peak where the β-peak is begining to come out at the right hand side. In 1.2.6-hexanetriol the JG-β- relaxation has very high amplitude in the measured temperature regime. So it interferes so much with the α-relaxation that the high frequency tail of the α-peak can not be observed at all, and the time temperature scaling is aparrantly broken. How α and JG-β interferes as they are merging cannot be known unless one assumes a model. It can not be considered as a simple superposition for, since JG-β has never been observed below α-peak at high temperatures.

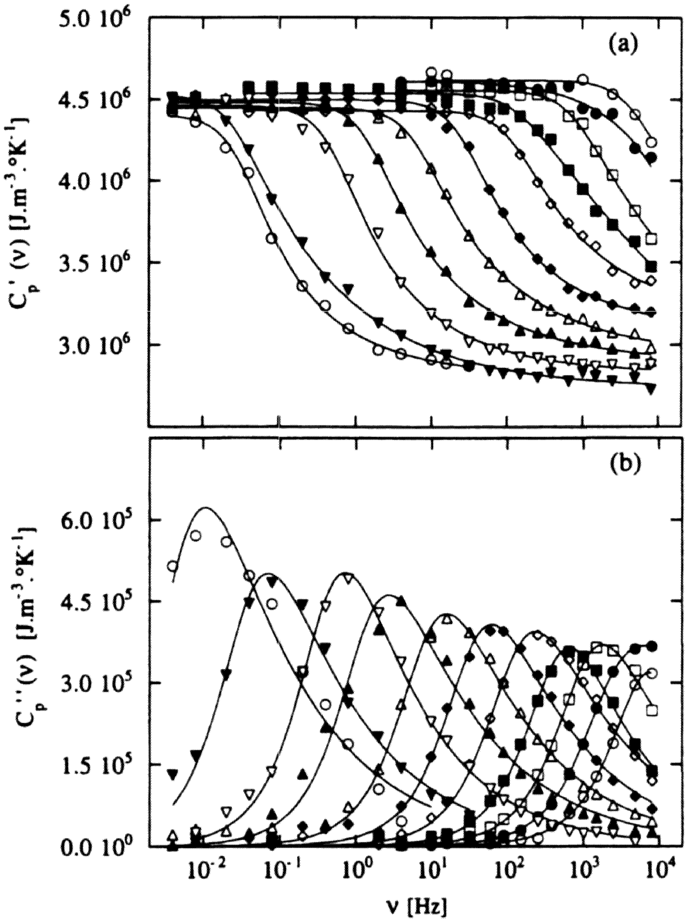

FIG. 5. Real and imaginary parts of $C_p(\nu) \equiv C_p'(\nu) + iC_p''(\nu)$ plotted against ν at 11 temperatures from 176.5 to 201 K showing the peak in $C_p'(\nu)$ (b) and the crossover in $C_p''(\nu)$ (a) moving to lower frequency as temperature is lowered. The solid lines are fits to the Davidson–Cole functional form: $C_p(\nu)=C_{p\infty}+\Delta C_p/[1+i(\nu/\nu_p)]^{\beta}$.

Figure 4.5: From N. Menon, J. Chem. Phys **105**, 5246 (1996). Specific heat of DBP. The relative broad spectra, is presumeably due to a JG-β peak separating from the α-peak in the observed temperature region, as it is seen in both dielectric and shear mechanical relaxation. The values of

given here the reason is that the α-peak and JG-β-peak are be overlapping in this substance, so that the slow declining high frequency tail of c'' in glycerole, which appears to be increasingly pronounced at lower temperature, is actually due to JG-β-relaxation which begins to separate out, in the same manner as in 1.2.6-hexanetriol. This is seen very clearly in the figure of [IV].

The experimental findings of $c_p(\omega)$ may be be interpreted in the light of this: There exists a low temperature limit where the α-peak of $c_p(\omega)$ has a temperature invariant shape, with $\beta_{\text{KWW}} \approx 0.58$, as it also are the case for $G_\infty(\omega)$ and $\varepsilon(\omega)$.

In the first four liquids of table (4.1), the JG-β peak is either so weak or so well separated from the α-peak, that this low temperature limit is actually reached at T_g. In the rest of the liquids the α and JG-β relaxations are beginning to separate at the meassured region, leading to a broadening of the spectra as temperature is decreased. Note that this interpretation implies that the increasing width of the spectra is only apparant, and caused by the β-peak, which is located in the tail of the α-peak, but does not move along with the alpha peak as temperature is decreased.

It is not my objective to show that the universality of publications [III] and [IV] are found exactly in real liquids, and I dont want to get to exited about it, since the models where universality occurs relies on a several doubious assumtions including that the liquid can be separated into non-interacting regions. I just want to note that its a fairly good approximation which may give a hint about the nature of the glass transition, and that the universallity in connection with the dielectric measurements gives a picture which includes time temperature scaling, and are consistent with measurements of all substances where both $c_p(\omega)$ and other responsefunctions has been measured.

4.3 Quasiuniversality and Energy Controlled Dynamics

In spite of the after all limited evidence for TTS, I shall now follow a line where time temperature scaling of the α-peak is considered valid, and thus a criterion for selection of models.

As far as I am concerned, there are no other zero parameter models which are that close to the experimental $c_p(\omega)$. To mention an example that does not work, consider a model with step DOS, but “metropolis” dynamics. Metropolis dynamcs is an computational tool used for sampling phase space points in montecarlo simulations. Metropolis dymamics only physical

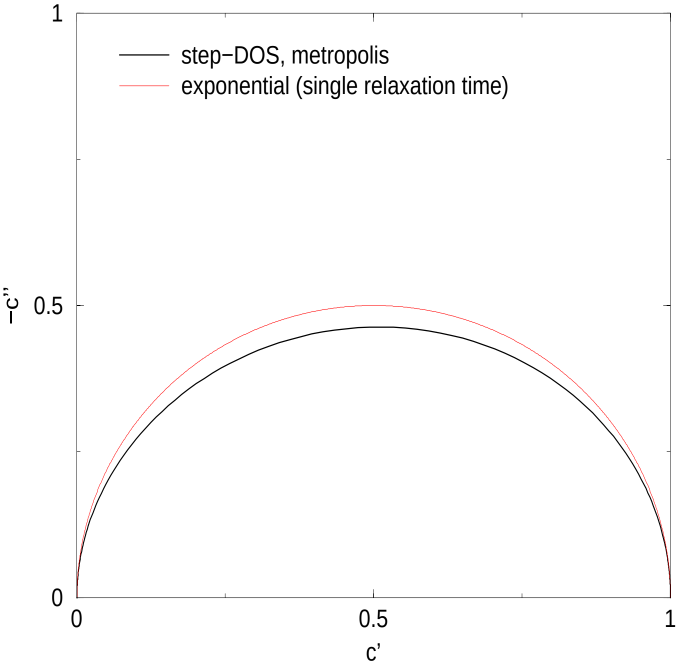

Figure 4.6: Specific heat of a model, in which Metropolis dynamics on step DOS is assumed. $c(\omega)$ is not close to experiments, thus the model is not of physical interest. However it shows time temperature scaling. $c(\omega)$ may be found analytically, and written on a simple form: $c(s) = -\int_0^\infty dt\ e^{-st}\frac{d}{dt}\frac{e^{-t}}{t+1} = 1 - se^{s+1}E_1(s+1)$, where $E_1(s+1)$ is the exponential integral $E_1(z) = \int_z^\infty dx \frac{e^{-x}}{x}$. For comparison the specific heat of a system with a single relaxation time is shown.

justification is that it obeys principle of detailed balance. The transition probabilities are defined as

$$\Gamma_{i\to j} = \Gamma_0 \left\{ \begin{array}{cl} e^{-\beta(E_j - E_i)}, & \text{if } E_j > E_i \\ 1, & \text{if } E_j \le E_i \end{array} \right. \tag{4.1}$$

This specific heat of this model is shown in figure (4.6)

Other types of collections of two level systems with zero parameters leads also to absurd or trivial results which are far from observations.

