

Does temperature fluctuate? The fluctuation-dissipation theorem considered as an equation describing quantum mechanical experiments, and application to the dynamic glass transition

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2000 J. Phys.: Condens. Matter 12 10371

(<http://iopscience.iop.org/0953-8984/12/50/302>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 08:13

Please note that [terms and conditions apply](#).

Does temperature fluctuate? The fluctuation-dissipation theorem considered as an equation describing quantum mechanical experiments, and application to the dynamic glass transition

E Donth

Fachbereich Physik, Universität Halle, D-06099 Halle (Saale), Germany

Received 19 April 2000

Abstract. In an earlier Letter to the Editor (Donth E, Hempel E and Schick C 2000 *J. Phys.: Condens. Matter* **12** L281) it was shown that the characteristic length of the dynamic glass transition in confined geometries favours the von Laue approach to thermodynamics over the Gibbs approach. In the present paper the two approaches are compared as regards their ability to describe temperature fluctuations and statistically independent nanometre subsystems representative for linear response of the whole sample. It is discussed why the dynamic glass transition can reflect properties of a quantum mechanical (qm) experiment (measurement process). The fluctuation-dissipation theorem (FDT) is interpreted as an equation describing a stationary succession of such experiments. The thermodynamics constructed from such an FDT is consistent with the second law: this law is inherent and the time arrow follows merely from the properties of the qm experiments.

1. Introduction

The glass transition belongs to the most important [1] group of physical problems for which no solution has been obtained in spite of intensive and expensive research over the last forty years—exploding since 1990 [2–4]. The problem is that of achieving an understanding of a *general* dynamic picture of traces in the Arrhenius plot with a clear architecture (figure 1), for a wide class of glass formers with *multifarious* molecular and liquid structures, not expected to be accessible to general theoretical methods.

I think it should therefore be permissible to question whether the theoretical methods available today are sufficient for clarifying this question or not. In particular, two observations are striking:

- (1) The compressibility paradox of the Fischer modes ϕ : for $Q \approx 2\pi/(100 \text{ nm})$, the structure factor $S(Q)$ is much larger than expected from the compressibility (κ_T) equation, $S(Q) \gg \bar{n}k_B T \kappa_T$ [5].
- (2) The size of the cooperativity for the α -process when calculated using the Gibbs distribution [6–8] is much too large for glass transitions in confined geometries, or for the crossover region [9] where the cooperativity is expected to become small [10].

In both cases the deviations are large, up to a factor of e.g. 50.

For the Fischer modes, thermodynamic explanations [5, 11] were announced. This contradicts the general feeling that the glass transition should have a dynamic explanation.

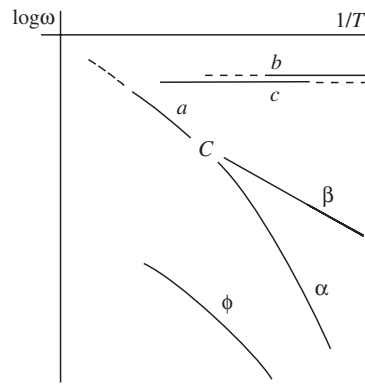


Figure 1. Traces of typical relaxation processes in an Arrhenius plot ($\log \omega$ is the mobility, $1/T$ the reciprocal temperature): a : the high-temperature Williams–Götze process; b : the boson peak; c : cage rattling; α : the cooperative process; β : the local mode Johari–Goldstein process; ϕ : the ultraslow-mode Fischer process.

A dynamic resolution of the compressibility paradox will be discussed elsewhere [12] that rests on the representativeness of the smallest statistically independent subsystems for the α -process: the cooperatively rearranging regions, CRRs [13]. A Levy-limit distribution with preponderant components (Levy exponent $\alpha < 1$) in an ensemble of many CRRs must be confronted with phenomenological requirements that are decisive regarding the experimental verification of Fischer modes [5].

For the confined geometries and the crossover region, an alternative evaluation with fluctuating temperatures—excluded in this length scale by the Gibbs distribution—gives consistent cooperativities [9]. This finding is also related to the definition and properties of representative subsystems and to the question of what is measured for subsystems. The existence of temperature fluctuation, however, leads [9] to the general problem of whether statistical mechanics must be derived from a more general thermodynamics, or the reverse.

To call into question the ability of present methods encourages one to look for gaps in present theoretical concepts. In the above series [1], understanding of quantum mechanical (qm) experiments (the measurement process) was also listed. I think we should seriously ask whether the ‘generation’ of thermodynamic variables, especially linear response correlations, from molecular situations is relevant to such experiments [14].

The bald statement that the collapse of a macroscopic CRR wave function $\psi(p, q)$ from the phase space $\{p, q\}$ onto thermodynamic variables in the Euclidean space \mathbb{R}^3 is the same as the mapping of the mechanical situation $H(p, q)$ of the phase space onto those variables, $\{p, q\} \mapsto \mathbb{R}^3$, seems too simple. The problem of qm experiments is largely repressed by many physicists for two reasons:

- (i) The formerly mysterious quantum jumps with $\Delta E_{fi} = \hbar\omega_{fi}$ could be built into quantum dynamics, e.g. in Fermi’s golden rule and later developments up to Feynman’s path integrals.
- (ii) The construction of a highly accurate and consistent quantum mechanics for solid-state physics, the verification of quantum electrodynamics up to ten decimals, and the consistency of the standard model for elementary particles up to four decimals seem not to leave gaps for unknown theoretical concepts.

Moreover, by way of compensation, the steadily repeated verification of qm by an enduring series of more and more refined experiments prompted by Bell’s artificial inequality concerning

there being no local hidden variables confirmed the assertion that a theory for qm experiments is really a philosophical problem. The problem e.g. of the twenty adjustable parameters in the standard model tends to be (perhaps unnecessarily) relegated as a problem for a new physics beyond the standard model rather than for qm experiments.

In terms of Bohr's first view on complementarity [15], we do not know which qm object (the hidden non-local world) is mapped onto our physical reality by the qm experiment. Here, we use only some commonly accepted aspects of the 'how', not the 'what', of the mapping. (Schrödinger conjectured as regards the 'what' [16] that the hidden world is made from eigensolutions of Maxwell's equation on a 'large' four-dimensional $S^1 \times S^3$ manifold. The particles may be an experimental reduction (collapse) of such non-local eigensolutions to points in the Minkowski space [17]. Lepton, baryon, and even quark [18] solutions can be obtained in such a model [19].)

Many statistical physicists concerned with liquids do not discuss CRRs. They obviously think that a good definition of CRRs and their size, if any, will be obtained *en passant* from computer simulations of the $\{p, q\} \mapsto \mathbb{R}^3$ map mentioned above.

The discussion of qm experiments has extremely sharp limits. I think that qm experiments have been from the beginning an inherent part of qm: any consequence for the predictability of qm must be excluded, especially for all situations where the accuracy of the qm is as high as mentioned above. This excludes all attempts to explain the qm experiments by qm (quantum mechanics) itself. Defining a Hamiltonian or Lagrangian for the experiment seems to constitute circular reasoning. Note the two variants—one beyond the fundamental scope and the other beyond the practical scope—used to justify the lack of reporting of qm experiments [20].

On the one hand, a fundamental way out is indicated by Bohr's complementarity [15]: before the experiment we have only the qm object with no space \mathbb{R}^3 and no time t ; after the experiment we have the result in \mathbb{R}^3 and t with no qm uncertainty. From this point of view the phase space $\{p, q\}$ with the Hamiltonian $H(p, q)$ is in principle a back-construction from the experimental results and not *a priori* a qm object. It is therefore, in principle, not a necessary consequence of qm that the Gibbs distribution based on a $\{p, q\}$ Hamiltonian and the application of the phenomenological zeroth law reflects exactly what is measured in a qm experiment as regards thermodynamic variables and linear response correlations. Details about the relationship between the qm object, the results (reality), and the virtuality of qm as obtained by the back-construction will be described elsewhere [19].

On the other hand, a practical and simpler way out is based merely on the assertion that the qm experiment is an inherent part of qm. We are then interested in 'phenomenological' properties of qm experiments as providing a method for approaching specific situations, especially thermodynamic situations. In other words, as mentioned above, we consider the qm experiment as part of qm that can be phenomenologically described in terms commonly used in this context [21].

I assume therefore that the statistical independence needed for the definition of CRRs is a part of a thermodynamic situation that can be directly reflected and displayed by phenomenological properties of the qm experiment for the α -relaxation of the dynamic glass transition. The experiment establishes the CRRs as representative subsystems for the α -relaxation. Both striking observations (1) and (2) can be explained by the representativeness. The Fischer modes will be investigated in [12]. The issue of fluctuating temperature will be discussed in this paper.

The Gibbs distribution does not refer to any definite subsystem. It starts from energy eigenvalues calculated using qm for a mechanically defined system with boundaries; e.g. for a series of given volumes V : $E_n(V)$. Its temperature T in $\exp(-H(p, q)/k_B T)$ is transferred from a large and given heat bath by means of the zeroth law and, being an

equivalence class index, cannot fluctuate if the heat bath temperature does not depend on V . The alternative von Laue approach to thermodynamics [22–24], however, refers to freely fluctuating, independent subsystems (figure 2) in a large homogeneous sample. The temperature can fluctuate. The sizes of fluctuations are determined by the sizes of these subsystems. Divide, as a *gedanken* experiment for representativeness, the sample into parts and look for changes in the linear response: obviously there exists a smallest one whose equilibrium-fluctuation correlation functions and spectral densities are representative for linear response of the whole sample. The representative subsystems are functional for the dispersion zone of a given trace (α, ϕ, \dots) in figure 1. The smallest one for the α -relaxation is the CRR.

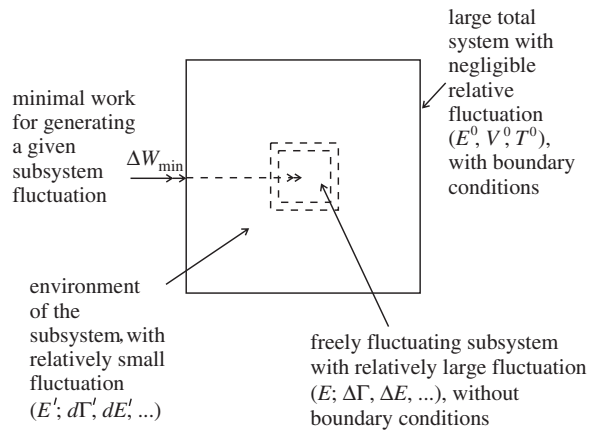


Figure 2. The freely fluctuating subsystem, environment, total system, and minimal work.

The *gedanken* experiment for representative subsystems only has meaning for liquids and disordered aspects of solids. The discrete translation invariance of a lattice would not allow the separation of a small subsystem from the large lattice. The unit cell of the lattice is not a representative subsystem in the sense of our construction.

The freely fluctuating subsystems of the von Laue approach are suited well to the system aspect of a qm experiment generating the observables of linear response. The aim of this paper is to show that the fluctuation-dissipation theorem containing temperature fluctuations can be interpreted as an equation describing qm experiments in thermodynamic situations.

The paper is organized as follows. Section 2 briefly describes the determination of cooperativity for the α -relaxation and discusses the question of why just the glass transition may be sensitive to the properties of qm experiments. Section 3 contains a short discussion of differences and relations between the Gibbs and the von Laue approaches to thermodynamic fluctuations. Section 4 provides the derivation of the FDT from the general properties of qm experiments. Section 5 shows that the thermodynamics derived from such an FDT is consistent with the second law. In the discussion (section 6) a further experimental test is suggested for providing the basis for a decision between the alternatives for thermodynamic fluctuations, and some developments in the literature are briefly commented on. Section 7 gives the conclusions; briefly: thermodynamics with temperature fluctuation is the wider concept as compared with the present statistical physics, and there is a theoretical foundation of such thermodynamics provided by general properties of qm experiments.

2. Why is the dynamic glass transition sensitive to qm experiments?

In the earlier Letter to the Editor [9], the alternatives for determining the cooperativity N_α (characteristic length ξ_α) were discussed. The result was that the formula [25] with temperature

fluctuation of CRRs (δT), stemming from the von Laue approach,

$$\xi_\alpha^3 = k_B T^2 \Delta(1/c_V)/\rho \delta T^2 \quad (2.1)$$

was the favoured one. This corresponds to a cooperativity

$$N_\alpha = RT^2 \Delta(1/c_V)/M_0 \delta T^2 \quad (2.2)$$

which is the number of particles (molecular mass M_0) in a CRR.

The cooperativity tends to $N_\alpha \approx 1$ (and $\xi_\alpha \approx 0.5$ nm) near the crossover region C of figure 1. Since in dense liquids each given particle has strong energetic interaction with at least the nearest neighbours, $N \approx 10$ or more, and since N_α was determined from the spatial statistical independence of temporal Fourier components in the α -process dispersion zone, our problem is that of the statistical independence of small functional subsystems with strong energetic interaction and correlation up to ranges with typical lengths larger than ξ_α . A similar problem was discussed by Fuchs within mode-coupling theory [26].

Let us discuss this question within the Nyquist approach to the FDT [27]; see figure 3. The transfer medium for measurements is a ‘cloud of quanta’ [28] in the adapted transmission lines (TL) between emitter E (the qm object) and the absorber A (the apparatus). The frequencies of these quanta reflect a fluctuating mobility field, $\log \omega(\mathbf{r}, t)$, introduced [29, 30] for the description of the dynamic heterogeneity of the α -process. The problem of statistical independence is thus relegated to that of the events of this field, called ‘attempts’. This ‘mesoscopic’ $\log \omega(\mathbf{r}, t)$ field seems very suitable for explanation of the generality-multifariousness problem mentioned in the first paragraph of section 1.

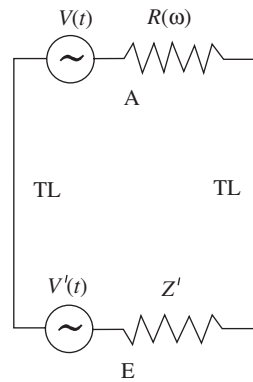


Figure 3. Nyquist's scheme for his derivation of the FDT. E: the emitter; A: the absorber; TL: the transmission lines.