It is remarkable that also a Gaussian density of states cannot reproduce the shape of the α-peak, since a Gaussian DOS is often assumed. For example in [53]. The reason is that energy landscape models are used as a way to model the non-Arrhenius behavior [46]. The step DOS results in a pure

Arrhenius law for the loss peak frequency, and is therefore not able to reproduce non-Arrhenius behavior (see the Appendix of IV). So one is lead to the conclusion that an energy master equation with transition state dynamics cannot explain both non-Arrhenius behavior and the shape of the α-peak. An important result so far is, that *if* one insists on an energy controlled model with transition state dynamics, one is led to a DOS with a low energy cut off, if the shape of $c(\omega)$ has to be in the neighborhood of experimental data. Roughly speaking, in the transition state picture, the shape of the α-peak is caused by a low energy cut off in DOS, combined with the Boltzmann distribution.

Again, all these conclusions are based on an assumption of transition state dynamics, which of course may be wrong. And also the fact that regions interact with each other is left out of consideration. The thing is, that there is not enough information in the experimental data to justify introduction of a more sophisticated form of the transition probabilities than that of equation (2.3), unless there is some physical reason for it. There are several unphysical one parameter models such as the KWW-form without physical explanation which can reproduce most response functions to excellent degree.

As an example consider a macroscopic system in contact, with a heat reservoir. In the macroscopic limit, the energy distribution is approximated by Gaussian with variance σ^2. The most simple way to assure principle of detailed balance is by assuming

$$\gamma_{i\to j} \propto e^{-\frac{1}{4\sigma^2}(E_j^2-E_i^2)+a(E_i+E_j)}, \tag{4.2}$$

where an (unmotivated) linear term has been introduced in the exponent. It is actually a one parameter model, since the energy axis may be rescaled without changing the shape of $c(\omega)$. The dynamic specific heat of this model is compared to the universal form in figure (4.7). The point is that this "model", which is totally different from transition state dynamics and step DOS can reproduce the quasi-universal curve with only 1 parameter. The physical interpretation of the "macroscopic master equation" is problematic. Clearly the parameter σ^2 must depend on temperature, since the zero frequency specific heat is $c(0) = \frac{\sigma^2}{k_B T^2}$, and the specific heats of supercooled liquids do not follow a T^{-2} law. In order to maintain time temperature scaling, the parameter a has to change as well ($a \propto \sigma^{-1}$). Since the variance σ^2 scales as N if we change the system size, it can also be concluded that $a \propto N^{-1/2}$ which makes it difficult to interpret the linear term as a Boltzmann factor of some sort. So one should not be to exited about this "model", unless a physical interpretation of a is found.

In connection to this I should mention, that the zero frequency specific

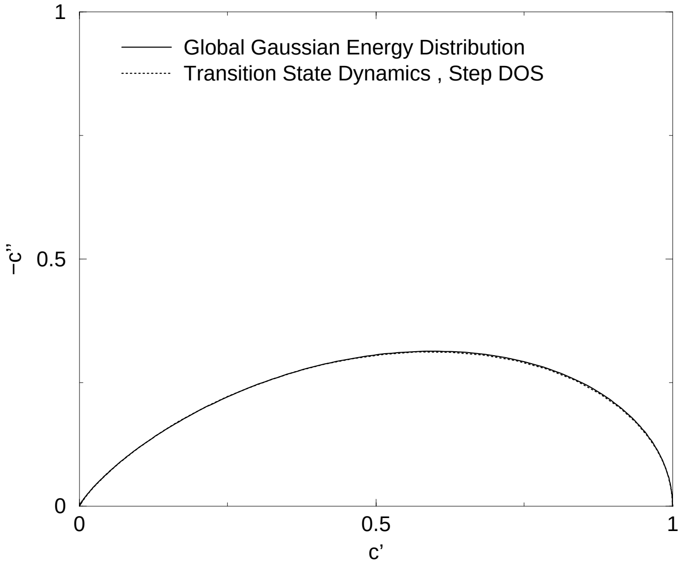

Figure 4.7: Specific heat of a “macroscopic” master equation, with Gaussian energy distribution, and transition rates chosen as $\gamma_{i \to j} \propto e^{-E_j^2+E_i^2+a(E_i+E_j)}$. The model is compared to the universal heat capacity, derived from the energy master equation with transition state dynamics, and step DOS. The parameter $a = 3.0$, is fitted with the eye.

heat $c(0)$ of the transition state model with step DOS, has a trivial temperature dependence, namely $c(0) = k_B$. This points towards a very small region size. If Gaussian DOS is chosen $c \propto \frac{1}{T^2}$, but since the specific heat of a region is still related to the width of the relaxation time distribution, one lead to conclude that the region size is on the order of magnitude of a molecule [63] also in this model. Generally supercooled liquids shows a declining overall specific heat, and an increasing (in few cases constant) relaxational part of the specific heat, as the temperature is lowered [8, 10, 14]. In order to justify the transition state model with step DOS, one has to put in an additional assumption, such as a total number of regions which are declining with temperature.

4.3.1 Consequences of universality

Even if the universality is only approximately obeyed of real liquids, the models may still carry some hint about what is going on in real liquids.

If we take the transition state models seriously, what may then be learned from these findings? First the relaxing unit, formerly named a "region", has a constant DOS $n(E)$ down to the ground state in both models. Since the models are considered as low temperature limits of real liquids, this implies, that in real liquids the DOS of a region near the ground state is almost constant within an energy interval at least as broad as the equilibrium distribution $P_{\mathrm{eq}}(E) = n(E)e^{-\beta E}$, i.e. an energy interval of at least same magnitude as β^{-1}. That $n(E)$ is constant means, that it varies little compared to the Boltzmann factor $e^{-\beta E}$. Further more, a nearly constant DOS must be interpreted as a system with very few degrees of freedom. A one dimensional harmonic oscillator for instance has constant DOS, and an N dimensional harmonic oscillator has $n(E) \propto E^{N-1}$. So if the model is interpreted naively, the "region" must be some simple entity in the liquid, e.g. a molecule or a bond. Alternatively the molecules motion may be restricted by surroundings in a way, so that even though a jump of a local region involves several molecules, the collective motion of all the molecules is confined to a certain region of phase space, which is the same as saying that the DOS is only apparent, and in reality it is actually due to interaction between regions.