The first question is then that of whether the density of attempts in each representative functional subsystem (cage c , Johari–Goldstein β , α -process, Fischer modes ϕ) is large enough to define the smallest statistically independent subsystems. To decide on this we use the diffusivities of a typical isothermal section of the Arrhenius plot in figure 1 (table 1). Both the ‘velocities’ and the ‘diffusivities’ are well ordered over many orders of magnitude, so a large temporal and spatial density of attempts is always guaranteed to provide a probability theory of events in the spectral density for every subsequent process (e.g. c for β , c and β for α , α for ϕ).

Mechanics has to do with particles and fields, whereas thermodynamics has to do with subsystems and environments. It seems that conventional qm is not well suited to finding small functional subsystems (related to β - or α - or ϕ -processes) that are statistically independent

Table 1. Typical molecular ‘velocities’ and ‘diffusivities’ as estimated from length scales and timescales for the different relaxation processes.

Process	Time (s)	Length (nm)	Velocity (m s ⁻¹)	Diffusivity (m ² s ⁻¹)
Cage c	1×10^{-12}	0.1	1×10^2	1×10^{-8}
Johari–Goldstein β	1×10^{-6}	0.5	5×10^{-4}	2.5×10^{-13}
α -process	1×10^{-1}	3	3×10^{-8}	9×10^{-17}
Fischer mode ϕ	1×10^6	100	1×10^{-13}	1×10^{-20}

and representative for these processes in the mobility field $\log \omega(\mathbf{r}, t)$. The qm experiments, however, seem well suited for this task because the concepts, the qm object and apparatus, can be adapted to our abstractly formulated mobility field for the dynamic glass transition of figure 1: its representative functional subsystems can be identified with both the qm object (with a ‘macroscopic’ wave function ψ) and the apparatus. This defines a succession of ‘self-experiments’ and I will show in section 4 that we actually get the phenomenological FDT as the equation describing this succession. Note that the representativeness *gedanken* experiment for the subsystem fluctuation indirectly induces a length scale, the characteristic length (e.g. ξ_α of equation (2.1) or ξ_ϕ [12]) in the linear response, depending otherwise only on the frequency ω . Note further that the term ‘phenomenological’ takes on a real meaning: measured by a succession of qm self-experiments.

First, in the next section (section 3), we shall compare the Gibbs and the von Laue approach to statistical physics as regards two questions: what about temperature fluctuation and what about subsystems suited for self-experiments?

3. Comparison of statistical mechanics without temperature fluctuation and thermodynamics with temperature fluctuation

All approaches to thermodynamics rest on the fundamental role of energy = heat + work. Defining the thermodynamic equilibrium as the same stationary state before and after isolation, i.e. undergoing no change over time, the role of energy results from the fundamental conjugation between conservation of energy and homogeneity of time (the Noether theorem). The conventional statistical mechanics starts from particles and fields and is, therefore, based on equations similar to

$$\dot{w} = (i/\hbar)(wH - Hw) \quad (3.1)$$

with w the statistical matrix and H the Hamiltonian (the Liouville equation).

The two variants under consideration are primarily distinct in the ways in which the energy is introduced.

3.1. The Gibbs treatment of statistical mechanics

Energy E comes here from *mechanics*. The actual degeneracy of eigenvalues in sets of many particles is counted by statistical weights $d\Gamma = \Delta\Gamma d\Gamma'$ in the probability distribution of the microcanonical ensemble:

$$dw = \text{constant} \times \delta(E + E' - E^0) \Delta\Gamma d\Gamma' \quad (3.2)$$

where E^0 is for the total system, $(E', d\Gamma')$ for the environment, and $(E, \Delta\Gamma)$ for the subsystem (figure 2). We use $\Delta\Gamma$ for the subsystem to indicate that $\Delta\Gamma$, or better $\Delta \ln \Delta\Gamma$, does not

need to be infinitesimally small in relation to the properties of the subsystem if the latter is small. Consider several statistically independent subsystems $w^{(1)}, w^{(2)}, w^{(3)}, \dots$. Then, from statistical independence, $w = w^{(1)}w^{(2)} \dots$, from the presumed additivity of their energies, $E = E^{(1)} + E^{(2)} + \dots$, and from the energy property of being a mechanical integral [23], we obtain

$$\log w_n = \alpha + \beta E_n \quad (3.3)$$

for the probability w_n of the n th state of any subsystem. *Thermodynamics* is introduced by the integral over the environment. The $S'(E')$ function for the environment entropy is a ‘sharp’ function of energy because of the infinitesimality of $d\Gamma'$ and of corresponding dE' . Forget temporarily the small subsystem and put for the system temperature $T^0 = T' = dE'/dS'$. The question is: what is the temperature of the subsystem?

Strictly speaking, the temperature of the subsystem is determined in the Gibbs approach by the zeroth law. The mutual equilibrium of any pair of systems (here the subsystem and environment) is an equivalence relation. This implies that any set of systems is partitioned into equivalence classes with the equivalence index T for equilibrating by heat exchange. Equilibrium means then $T = T'$ (sharp). Such a subsystem temperature cannot fluctuate:

$$\overline{\Delta T^2} = 0 \quad (3.4)$$

and the Gibbs distribution

$$w_n = A \exp(-E_n/k_B T) \quad (3.5)$$

is obtained from equation (3.3).

This procedure for finding T as described in [23] is based on the questionable assumption that there should exist, ‘by definition’, a sharp function $\Delta\Gamma(\bar{E})$, and therefore a sharp function $S \equiv k_B \ln \Delta\Gamma = S(\bar{E})$ for the subsystem, with \bar{E} the mean value of the subsystem energy. This assumption does not correspond to the ability to fluctuate of small subsystems far from the boundaries of the large total system: the freely fluctuating subsystems (figures 2 and 4). Formally, the ability to fluctuate is still expressed in the Dirac delta of the microcanonical distribution by $E = E^0 - E'$ being a small difference between huge numbers. The possibility of different paths across subsystem fluctuation regions (figure 4(a)) corresponds to different subsystem temperatures, i.e. to individual temperature fluctuations, $\delta T \neq 0$.

Let us restate this important issue in other words. The statistical weight $\Delta\Gamma$ is defined in [23] as ‘the number of quantum states corresponding to the interval ΔE ’, of the order of the mean energy fluctuation. The use of $\Delta\Gamma$ for the entropy $S = k_B \ln \Delta\Gamma$, however, is factual as always in science: $\Delta\Gamma$ is based on actual occupation numbers that do not define, as pure numbers from a distribution, any exact E -value *inside* the ΔE interval. Different E -values can be realized for given $\Delta\Gamma$ by different occupation distributions. As both $\Delta\Gamma$ and ΔE are stochastic functions of time, $\Delta\Gamma(t)$ and $\Delta E(t)$, the quotient $\Delta\Gamma(t)/\Delta E(t)$ is again a stochastic function, not a sharp value. (Mathematical example from p 133 of [31]: if $A(t)$ and $B(t)$ are symmetrically Gauss distributed, then the quotient $A(t)/B(t)$ is Cauchy distributed.) Thus both $\Delta\Gamma$ and ΔE are real fluctuations with no one-to-one dependence $\Delta\Gamma(\Delta E)$ inside the small system. Equation (7.4) from the textbook [23], $\Delta\Gamma = (d\Gamma(E)/dE) \Delta E$, is therefore not suitable for application to the fluctuation of subsystems if $\Delta\Gamma$ and ΔE are actual fluctuations. It was this equation that finally eliminated the temperature fluctuation from the Gibbs distribution.