Then there is a third possibility, namely that there is local inhomogeneities in the liquid, so that there actually exists such a thing like isolated regions. This is a topic which is very much discussed in literature at the present (see e.g. [64]), but still unsettled though. The idea is that a liquid at low temperatures may be heterogenous in a dynamical sense, so that the particles which are relaxing fast is clustered in space, a phenomenon which is very hard to measure experimentally, since it cannot be monitored in the static structure factor. However, if this is the case, it can help to justify the disregard of region-region interaction, which is the main flaw of the region picture in general; the energy fluctuations of different dynamic clusters may be considered as uncorrelated, and thus the cross correlation terms in equation (3.9) are equal to zero. On the other hand this leaves one with a paradox, i.e. that the regions still has to be on the size of a molecule.

Chapter 5

Hydrogen Bond Dynamics in Supercooled Water

5.1 Brief introduction

The research in pure water is major topic itself. The great interest in this particular liquid is partly motivated by pure physical interest, and partly motivated by the fact that understanding of water is important for biochemistry and biophysics, because of its presence in all biological processes. [1, 84, 85].

Of course the anomalous thermodynamic behaviors are the most striking features of water. There is not yet consensus about the reason for the negative expansion coefficient $\alpha(T)$ below 4°C and the compressibility minimum at 46° C, which are very rarely found in other liquids. These phenomena has been tried correlated with an apparent power law divergence of susceptibilities, as well as relaxation times at a low temperature about $T_A \approx -45°$ [86].

Unfortunately water crystallizes at around $-35°$. This limits the evidence of power law divergence to a narrow region pretty far from T_c, thus this evidence is not out ruling the possibility that the apparent divergence in relaxation times is just the non-Arrhenius behavior, seen in other liquids.

An interesting explanation scheme proposed by H. E. Stanley [87], views supercooled water as a heterogeneous liquid: Locally water can pack in two different configurations. 1) A low density tetrahedral structure , with low entropy and low enthalpy, and 2) a high density structure with high entropy. The low density configuration is associated with a high degree of hydrogen bonding. The idea is that this structure which looks very much as normal ice (ice VI) becomes more and more dominant as water is cooled along an isobar $P = 0$, and causes an expansion of the supercooled liquid. The apparent divergence in relaxation times is explained by the existence of a high density

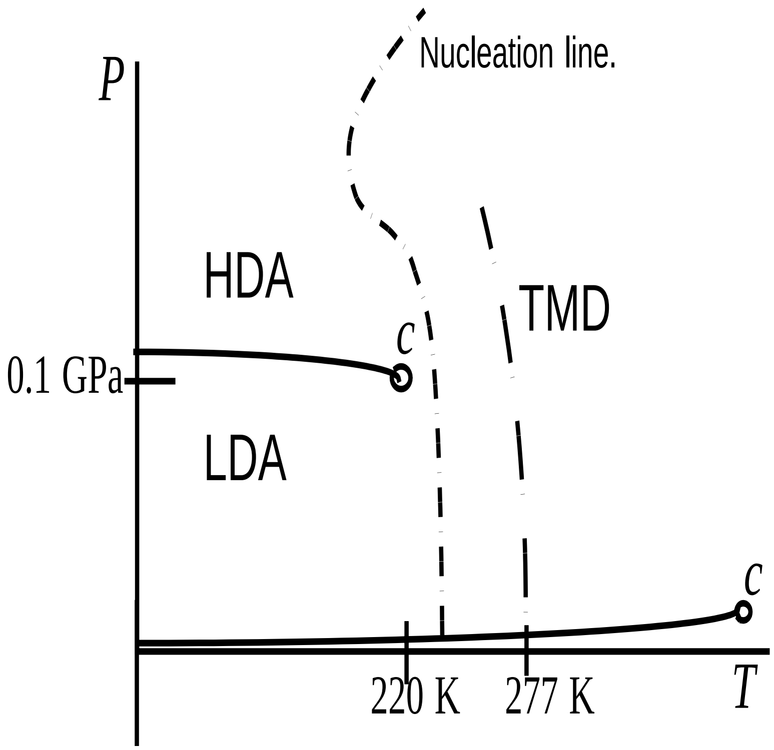

Figure 5.1: Schematic phase diagram of liquid water. LDA and HDA refers to Low / High Density Amourphous water. TMD refers to “Temperature of Maximum Density”.

liquid - low density liquid phase transition, terminating in a critical point c' located at $T = 220$K and $P = 100$ MPa. The fluctuations origining from c' can also account for the increase of κ_T as T is decreased. See the schematic drawing in figure (5.1). The hydrogen bonds are believed to be of great importance for the scenario sketched above. This may be the reason for a discussion in literature [88, 89] about the time correlation of hydrogen bonds in supercooled water. It is this particular topic which is addressed in publication [V].

5.1.1 Summary of V

The initial motivation for the work presented in publication [V] sec (7.5), was that there has been some discussion [88, 89] about how to define hydrogen bonds, and the way of analysing their time correlation as well. In [V] we cleared out the differences between the life time distribution method of [89] and the reactive flux method described by [88]. The reactive flux defined as

$$k(t) = -\frac{d}{dt}c(t), \tag{5.1}$$

where

$$c(t) = \frac{1}{\langle h \rangle}\langle h(0)h(t)\rangle. \tag{5.2}$$

Here h is a "bond indicator" (see [V] and [88]) of an arbitrary pair of molecules. $k(t)$ turned out to be independent on the bond definition at long times. In opposition to this, the bond life time distribution $P(\tau)$ turned out to be very sensitive to the bond definition. We found that in the SPC/E model $c(t)$ showed qualitatively the same time dependence as the intermediate scattering function reported in [91], with a relaxation time τ_R departing from the Arrhenius law. The non-Arrhenius behavior was equally well/bad fitted with a power law or an Vogel Fulcher law, which both diverges too fast at low temperature. Which is also the case for normal fragile liquids. On the other hand the characteristic time of $P(\tau)$ τ_{HB} showed Arrhenius behavior. The results matches simulations on saturated square-well models of R. Speedy et al. [90], who actually did the same analysis as we did, on an other potential. We did not find a power law with exponent 0.5 in $P(\tau)$, as it is the case for the more structured model ST2 [89]. Since the $P(\tau)$ analysis counts a bond as broken as soon as it has been exited in to a broken state for even a very short time, it seems reasonable that this function is thermally activated (the most obvious interpretation of the found Arrhenius law). To brake a bond for good requires that the liquid is reorganised in a more collective way locally, an therefore τ_R is related to the viscous relaxation. It remains to be seen whether the power law found by [89] is persistent at lower temperature.

5.2 Time Temperature Scaling

I shall just add a few further comments to the simulation results of [V]. It appears that the long time behavior of $c(t)$ shows time temperature scaling to quite good agreement. In figure (5.2) $c(t)$ has been plotted for 5 different temperatures each with two bond definitions. The curves clearly collapses in the long time limit.

In order to model this interesting behavior I propose the following simple model. Consider the decay of $c(t)$ as the probability of two molecules being bonded, given that they where bonded at $t = 0$.