Since pressure p and chemical potential μ are also equivalence class indices (for equilibration by work and by particle exchange, respectively), one could ask why the pressure fluctuation Δp^2 , e.g., can be calculated from the Gibbs distribution. This is possible because work can be externally parametrized, e.g. by the series of volumes for $E_n(V)$ as mentioned

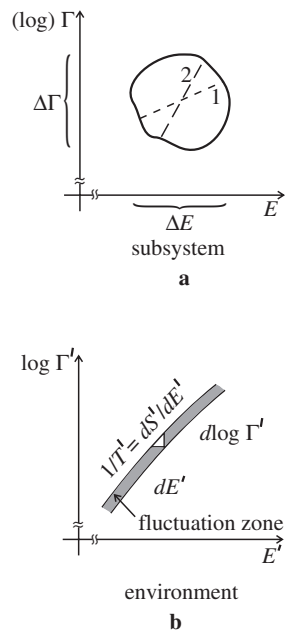


Figure 4. The handling of state and energy fluctuations ($\Delta \Gamma$, ΔE) in the derivation of the Gibbs distribution. (a) Different ‘paths’ (e.g. 1 or 2) are possible across the fluctuation region for a small subsystem. (b) A relatively sharp fluctuation zone is formed for large systems, as for the environment. The path possibilities defining the temperature are then restricted to the derivatives along the zone.

above, and heat cannot. Heat can only be reduced to an equilibrium energy change by the entropy, $\delta Q = T dS$, finally giving the heat ($k_B T$) numerator in the Gibbs distribution. There is no corresponding work ($k'_B p$) numerator. Thus, a pressure fluctuation can be calculated from the canonical ensemble (see e.g. equation (19.9) in Hill’s book [32]), but it depends on boundary conditions needed for the application of any ensemble calculation of fluctuation. Application of boundary conditions does not correspond e.g. to a small representative scattering volume inside a large sample cell (figure 2). It also does not correspond to calorimetry of samples with small CRRs, because any CRR is representative for linear response of the total sample, and the overwhelming number of CRRs correspond to the freely fluctuating situation of figure 2. The few CRRs that are affected by the boundary of the total sample can be neglected [22].

In the Gibbs approach, the only way to define statistically independent subsystems seems to be by means of energetical decoupling: equation (3.3) implies that $E = E^1 + E^2 \iff w = w_1 w_2$. Energetical decoupling is, as mentioned above, useless for explaining small cooperativities $N_\alpha \approx 1$ for statistically independent CRRs near the crossover.

Starting from the Gibbs distribution, thermodynamics is a relatively simple construction from the mechanics of particles and fields.

3.2. The von Laue treatment of thermodynamics

Energy is from the beginning introduced from *thermodynamics* as the internal energy U for subsystems:

$$dU = T dS - p dV. \quad (3.6)$$

The environment (as a necessary complement to any system) is introduced by the concept of minimal work ΔW_{\min} (the Stradola formula; figure 4(b); see also sections 19, 20 of [23]):

$$\Delta S_{\text{total}} = \Delta W_{\min}/T^0 \quad (3.7)$$

with $S_{\text{total}} = S + S'$, subsystem plus environment. For fluctuations (figure 2) we consider the minimal work necessary for generating a subsystem fluctuation away from the average. The heart of the von Laue approach is the application of Boltzmann probability directly to the figure 2 situation:

$$w_{\text{fluctuation}} = \text{constant} \times \exp(\Delta S_{\text{total}}/k_B). \quad (3.8)$$

Let the total system be defined by $V^0 = \text{constant}$. Otherwise a second term in ΔW_{\min} ($\propto \Delta V^0$) is necessary. We thus have $\Delta V = -\Delta V'$. Beyond this calculation procedure, the $V^0 = \text{constant}$ condition is not important for fluctuations of a small freely fluctuating subsystem inside and practically [22] does not affect their statistical independence. Minimal work is for reversible processes: $\Delta S = -\Delta S'$. Then, from equation (3.6),

$$\Delta W_{\min} = \Delta U - T \Delta S + p \Delta V \quad (3.9)$$

where again the Δ for the subsystem need not be infinitesimally small. This opens the way to calculating subsystem fluctuations. The formal treatments of $T \Delta S$ and $p \Delta V$ are the same, so temperature fluctuations are not excluded. From a second-order series expansion in Δ we obtain

$$w_{\text{fluctuation}} = \text{constant} \times \exp[(\Delta p \Delta V - \Delta T \Delta S)/2k_B T]. \quad (3.10)$$

We put now $T^0 = T$ since the treatment of fluctuations is separated from the average temperature of equilibrium. Equation (3.10) implies [22, 23], in contrast to equation (3.4), a non-zero temperature fluctuation:

$$\overline{\Delta T^2} = k_B T^2 / C_V. \quad (3.11)$$

Starting from representative, freely fluctuating, and statistically independent subsystems, the insertion of mechanics of particles and fields seems to be non-trivial.

3.3. Differences and relations between the two treatments

First, the differences. The Gibbs treatment starts from mechanics, the subsystem fluctuations are restricted by the zeroth law that excludes temperature fluctuations, and the other fluctuations are governed by boundary conditions. On the other hand, the von Laue treatment starts from thermodynamics (i.e. the mechanics must afterwards be introduced by means of minimal work; see below), the subsystem fluctuations are not restricted (temperature can fluctuate) because the zeroth law is only applied to the large total system (T^0 in equation (3.7)), and the fluctuations are not governed by boundary conditions.

The possibility of defining statistically independent subsystems in the Gibbs approach is restricted to energetic decoupling. There is no such restriction in the von Laue approach, except that they must be large (or dense; cf. table 1) enough to support thermodynamics.

Second, the relations. The von Laue treatment implies the Gibbs treatment:

$$\text{von Laue} \implies \text{Gibbs} \quad (3.12)$$

but the inverse, of course (equation (3.4) and equation (3.11)), is not true.

A starting point for understanding the implication of equation (3.12) may be Fermi's golden rule of quantum mechanics (qm). The heat exchange between the subsystem and environment is mediated by Planck quanta:

$$\hbar \omega_{fi} = E_f - E_i. \quad (3.13)$$

Absorption and emission are microscopically equivalent. This implies that the (reversible by definition) minimal work is equivalent to a change of mechanical subsystem energy E in the microcanonical qm ensemble (equation (3.2)):

$$\Delta W_{\min} = \Delta E_{\text{qm}}. \quad (3.14)$$

In the Gibbs treatment, figure 4, the equation (3.14) equivalence is reduced to an implication by the restriction originating from the application of the zeroth law to the subsystem before the fluctuations are separated.

The difference between the alternatives is important when representative subsystems in the nanometre range must be considered, e.g. for linear response or scattering in liquids, especially below the crossover region. The difference is not important if the consideration of large phases is sufficient, as for many properties of gases or crystalline solids, because $(\overline{\Delta T^2})^{1/2}/T \sim 1/N^{1/2}$ is small there, e.g. $1/N^{1/2} \approx 10^{-5}$ for a subsystem of μm size.