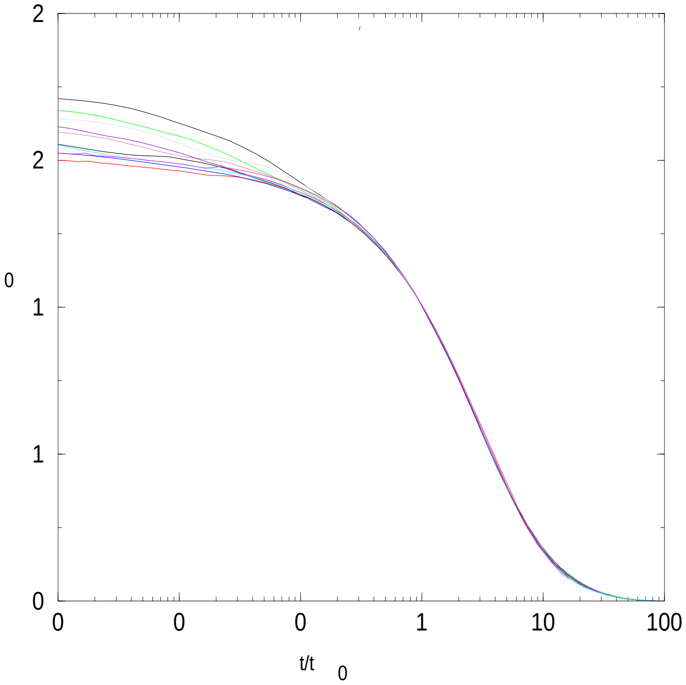

Figure 5.2: $c(t)$ calculated both from geometric and energetic bond definition for 5 separate temperatures 210-300 K. The time has been divided with t_0, found by monitoring t times the logarithmic derivative, $t\frac{d}{dt}\ln[c(t)]$, which is invariant to a possible scaling of $c(t)$ and $c(t)$ has been devided by its value at t_0.

If one describes the position of particle 2 relative to particle 1, the problem is reduced to diffusion of one particle in 3 dimensions. Now, the particle is not diffusing by simple random walk, since its surroundings are structured. As a first attempt to overcome this problem I propose to consider the particles movement as random walk in a non-homogeneous DOS, and that DOS is proportional to the pair correlation function $g(r)$. In equilibrium the probability distribution $f(r)$ has to be equal to $g(r)$. The most simple dynamical equation one can make on these premises is one where the jump probability between two neighboring sites is

$$p_{i \to j} = \gamma_0 g(r_j). \tag{5.3}$$

In the continuous limit this leads to the following modified diffusion equation:

$$\frac{\partial f}{\partial t} = D(g\nabla^2 f - f\nabla^2 g) \tag{5.4}$$

This model was simulated with the initial distribution

$$f_0 = \begin{cases} g(r), & r < 3.5\text{Å} \\ 0, & r > 3.5\text{Å} \end{cases}, \tag{5.5}$$

and $c(t)$ was calculated as the probability of still being inside the 3.5 Å shell at time t. In figure (5.3) $t\frac{d}{dt}\ln[c(t)]$ derived from this model at $T = 225$ K is shown together with the result from the simulations. The agreement at long time scale is good, as it is forced to by the construction of the model, while the short time behavior is not that well reproduced by the model, as the $c(t)$ of the model has a knee which is sharper than that of the simulation. The model is not expected to depedent to much on the relatively small changes of $g(r)$ as function of temperature, though I have not analysed this carefully. This is a zero parameter model, and in the light of this it works good. It confirms, what should be expected, that the long time tail of $c(t)$ is determined by diffusional motion.

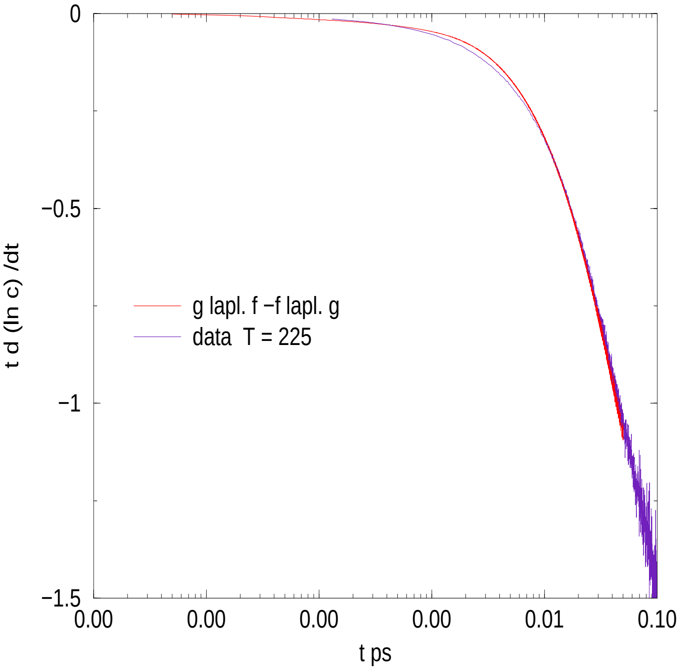

Figure 5.3: t times the logarithmic derivative of $c(t)$, $t\frac{d}{dt}\ln[c(t)]$ calculated from a modified diffusion model, with $g(r)$ as input, compared to the same property calculated from MD simualtion at 225 K

Chapter 6

Conclusions

The frequency dependent specific heat $c_p(\omega)$ reflects macroscopic energy fluctuations of a system, expressed through fluctuation dissipation theorems, specific for a given ensemble. The fluctuation dissipation theorems includes other thermodynamic response functions as well.

If external constraints like constant volume or energy is acting on a system, the macroscopic energy correlations cannot be separated into sums of local microscopic correlations, since global particle-particle correlations contributes significantly to the macroscopic response functions. $c_p(\omega)$ reflects only microscopic local correlations, but these include correlations between regions located close in space.

Because of the global correlations thermodynamic response functions are difficult to sample from computer simulations. By means of very long runs, the full response matrix of a 256 molecule binary Lennard Jones system was found. All response functions had a relaxational part, but the relaxation strength of the adiabatic compressibility was rather weak. Generally the susceptibilities was increasing with decreasing temperature.

The shape of the α-peak of $c_p(\omega)$ in the low temperature limit is well described by an energy master equation with a cut of in the density of states at the ground state, and a common absolute barrier energy for all states. The model shows time temperature scaling, which is in consistence with experiments of $c_p(\omega)$, provided that an interpretation of the high frequency tail of $c_p(\omega)$ as associated with JG-β relaxation, is adopted.

The interpretation of microscopic energy master equation models in terms of macroscopic specific heat, relies on an assumption of essentially non-interacting regions, which can only really be true if there is some physical separation of such entities, i.e. an inhomogeneous liquid at microscopic level, or if the regions are so large that their interaction may be ignored. The last possibility seems to be in contradiction with an almost constant DOS near the ground level, which implies a very small region size. But if the assumption of non-interacting regions is taken literary, one is led to the conclusion, that transition state dynamics implies constant DOS with a low energy cutoff.

Since there are other energy controlled models, with more poor physical foundation, which also reproduce $c_p(\omega)$, it can not be out ruled, that the striking agreement between the quasi-universal $c(\omega)$ and measurements of $c_p(\omega)$, may be coincidental.

MD simulations of supercooled SPC/E water shows that the bond correlation function $c(t)$ is quite independent on the bond definition, and have the same qualitative behaviour as the intermediate scattering function. $c(t)$ are connected to the glassy behavior of SPC/E, and $c(t)$ shows time temperature scaling at long times. The shape of $c(t)$ at long times can be rationalized by a simple zero-parameter modified diffusion model.

On the other hand the bond lifetime distribution depends on the bond definition. The glassy behavior of SPC/E is not reflected in the mean bond lifetime, which continues to grow as an Arrhenius law deep in the supercooled regime.

Chapter 7

Publications

7.1 PUBLICATION I

Chapter 7

Publications

7.1 PUBLICATION I

ELSEVIER

Journal of Non-Crystalline Solids 235–237 (1998) 346–348

JOURNAL OF NON-CRYSTALLINE SOLIDS

Frequency dependent thermodynamic response functions from computer simulations

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Abstract

Information about frequency dependent thermodynamic properties such as the isocoric specific heat, $\tilde{c}_V(\omega)$, or the isobaric thermal expansion coefficient, $\tilde{\alpha}_P(\omega)$, is important for understanding the dynamics of supercooled liquids. A special fluctuation–dissipation (FD) theorem is developed. It establishes the connection between equilibrium fluctuations in a microcanonical ensemble and response functions of macroscopic entities upon perturbation of energy or volume. Using this theory, information of all thermodynamic response functions can be calculated from one molecular dynamics simulation. © 1998 Elsevier Science B.V. All rights reserved.

7.2 PUBLICATION II

7.2 PUBLICATION II

Linear Response Theory for Thermodynamic Properties

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(September 24, 1998; lr9.tex)

Abstract

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.

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I. INTRODUCTION

Properties like specific heat, thermal expansivity and compressibility become dynamic in systems with slow internal relaxation processes. If, for instance, an instant volume increase δV 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 experiments 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 it 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 δT_0 at time zero. The time dependent isocoric 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 $\langle\cdot\rangle_{T,P}$ means averaging over the isothermal-isobaric ensemble, and $\Delta H(t) = H(t) - \langle H\rangle_{T,P}$. k_B is Boltzmanns constant, which in the rest of this paper is put equal to 1.

In this article the focus is on the connection between on 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 reflects 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]. But 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 can not 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 δQ_0 is imposed by applying a voltage 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 q_i are the charges, $\mathsf{E} = -\frac{d}{dx}\mathsf{V}$ the electric field and x_i particle i's position in the x-direction. But the heat perturbation δQ_0, is quadratic in the perturbing field, instead of linear, thus the temperature response which is linear in δQ_0 will also be quadratic in E. Besides 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 are only including 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,

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

where the kinetic energy and the virial is

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

v_{ij} and r_{ij} are the pair potential and the pair distance respectably. 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 H. H. Rugh [27]. It is shown that several choices of dynamic variables are possible, each on average equaling the microcanonic temperature $\frac{1}{T} = \frac{\partial S}{\partial E}$, 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, or as a "thermometer" if one 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 $\delta Q(\omega, t) = \delta Q_0 e^{\imath\omega t}$, 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 δQ_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

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

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 on 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 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 on how one actually heat the system up.

1. Heat perturbation

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

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

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

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

Of course this choice gives rise to an instant overshoot of the temperature $\delta T_0 = \frac{2\delta Q}{3N-n}$. However, the heat is immediately transfered into the configurational degrees of freedom, and within a few vibration times, the heat δQ 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 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 example the system is evolving in a cubic cell under periodic boundary conditions, then H_V can be constructed by inserting a modified position vector $d_{V(L)}(r) = \{L \cdot \mathrm{mod}(\mathbf{r}_i/L)\}$ 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,

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

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

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

one observes that

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

to first order in δ. 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 Γ, 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/volume response functions. As the volume is the actual control parameter, the quantities δ and ε is better expressed in terms of δV,

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

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 iso-energetic 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 previous section, perturbations are constructed so that δE does not depend on the initial state Γ, 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 non-uniform distribution on the energy surface $H_{V+\delta V}(\Gamma') = E + \delta E$. The Jacobian $\left|\frac{\partial(\Gamma' - \delta\Gamma(\Gamma'))}{\partial \Gamma'}\right|$ ensures proper normalization of f_0. It compensates for the immediate phase space expansion following the disturbance. Note that the determinant depends on Γ'. $f_0(\Gamma')$ 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:

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

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 like

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

where $L = -\imath\{H, \cdot\}$ 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 $\delta B_0 = \left\langle \frac{\partial B}{\partial\Gamma}\delta\Gamma \right\rangle_{E,V}$, plus a time dependent decay $(B(t) - B(0))$, 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

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

Expansion of $\frac{1}{\Omega_{E+\delta E, V+\delta V}}$ in δE and δV 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 $\frac{1}{\Omega_{E,V}}$ in Eq. (26) one gets,

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

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 $(\frac{\partial \ln \Omega_{E,V}}{\partial E} \delta E + \frac{\partial \ln \Omega_{E,V}}{\partial V} \delta V)$ 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. $\langle \cdot \rangle_{E+\delta E, V+\delta V}$ 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 $\langle\cdot\rangle$ is used for $\langle\cdot\rangle_{E,V}$.

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

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

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 Eq. (7) and Eq. (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. Eq. (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 ε and δ 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

$$\begin{aligned} G_{BV}|_E(\omega) = \left.\frac{\delta B_0}{\delta V}\right|_E &+ \frac{3N}{V(3N-n)}\left\{\left\langle \Delta\frac{W}{T}\Delta B\right\rangle\right. \\ &\left.-\imath\omega\int_0^\infty dte^{-\imath\omega t}\left\langle \Delta\frac{W}{T}(0)\Delta B(t)\right\rangle\right\}. \end{aligned} \tag{39}$$

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

$$\begin{aligned} \left.\frac{\delta P}{\delta V}\right|_E &= \langle \delta P(\delta\Gamma)\rangle \\ &= \frac{-1}{V}\left\langle \frac{2K}{3} + \frac{1}{9V}\sum_{\imath\neq\jmath}\frac{\partial^2 v(r_{\imath\jmath})}{\partial r_{\imath\jmath}^2}r_{\imath\jmath}^2\right\rangle . \end{aligned} \tag{40}$$

D. Laboratory response functions

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

$$\begin{pmatrix} \delta T \\ \delta P \end{pmatrix} = \begin{pmatrix} G_{TE}|_V & G_{TV}|_E \\ G_{PE}|_V & G_{PV}|_E \end{pmatrix}(\omega)\begin{pmatrix} \delta E \\ \delta V \end{pmatrix}. \tag{41}$$

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 δV 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 like

$$\begin{aligned} G_{BV}|_Q(\omega) &= (G_{BV}|_E(\omega) - \langle P\rangle G_{BE}|_V(\omega)) \\ &= \left.\frac{\delta B_0}{\delta V}\right|_E - \langle P\rangle \left.\frac{\delta B_0}{\delta E}\right|_V + \\ &\quad \frac{1}{V}\frac{3N}{3N-n}\left\{\left\langle \Delta\frac{W-\langle P\rangle V}{T}\Delta B\right\rangle\right. \\ &\quad \left. -i\omega\int_0^\infty dt\; e^{-\imath\omega t}\left\langle \Delta\frac{W-\langle P\rangle V}{T}(0)\Delta B(t)\right\rangle\right\}. \end{aligned} \tag{42}$$

In large systems

$$\begin{aligned} G_{BV}|_Q(t) = \left.\frac{\delta B_0}{\delta V}\right|_E - \langle P\rangle \left.\frac{\delta B_0}{\delta E}\right|_V + \frac{1}{\langle T\rangle}\{\langle \Delta P\Delta P\rangle \\ -\imath\omega\int_0^\infty dt\; e^{-\imath\omega t}\langle\Delta P(0)\Delta P(t)\rangle\}. \end{aligned} \tag{43}$$