A ‘microscopic von Laue distribution’ with $\delta T \neq 0$ that could be substituted for the Gibbs distribution with $\overline{\Delta T^2} = 0$ has yet to be invented. Only preliminary attempts to enlarge the Gibbs distribution correspondingly have been described [33].

Let us list some problems encountered in trying to find a microscopic von Laue distribution:

- (i) The calculation of fluctuation formulae for three thermodynamic dimensions, e.g. with an additional shear term $-\sigma V d\gamma$ in equation (3.7), needs additional assumptions.
- (ii) The formulation of statistical independence in a mechanical system seems delicate.
- (iii) The classical (non-qm) Maxwell–Gibbs separableness, $E(p, q) = T(p) + V(q) \implies \rho = \rho_p \rho_q$, may be lost.
- (iv) The non-infinitesimal changes $(\Delta T, \Delta S, \dots)$ in small subsystems open the way for insertions beyond the Gaussian character of the Gibbs distribution, e.g. for Levy statistics with preponderant partial systems or subsystems [12].

3.4. Frequency partition

Application of the fluctuation formulae to the glass transition needs a partition of time or frequency domains, because only Fourier components in a frequency region around a slow ‘glass frequency’ are relevant. This region is called the ‘dispersion zone of the dynamic glass transition’ (figure 5). The partition of an entropy fluctuation, $\overline{\Delta S^2} = k_B C_p$, leads to a compliance with a relevant step $\propto \Delta c$ at the glass transition, whereas the partition of the temperature fluctuation equation (3.11) leads to a modulus with a step $\propto \Delta(1/c)$ (c = heat capacity). This reciprocity is an implication of the linear response equation $J^* G^* = 1$. In general, compliances J^* correspond to thermodynamically extensive (additive) variables, and moduli G^* to intensive ones. The partition of thermodynamic fluctuation formulae such as $\overline{\Delta S^2} = k_B C_p$ is called the fluctuation-dissipation theorem, FDT; its forms are nearly identical for intensive and extensive variables. For $\hbar\omega \ll k_B T$ we obtain for extensive variables

$$x^2(\tau) = -k_B T (J(\tau) - J_{\text{equil}}) \quad x^2(\omega) = k_B T J''(\omega) / \pi \omega \quad (3.15)$$

and for intensive variables

$$f^2(\tau) = k_B T (G(\tau) - G_{\text{equil}}) \quad f^2(\omega) = k_B T G''(\omega) / \pi \omega \quad (3.16)$$

where the spectral densities $\{x^2(\omega), f^2(\omega)\}$ in the frequency domain are connected to the correlation functions $\{x^2(\tau), f^2(\tau)\}$ in the time domain by a Fourier transformation:

$$x^2(\omega) = (1/\pi) \int_0^\infty d\tau x^2(\tau) \cos(\omega\tau) \quad f^2(\omega) = (1/\pi) \int_0^\infty d\tau f^2(\tau) \cos(\omega\tau). \quad (3.17)$$

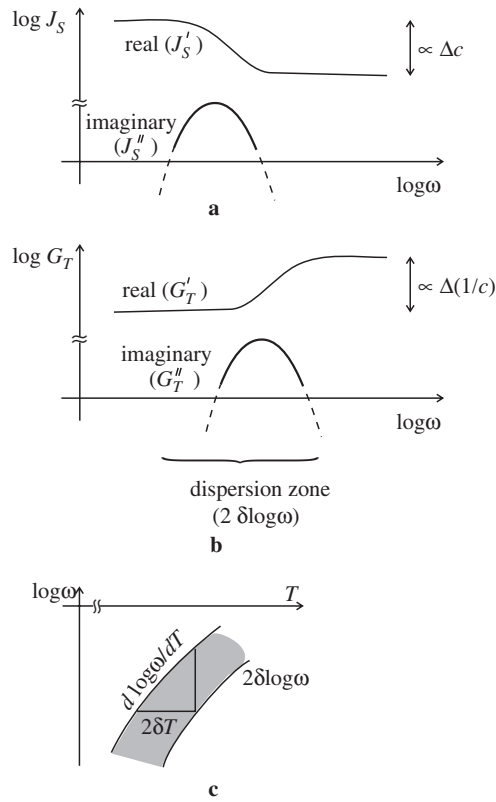


Figure 5. The dynamic entropy compliance $J_S^* = J'_S - iJ''_S$ (a) and temperature modulus $G_T^* = G'_T + iG''_T$ (b) as functions of (the log of) frequency ω in the dispersion zone of the dynamic glass transition. Part (c) shows the (log of the) frequency–temperature equivalence, equation (3.18), mediated by the ω -identity of the FDT. Different experimental scans across the dispersion zone are now determinable by the external parameters T and ω . Note the difference from the subsystem fluctuation region of figure 4(a) for the Gibbs approach.

The α -process dispersion zone in the $\log \omega$ – T plot (figure 5(c)) reflects the fluctuation properties of the smallest representative subsystems for the α -process (CRR). The dispersion zone is not sharpened by system enlargement. Note the difference from the fluctuation region of figure 4(a) for the Gibbs approach. In the $\Delta\Gamma$ – ΔE region, no determination of a definite physical path is possible apart from the zeroth-law artifact. In the $\Delta \log \omega$ – T zone, however, paths can be defined also for one single CRR by linear response experiments, since $T = T^0$ can now be used without affecting the fluctuations, and the fluctuation frequency ω (in the l.h.s. of the second of equations (3.15) and the second of equations (3.16)) is exactly the same as the susceptibility frequency ω applied in the measurement (in the r.h.s.). This important property is called the ω -identity [28] of the FDT. It is in the final analysis based on the indistinguishability of quanta in Nyquist’s transmission lines (figure 3). This property can be used [25] to determine the temperature fluctuation δT of CRRs from the dispersion of the log of the frequency, $\delta \log \omega$, for the glass transition:

$$(d \log \omega / dT)_{\text{along}} = \delta \log \omega / \delta T \quad (3.18)$$

where ‘along’ means along the dispersion zone. A more direct proof will be published elsewhere.

Equations (3.15)–(3.18) show that the linear response informs us exclusively about microscopic fluctuations. Suppressing temperature fluctuations by using the Gibbs distribution could mean that important information about the glass transition remains hidden.

4. The FDT considered as an equation describing qm self-experiments on thermodynamic subsystems

The FDT including temperature fluctuation can be considered as an equation describing quantum mechanical (qm) experiments that identify the subsystem with both the qm object and the measuring apparatus. In a way, our analysis is a synthesis of Nyquist’s derivation of the FDT [27] and Szilard’s discussion of thermodynamic experiments [21] in the context of von Laue’s approach to the fluctuation [22]. The new element here is the identification of the object and the apparatus with the subsystem.

Szilard described the experiment as ‘made by demons’ in simple thermodynamic systems, and this could reflect many aspects of the direction in which we intend to go. Our qm experiment is based on Bohr’s wholeness [15]: we must consider two things—the object and the apparatus. We identify a somewhat large qm object and a somewhat miniaturized apparatus with the same subsystem (figure 6). A qm experiment with this identification will be called a self-experiment. It seems interesting that the original derivation of the FDT by Nyquist [27] can easily be discussed in such terms (figure 2). The identification is there realized by the adjusted transmission lines between the emitter and absorber resistors.