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

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

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

$$\begin{aligned} \tilde{G}_{Tq}|_v(\omega) &= \tilde{c}_v(\omega)^{-1} = \frac{2}{3} + N\left\{\left\langle\Delta\frac{1}{T}\Delta T\right\rangle\right. \\ &\qquad \left. -i\omega\int_0^\infty dte^{-\imath\omega t}\left\langle\Delta\frac{1}{T}(0)\Delta T(t)\right\rangle\right\} \\ \tilde{G}_{Tv}|_q(\omega) &= -T\tilde{G}_{Pq}|_v(\omega) \\ \tilde{G}_{Pq}|_v(\omega) &= \frac{2}{3}\rho + N\left\{\left\langle\Delta\frac{1}{T}\Delta P\right\rangle\right. \end{aligned} \tag{45}$$

$$-i\omega\int_0^\infty dt\, e^{-\imath\omega t}\left\langle\Delta\frac{1}{T}(0)\Delta P(t)\right\rangle\Bigg\} \tag{46}$$

$$\tilde{G}_{Pv}|_q(\omega) = \rho\left\{\frac{\langle W\rangle}{V} - \frac{5}{3}\langle P\rangle - \frac{1}{9V}\left\langle\sum_{\imath\neq\jmath}\frac{\partial^2 v_{\imath\jmath}}{\partial r_{\imath\jmath}^2}r_{\imath\jmath}^2\right\rangle\right\}$$

$$+\frac{N}{\langle T\rangle}\left\{\langle\Delta P\Delta P\rangle - i\omega\int_0^\infty dte^{-\imath\omega t}\langle\Delta P(0)\Delta P(t)\rangle\right\}. \tag{47}$$

This constitutes the FD-theorem for thermodynamic response functions. Eq. (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),

$$\begin{pmatrix}\delta\tilde{q}\\ \delta\tilde{v}\end{pmatrix} = \begin{pmatrix}\tilde{c}_P(\omega) & -T\tilde{\alpha}_P(\omega)\\ \tilde{\alpha}_P(\omega) & -\tilde{\kappa}_T(\omega)\end{pmatrix}\begin{pmatrix}\delta\tilde{T}\\ \delta\tilde{P}\end{pmatrix}$$

$$= \frac{1}{\tilde{D}(\omega)}\begin{pmatrix}\tilde{G}_{Pv}|_q(\omega) & -\tilde{G}_{Tv}|_q(\omega)\\ -\tilde{G}_{Pq}|_v(\omega) & \tilde{G}_{Tq}|_v(\omega)\end{pmatrix}\begin{pmatrix}\delta\tilde{T}\\ \delta\tilde{P}\end{pmatrix}, \tag{48}$$

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

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 is 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 $\delta V(t) = \Re\{V_0 e^{\imath\omega t}\}$ is forced on the system, the work done on the system during one cycle is given by the integral

$$\delta E = \int_0^{T_{\text{cycle}}} -P(t)\dot{V}dt = \int_0^{T_{\text{cycle}}} -(P_0 + \delta P(t))\dot{V}dt$$

$$
\begin{aligned}
&= \int_0^{T_{\text{cycle}}} -(P_0 + \Re\{\delta V_0 \tilde{G}_{Pv}|_q(\omega) e^{\imath\omega t}\})\Re\{i\omega\delta V_0 e^{\imath\omega t}\} \\
&= \frac{\delta V_0^2 \pi}{N} \Im\{\tilde{G}_{Pv}|_q(\omega)\} = \frac{\delta V_0^2 \pi}{N} \Im\{\frac{1}{\tilde{\kappa}_S(\omega)}\}
\end{aligned}
\tag{49}
$$

Since $\Im\{\tilde{G}_{Pv}|_q(\omega)\}$ is non-negative this means that if there is an imaginary part of $G_{Pv}|_q$ 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 $\delta Q(t) = \Re\{\delta Q_0 e^{-\imath\omega t}\}$ 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 does not depend on the choice of heat perturbation, as well as the linear response does not. However the entropy increase resulting from a perturbation of the sort specified in Eq. (10) and Eq. (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 $S[f] = -\int drdpf(r,p)\ln h^{3N} f(r,p)$, where h is some constant with 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

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

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

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

as it should 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_{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 δQ 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 integrate to 0. Since $\delta T(t) = \Re\{\frac{\delta Q_0}{(N\tilde{c}_v(\omega))} e^{\imath\omega t}\}$, the entropy flow into the system to second order in δQ_0, is found to

$$\delta S_{\text{cycle}} = -\pi \frac{\delta Q_0^2}{N T_0^2} \Im\{\frac{1}{\tilde{c}_v(\omega)}\}. \tag{55}$$

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 α and β 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 σ_{AA}, energy in dimensionless units of ϵ_{AA} and time is given in dimensionless Lennard-Jones Units (LJU). 1 LJU $= (m\sigma_{AA}^2/\epsilon_{AA})^{1/2}$. A characteristic vibration time is around 1/10 LJU. 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 $P = 2.43, 3.20, 4.40, 5.61 \pm 0.02$ respectively. 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 4 different samples with 256 particles in each were prepared by first quenching a random configuration, then equilibrating with a Nose Hoover thermostat [31], and there upon tuning the energy to make sure that all 4 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 LJU in the cases $T = 0.614, 0.711$, 4000 LJU in the case $T = 0.527$ and 8000 LJU 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 $\sum \frac{\partial^2 v_{ij}}{\partial r_{ij}^2} r_{ij}^2$ was sampled during runs at 1.6×10^5 LJU (4×10^7 time steps) for $T = 0.464$, 8×10^4 LJU for $T = 0.527$ and 8×10^3 LJU 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 5 samples of 800 particles each, and the same density as above were prepared at $T = 0.527$, and runned for 4×10^4 LJU to check for finite size effects.

B. Simulation Results

In Fig. 2 the time correlation function $-N\left\langle \frac{1}{T}(0)T(t)\right\rangle$ 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 fitting formula. Relaxation times grows in a non Arrhenius way [34], common to supercooled liquids, as shown in the inset of Fig. 2. The β-exponents change from approximately 1 at $T = 0.711$ down to 0.7 at $T = 0.464$.

β measures the sharpness of the relaxation time distribution. Lower values of β correspond to broader spectra. In laboratory measurements on organic liquids [2–5,16,35] the specific heat spectres have in general been found to be broader, with β lying in the range from 0.4-0.65. However, these measurements were done much closer to the glass transition temperature T_G, and for molecular liquids. In general β for other sorts of 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].

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 were 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 systematic larger by 3% percent 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.

The 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 (α)decay is moving approximately 2 decades down, as the temperature is lowered. In general the configurational part (or relaxation strength) is increasing with decreasing temperature, but while $\tilde{c}_P$ and $\tilde{\alpha}_P$ have relatively high configurational part, $\frac{c'_P(0)-c'_P(\infty)}{c'_P(\infty)} \approx 0.4-0.6$, $\frac{\alpha'_P(0)-\alpha'_P(\infty)}{\alpha'_P(\infty)} \approx 0.5-0.8$, the same property calculated for $\tilde{\kappa}_T$ is somewhat lower, $\frac{\kappa'_T(0)-\kappa'_T(\infty)}{\kappa'_T(\infty)} \approx 0.15 - 0.3$.

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 the figures 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 shape of the relaxational parts of the response functions $\frac{c'(\omega)-c'(\infty)}{c'(0)-c'(\infty)}$ is very much alike each other, but $\tilde{c}_P(\infty)$ is 20 % bigger than $\tilde{c}_v(\infty)$, and the relaxation strength 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 relaxation strength of the configurational part of $\tilde{\kappa}_s(\omega)$ is only between 3 and 5%.

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. Besides 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. Secondly 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.

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 like 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 a much bigger statistical material to perform the averaging on, 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 ad these parts up to give better statistics. This is simply because the kinetic energies of two particles in a system with constant energy are in general anti-correlated even if the particles are very far from each other. This anti-correlation contributes significantly to the correlation function. In fact it reflects the nature of a systems response under iso-energetic/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 more simple 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 methods 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 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 additional term in the Hamiltonian, as in usual response theory. It is introduced as an 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 section II A). This is justified with analogy to laboratory experiments where one does not expect the actual choice of heating aggregate to influence on the specific heat of the system. *iii)* The derivation of the FD-theorem is done under strictly iso-energetic 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 the equations (44)-(47), connects all thermodynamic response functions to equilibrium fluctuations of the isocoric/iso-energetic ensemble. The dissipation has to be be considered carefully when dealing with heat flow as a control parameter. It was demonstrated in section 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].

V. ACKNOWLEDGMENTS

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bility is evaluated from unperturbed (autonomous), Hamiltonian or general stochastic dynamics, thus avoiding the assumption of microscopic linearity.

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FIGURES

NIELSEN FIG. 1

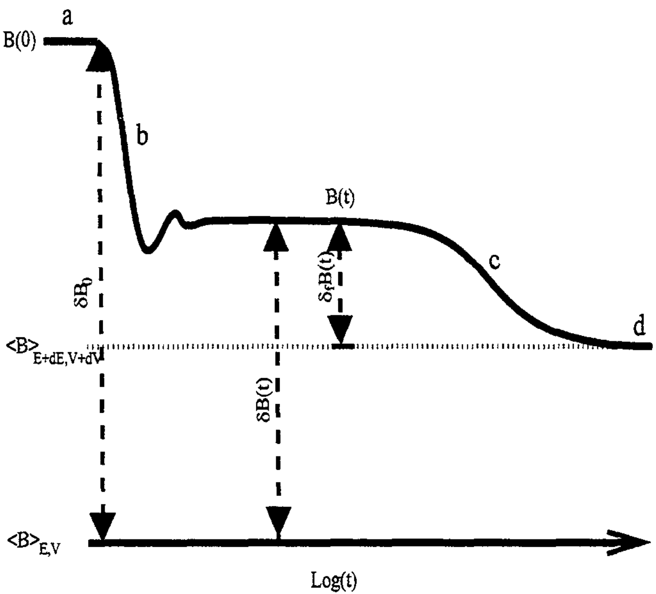

FIG. 1. Schematic illustration of a response experiment. The instant response δB_0 (a) is followed by a fast decay (b) to a state where the fast degrees of freedom are equilibrated. The slow decay (c) follows, and the system finally reaches equilibrium under the new constraint $(E+\delta E, V+\delta V)$ (d). It doesn't 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

NIELSEN FIG. 2

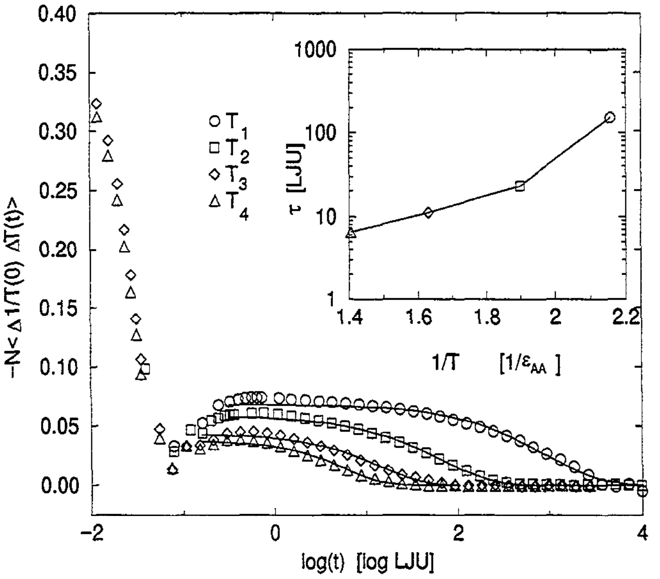

FIG. 2. The correlation functions $\left\langle -N\Delta\frac{1}{T}(0)\Delta T(t)\right\rangle$ for four different mean temperatures, on a logarithmic time axis. Each correlation function is based on 8 different runs with 10^6 sample points each. No smoothing has been employed. The data points has been logarithmic 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 τ.

NIELSEN FIG. 3

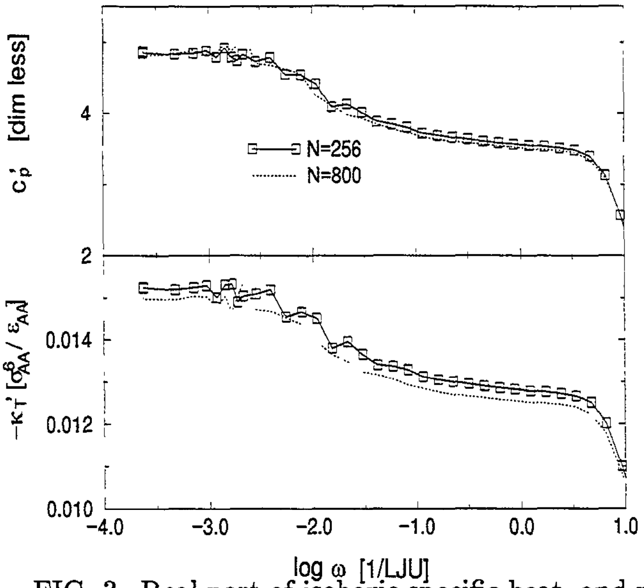

FIG. 3. Real part of isobaric specific heat, and negative real part of isothermal compressibility at $T_2 = 0.527$, for two different sample sizes. The samples were prepared so that the total energy per particle is the same in each case. The temperature appeared to be the same within an insignificant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

NIELSEN FIG. 4

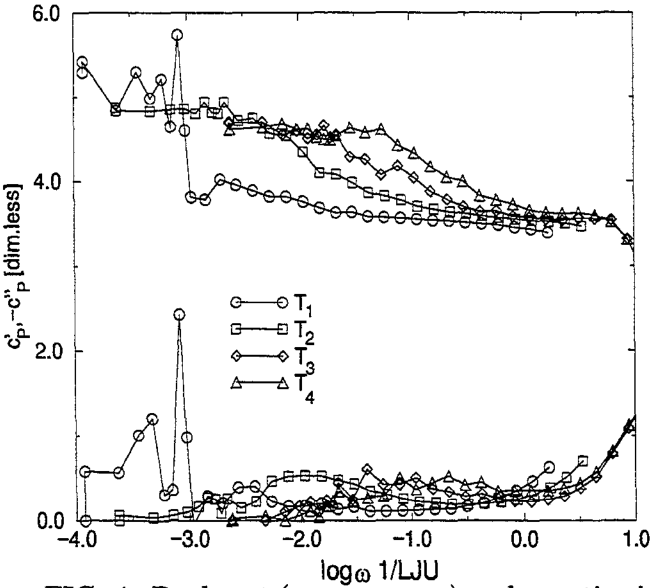

FIG. 4. Real part (upper curves) and negative imaginary part (lower curves) of isobaric specific heat per particle. The four temperatures are the same as in figure (2). Logarithmic averaged data.