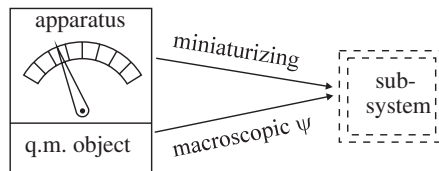


Figure 6. Identification of the apparatus and the object of a quantum mechanical experiment with the same representative thermodynamic subsystem. The collapses of a succession of such ‘self-experiments’ in freely fluctuating subsystems yield the fluctuation-dissipation theorem that includes temperature fluctuation.

As mentioned in section 3, the stationarity of thermal fluctuations corresponds to the time homogeneity of quantum mechanics. The central role of the Hamiltonian for qm systems is to be transferred to the energy form of thermodynamics for subsystems. This is, for subsystems that are not too small, the fundamental form of the first law and the first part of the second law:

$$dU = T dS - p dV \pm \dots = \sum_i f_i dx_i. \quad (4.1)$$

This form includes heat and work, and there is no reason for a different treatment of their fluctuations. Both stem from qm fluctuations of the underlying mechanical system. Starting from equation (4.1) means that fluctuations of temperature and pressure can be treated in the same way for the measurement.

The main requirement for a subsystem to be an apparatus is representativeness: this allows homogeneity in space and time and functionality, i.e. specific application to a given dispersion zone. All representative apparatus subsystems measure the same susceptibilities as the smallest ones, e.g. the CRRs for the α -process.

The FDT is derived from a stationary stochastic succession of qm self-experiments. A virtual thermodynamic step corresponds to one collapse of the wave function ψ for a CRR.

According to equation (4.1), the only variables which are important for thermodynamics and the linear response of our subsystems are the energy-conjugate variables f and x . It follows that the ψ -collapse corresponds to a certain jump in the $\{f, x\}$ variables.

Consider the product $x(t')f_B(s)$ [14] with $x(t')$ characterizing the extensive aspect of the state (e.g. entropy, $x = S$) and f the intensive aspect (e.g. $f =$ temperature T); t' and s are two times. The index B indicates that f_B is the quantity after measurement; the stochastic integral

$$f_B(t) = \int_{-\infty}^t G(t-t')\dot{x}(t') dt' \quad (4.2)$$

means linear and causal determination from stochastic entropy fluctuations $x(t')$ before the measurement: $x(t')$ without the index B is not yet measured; x and f_B are complementary in Bohr's sense. In terms of the fundamental way out described in section 1, nothing is known about the behaviour of the variables x or f of the qm objects, without the index B , i.e. before they are measured. In our treatment we do not need detailed information about their stochastics. The stochastic succession of collapses may be described by associated processes with uncorrelated increments [34].

Confined to x - and f -variables, there is no other way for stationary reflection of an arbitrary mechanical response in the macroscopically linear region other than by means of a $G(t-t')$ memory of the subsystem. To derive the FDT for f we need the expectation value (denoted by script \mathcal{E} in this paper) of the product xf_B . I will show that

$$\mathcal{E}x(t')f_B(s) \propto \varepsilon(s-t') \quad \varepsilon(\tau) = \begin{cases} 1 & \text{for } \tau > 0 \\ 0 & \text{for } \tau < 0 \end{cases} \quad (4.3)$$

with $\varepsilon(\tau)$ the Heaviside step function.

Without experiment, we would have zero correlation between the observable f_B and a non-measured stochastics of x . Let t' be the time of the experiment considered and take s different times. *Before* the experiment, $s < t'$, the state $x(t')$ is 'not measured' and the state $x(t')$ has no influence on $f_B(s)$; $\mathcal{E}x(t')f_B(s) \equiv 0$ for $s < t'$. *At* the experiment, $s = t'$, the state $x(t')$ realizes its part on the 'apparatus pointer' for $f_B(s)$. *After* the experiment, $s > t'$, the pointer is fixed at $f_B(s)$ [21]. We have a fixed relation between $f_B(s)$ for all $s > t'$ and the realized state $x(t')$ at t' : $\mathcal{E}x(t')f_B(s) = \text{constant}$ for $s > t'$. The ε -step in equation (4.3) describes the quantum jump of the experiment at t' as being one event in a $\{t'\}$ -succession of such self-experiments of the subsystem. Stationarity of this succession and of the equilibrium fluctuations implies the reduction $\{t', s\} \rightarrow \{(s-t')\}$. These time differences generate the two-time correlation functions of the FDT, irrespective of the dimension of mechanical correlations, e.g. three- or four-time correlations.

It is easy to derive the FDT from $\mathcal{E}f_B(t)f_B(s)$ using equation (4.3) in the stochastic integral. After Fourier transformation, we obtain

$$\Delta T^2(\omega) = \bar{E}(\omega, T)G_B''(\omega, T)/\pi\omega \quad (4.4)$$

for the spectral density of the temperature fluctuation, $\Delta T^2(\omega)$, including the Bose factor $\bar{E}(\omega, T) = (1/2)\hbar\omega \coth(\hbar\omega/2k_B T)$. This factor follows from exchange of quanta; this factor must have the dimension of an energy. The measuring process must be mediated by quanta from oscillators with corresponding energies, on average $\bar{E}(\omega_0, T)$, where ω_0 is the frequency of the relevant oscillator. From the ω -identity of the FDT (section 3.4) we get $\omega_0 = \omega$. For $\hbar\omega/k_B T \gtrsim 1$ the ω -identity implies that the FDT in the ω -domain is the basic one; the correlation function in the time domain must be calculated afterwards.

The subsystem memory $G(t-t')$ in equation (4.2) advances to an observable dynamic temperature modulus, $G \rightarrow G_B$, with the imaginary part $G_B''(\omega, T)$ and the glass transition

step $\Delta G_B \sim \Delta(1/C_V)$. Starting from the product $f(t')x_B(s)$ we would get the compliance step $\Delta J_{SB} \sim \Delta C_p$. Comparing with section 3 we see that the Gibbs distribution can reflect the FDT for extensive fluctuation, $\overline{\Delta S^2} = k_B \Delta C_p$, but not for the intensive fluctuation, $\overline{\Delta T^2} = k_B T^2 \Delta(1/C_V)$.

In the classical derivation of the FDT [23, 35], the measurement is simulated by equation (3.13) for exchange quanta in the qm perturbation theory. Using the Gibbs distribution, however, excludes temperature fluctuation from the FDT in this derivation.

5. Discussion of thermodynamics from the point of view of the FDT

In this section, thermodynamics is defined as the relation between those variables whose changes are measured by the FDT.

- (i) The second law. The increase of internal entropy is a purely mathematical implication of our stochastic derivation of the FDT. Since we get a stationary correlation function for any linear response variable $\{x_B, f_B\}$, we obtain inevitably a non-negative spectral density for all observable fluctuation. This follows from the mathematical Khintchine theorem (p 307 of [31]): a function $R(t)$ is a correlation function of a continuous stationary stochastic process if it can be represented as $R(t) = \int \cos(t\omega) dF(\omega)$ with a certain distribution function $F(\omega)$. In our case, $F(\omega) \propto \rho(\omega) d\omega$ with $\rho(\omega) =$ spectral density, $\rho(\omega) \geq 0$ as for all probability densities; the continuity of our stochastic process $f_B(t)$ follows from the stochastic integral in equation (4.2). Since also $\bar{E}(\omega, T) > 0$, non-negativity of spectral densities implies non-negativity of loss susceptibilities. This is sufficient for ensuring that there is always non-negative entropy production in the linear stage around any equilibrium situation, i.e. the second law.