NIELSEN FIG. 5

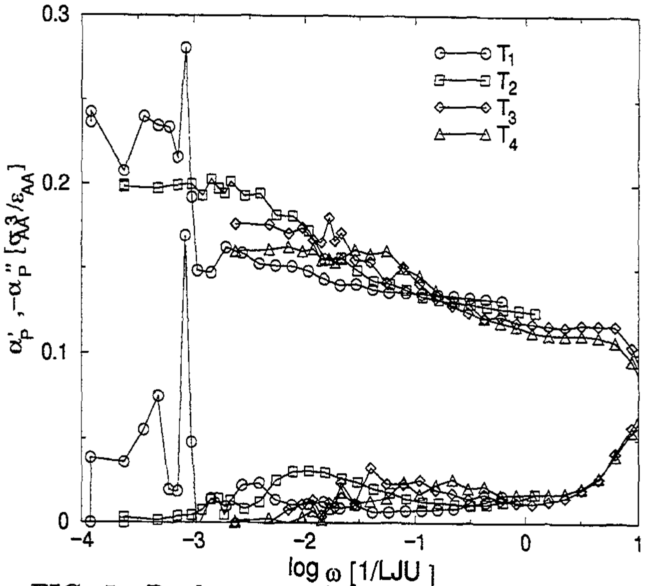

FIG. 5. Real part and negative imaginary part of isobaric expansivity per particle. Same temperatures as in figure (2). Logarithmic averaged data.

NIELSEN FIG. 6

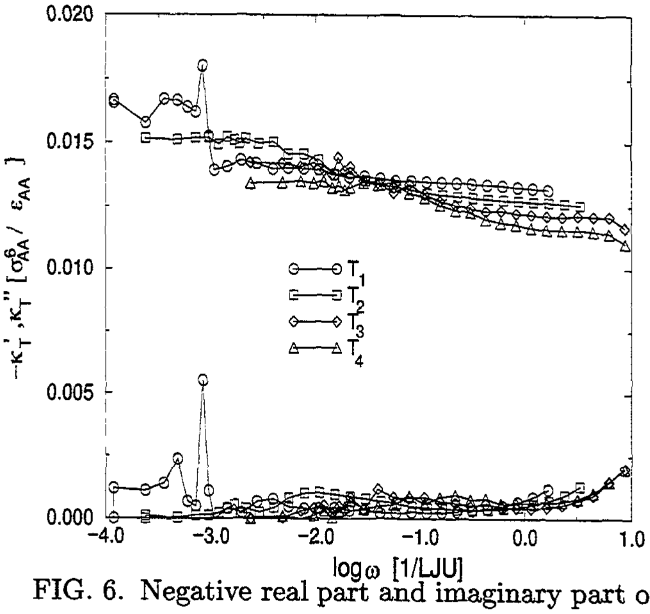

FIG. 6. Negative real part and imaginary part of isothermal compressibility per particle. Temperatures are the same as figure (2). Logarithmic averaged data.

NIELSEN FIG. 7

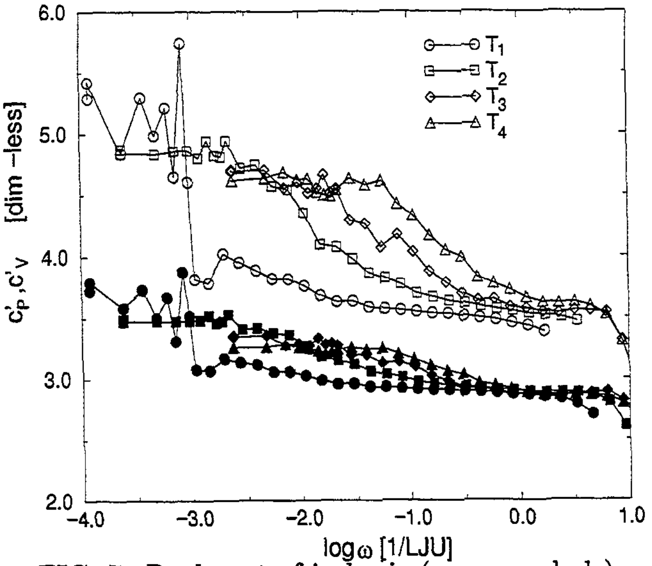

FIG. 7. Real part of isobaric (open symbols) and isocoric (filled symbols) specific heat. Same temperatures as in figure (2).

NIELSEN FIG. 8

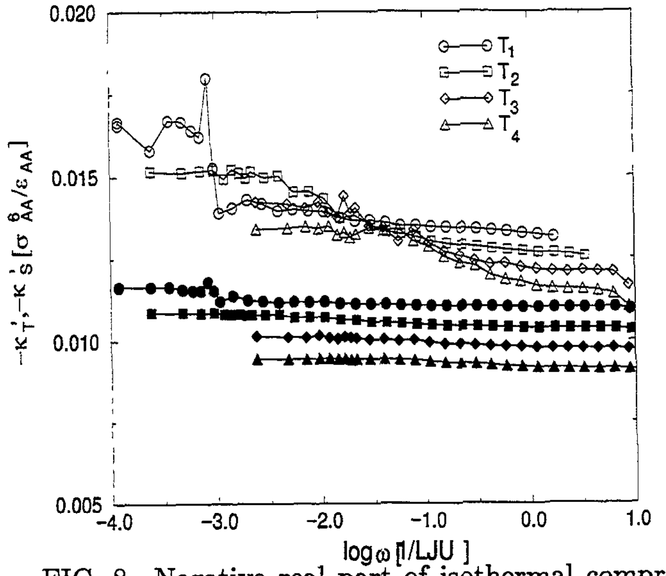

FIG. 8. Negative real part of isothermal compressibility (open symbols) and adiabatic compressibility (filled symbols). Temperatures as in figure 2.

7.3 PUBLICATION III

7.3 PUBLICATION III

MASTER EQUATION MODELS OF THE GLASS TRANSITION.

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ABSTRACT

A generalization of the Energy Master Equation (EME) dealing with both the internal configurational region energy and the region *volume* as stochastic variables is investigated. The frequency-dependent linear response functions can be calculated without approximations for this model, as for any separable master equation model.

7.4 PUBLICATION IV

7.4 PUBLICATION IV

PHYSICAL REVIEW B VOLUME 54, NUMBER 22 1 DECEMBER 1996-II

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. [S0163-1829(96)06446-6]

7.5 PUBLICATION V

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Fast and slow dynamics of hydrogen bonds in liquid water

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Abstract

We study hydrogen-bond dynamics in liquid water at low temperatures using molecular dynamics simulations. We find that bond lifetime ("fast dynamics") has Arrhenius temperature dependence. We also calculate the bond correlation function and find that the correlation time ("slow dynamics") shows power-law behavior. This power-law behavior, as well as the decay of the bond correlations, is consistent with the predictions of the mode-coupling theory. The correlation time at the lowest temperature studied shows deviation from power-law behavior that suggests continuity of dynamic functions between the liquid and glassy states of water at low pressure.

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