Let us reformulate [14] the most important aspects. The time order of each quantum mechanical self-experiment is sufficient to explain the increase of internal entropy during and after an external (index B) disturbance. *Although* any self-experiment has a time order, the succession of self-experiments is thermodynamically reversible [21] for spontaneous equilibrium fluctuations without external disturbance [14]. *Although* internal (x) and external (x_B)—the same holds for f and f_B —quantities are of the same physical nature in the linear region, it is their complementarity (only one B -index in the product $x_B f$ or $x f_B$ considered above) that is responsible for irreversibility. *Although* the qm Hamiltonian of an independent subsystem is symmetric with respect to time reversal, for real thermodynamic subsystems with a succession of self-experiments the spontaneous recurrence of a state with smaller internal entropy is not possible.

For cross-fluctuations we must consider $x_{iB} f_j$ or $x_i f_{jB}$ with $i \neq j$. Example: one gets a dynamic thermal expansivity $\alpha^*(\omega)$ from the ω -domain partition of $\overline{\Delta S \Delta V} = k_B T (\partial V / \partial T)_p$ [36]. For glass transition Fourier components, it also seems interesting to consider the products $f f_B$ and $x x_B$.

- (ii) The character of the qm experiment. Define the term ‘virtual’ in the sense of section 1: the phase space $\{p, q\}$ with the Hamiltonian $H(p, q)$ is considered as a back-construction from the results, from reality, not as a qm object to be measured. We may then ask which virtual mechanical property is ‘demolished’ by the self-experiments. Since the virtual mechanical system without self-experiments has time-reversal symmetry, Poincaré recurrence is inevitable for it. Since negative internal entropy production is implied by this recurrence, the mechanical system contradicts the second law. Since our qm experiment excludes negative entropy production, we conclude that at least the Poincaré recurrence is demolished by the experiment. I suggest calling the time concept that is connected

with the stationary succession of self-experiments, i.e. with this demolition, the *vital time*. No justification from gravitation, cosmology, or violation of T -invariance in elementary particle physics is necessary for the time arrow of vital time. Its arrow can be generated by the FDT self-experiments alone.

Incidentally, three time concepts are thus used in thermodynamics: the real time t' measured by a clock near to the apparatus; a large set of time differences $\{t' - s\}$ needed for the definition of time in correlation functions and frequency in spectral densities; and the vital time for the stochastic succession of self-experiments. Referring to the more fundamental form of equation (4.4) in the frequency domain, we have the apparatus time, the quantum frequencies, and the vital time.

- (iii) The zeroth law. This law failed in application to mechanical fluctuation in the fluctuation region of small subsystems (figure 4(a)). Insisting on the zeroth law, a new thermodynamic principle must be introduced to gauge virtual fluctuations that are forbidden by the zeroth law (the principle of local equilibrium, PLE [28, 37]). Gauging is not necessary for the von Laue fluctuation approach to thermodynamics, since both the equation of state and the fluctuations are directly generated by the same fundamental form, equation (3.6) or equation (4.1).

The temperature–frequency equivalence (the Boltzmann superposition principle for linear response), being a special kind of PLE with inclusion of $\ln \omega$ or $\ln \tau$, can be applied to small subsystems such as to CRRs, since the ω -identity ensures the existence of paths in the dispersion zone of the dynamic glass transition for small systems also (section 3.4).

6. Discussion

6.1. A further test for the von Laue approach

The behaviours of the characteristic length or of the cooperativity near the crossover region of figure 1 are different when calculated by the von Laue and by the Gibbs treatment (figure 4 for a poly(n -alkyl methacrylate) series (PnAMA) in reference [9]). In the former case, the square root of the cooperativity, equation (2.2), tends linearly to 1: $N_\alpha^{1/2}(T) \rightarrow 1$ [38], whereas in the latter case, the cooperativity near the crossover remains large, $N_\alpha^{1/2} \approx 8.5$, i.e. $N_\alpha \approx 70$, corresponding to a ξ_α (Gibbs) four times larger than ξ_α (von Laue) ≈ 0.5 nm. The alternatives can be distinguished when dynamic neutron or x-ray scattering embraces the range of time and wave-vector (Q) of the crossover region (figure 7). According to a suggestion by Stefan Kahle [39], the dielectric traces of the α -, α -, and β -processes in the Arrhenius plot should be directly compared to the iso- Q lines from dynamic scattering. If the increase of Q for the α -process starts with $Q \approx 2\pi/0.5 \text{ nm} \approx 12 \text{ nm}^{-1}$, then the von Laue approach is indicated; if the Q -increase starts with $Q \approx 2\pi/2 \text{ nm} \approx 3 \text{ nm}^{-1}$, then the Gibbs approach is indicated.

Several details must be discussed as regards application of the test:

- (i) Transferability of the calorimetric results from the homologous PnAMA series to other substances where the crossover frequency is high and at present not accessible to precise heat capacity spectroscopy.
- (ii) Distinction between two crossover scenarios [40].
- (iii) Evaluation of dielectric data suitable for a comparison with dynamic scattering and for the application of the FDT [41–44].
- (iv) Separation of an additional length scale in the crossover region as indicated by computer simulations [45].

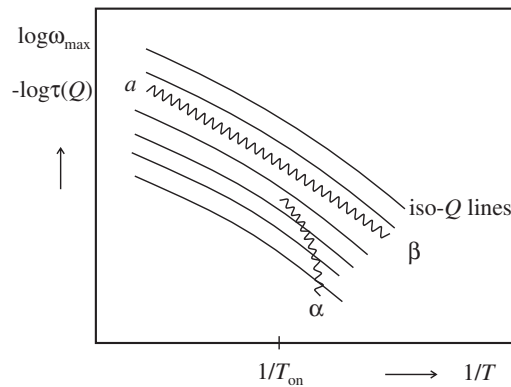


Figure 7. The Arrhenius plot expected for comparison of dielectric traces $\log \omega_{\max}$ (wavy lines) for the high-temperature process a , the cooperative process α , and the local mode β in the crossover region for splitting scenario I [40] with iso- Q lines ($-\log \tau(Q)$) from dynamic neutron scattering (schematically, as suggested by Stefan Kahle [39]).

6.2. Three comments on some recent activities described in the literature

- (1) Molecular dynamics computer simulation can today determine a pattern of kinematic dynamical heterogeneity above and near the crossover region, e.g. the spatial shift of any particle during a typical a -process time [46]. The length scale of this pattern (the ‘kinematic length’) is much larger than the ‘characteristic length’ determined from stationary periodic calorimetry using equation (2.2). This characteristic length is different from the mechanical length because of representativeness, thermodynamic definition, and functionality: the corresponding dynamic heterogeneity is e.g. determined by representative stationary entropy fluctuations relevant for the a - or α -process. Since the mechanical heterogeneity may also involve dynamic regions with no entropy fluctuation, the characteristic length is expected to be smaller than the mechanical length.
- (2) A violation of the FDT for partly frozen glasses was observed by molecular dynamics computer simulation [47–49] and by dielectric-noise experiments on glycerol [50]. The result is that the response after a quench into the glass state is smaller than expected from the fluctuation remaining in a non-equilibrium state. From the standpoint of FDT viewed as an equation describing the qm experiment, this result would mean that a fraction of the fluctuation quanta (in the transmission lines of figure 3) are used to stimulate the structural relaxation and are therefore missing for the linear response measured.
- (3) To give the glass transition a thermodynamic basis, Mézard and Parisi used a replica-coupling method to find a certain crossover temperature [51] which corresponds to the edge of a metastability region. The authors tried to show how the glass transition can be described in the framework of coupled replicas as an ordinary phase transition. Enlarging the space of parameters to include the hidden coupling of replicas, they find a first-order transition line terminating at a critical point. There seems also to be a problem with dynamic heterogeneity. As long as the dynamic glass transition is described using the Gibbs-distribution thermodynamics as a ‘static’ boundary condition, then dynamic heterogeneity when accompanied by free-volume heterogeneity must be reflected by the equilibrium Gibbs distribution, and a thermodynamic approach to the glass transition seems inevitable. If, however, the von Laue approach is taken as the basis, and if thermodynamics is the consequence of a FDT with genuine temperature

fluctuation, then the dynamic heterogeneity need not inevitably be reflected by Gibbs equilibrium thermodynamics: if the thermodynamics contains temperature fluctuation, then dynamical elements of the momentum $\{p\}$ -space—additionally to the Maxwell factor—seem inevitable in the classical microscopic von Laue distribution. Computer physicists interested in temperature fluctuation for molecular dynamics (MD) might try to simulate the equations (3.7), (3.8), and (3.10) of the von Laue approach for freely fluctuating subsystems.

7. Conclusions

Phenomenological thermodynamics can be deduced from the fluctuation-dissipation theorem considered as an equation describing a stationary succession of quantum mechanical experiments on and with representative subsystems. This thermodynamics has a fluctuating temperature. The basic concept of representative subsystems has consequences for the dynamics and thermodynamics of liquids and other disordered materials. The distribution function derived from this thermodynamics is called the microscopic von Laue distribution. Although not yet invented, it must be different from the Gibbs distribution. The time arrow of the second law is an inherent property of such a thermodynamics. The behaviour of the characteristic length of the dynamic glass transition, especially near the crossover or in confined geometries, seems to give strong support to such a view of thermodynamics.

Acknowledgments

I thank Professor A Heuer (Münster) for a discussion of the kinematic length, and the Deutsche Forschungsgemeinschaft (DFG) and the Fonds Chemische Industrie (FCI) for financial support.

References

- [1] Anderson P W 1995 *Science* **267** 1615
- [2] Angell C A 1995 *Science* **267** 1924
Frick B and Richter D 1995 *Science* **267** 1939 and other papers in that issue
- [3] Weeks R A (ed) 1998 *3rd Int. Discussion Mtg on Relaxations in Complex Systems (Vigo, Spain, 1997)*; *J. Non-Cryst. Solids* **235–237** (Special Issue)
- [4] Giordano M, Leporino D and Tosi M (ed) 1999 *2nd Workshop on Non-Equilibrium Phenomena in Supercooled Fluids, Glasses and Amorphous Materials (Pisa, Italy, 27 September–2 October 1998)*; *J. Phys.: Condens. Matter* **11** A1–377 (Special Issue)
- [5] Fischer E W 1993 *Physica A* **201** 183
- [6] O'Reilly J M 1987 *CRC Crit. Rev. Solid State Mater. Sci.* **13** 259
- [7] Moynihan C T and Schroeder J 1993 *J. Non-Cryst. Solids* **160** 52
- [8] Sillescu H 1994 *Acta Polym.* **45** 2
- [9] Donth E, Hempel E and Schick C 2000 *J. Phys.: Condens. Matter* **12** L281
- [10] Johari G P 1976 *Ann. NY Acad. Sci.* **279** 117
- [11] Kivelson S A, Zhao X, Kivelson D, Fischer T M and Knobler C M 1994 *J. Chem. Phys.* **101** 2391
- [12] Donth E 2001 *Europhys. Lett.* at press
- [13] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **43** 139
- [14] Donth E 1982 *Wiss. Z. Tech. Hochsch. Leuna-Merseburg* **24** 475
- [15] Jammer M 1967 *The Conceptual Development of Quantum Mechanics* (New York: McGraw-Hill) p 351
- [16] Schrödinger E 1940 *Proc. R. Irish Acad. A* **46** 32
- [17] Donth E 1988 *Int. J. Theor. Phys.* **27** 1461
Donth E 1991 *Wiss. Z. Tech. Hochsch. Leuna-Merseburg* **33** 89
- [18] Busse K 1998 *PhD Thesis* Universität Halle
- [19] Donth E 2001 unpublished

- [20] Pearle P 1991 *Encyclopedia of Physics* 2nd edn, ed R G Lerner and G L Trigg (New York: VCH) pp 995–9
- [21] Szilard L 1929 *Z. Phys.* **53** 840
- [22] von Laue M 1917 *Phys. Z.* **18** 542
- [23] Landau L D and Lifshitz E M 1980 *Statistical Physics* part 1, 3rd edn (Oxford: Pergamon) sections 4, 7, 8, 19, 28, 112, 124
- [24] Kondepudi D and Prigogine I 1998 *Modern Thermodynamics* (New York: Wiley) ch 14.2
- [25] Donth E 1982 *J. Non-Cryst. Solids* **53** 325
- [26] Fuchs M 1994 *J. Non-Cryst. Solids* **172** 241
- [27] Nyquist H 1928 *Phys. Rev.* **32** 110
- [28] Donth E 1992 *Relaxation and Thermodynamics in Polymers. Glass Transition* (Berlin: Akademie) section 3.7
- [29] Donth E 1979 *Acta Polym.* **30** 481
- [30] Donth E 1999 *Acta Polym.* **50** 240
- [31] Gnedenko B W 1997 *Lehrbuch der Wahrscheinlichkeitstheorie* 10th edn (Frankfurt: Deutsch)
- [32] Hill T L 1956 *Statistical Mechanics* (New York: McGraw-Hill) ch 4 (reprinted 1987 (New York: Dover))
- [33] Nielsen J K 1999 *Phys. Rev. E* **60** 471
- [34] Feller W 1971 *An Introduction to Probability Theory and Its Applications* vol II, 2nd edn (New York: Wiley) ch XIX
- [35] Callen H B and Welton T A 1951 *Phys. Rev.* **83** 34
Callen H B and Greene R F 1952 *Phys. Rev.* **86** 702
Greene R F and Callen H B 1952 *Phys. Rev.* **88** 1387
Greene R F and Callen H B 1951 *Phys. Rev.* **83** 1231
- [36] Bauer C, Böhmer R, Moreno-Flores S, Richert R, Sillescu H and Neher D 1999 *Phys. Rev. E* **61** 1755
- [37] Prigogine I 1967 *Introduction to Thermodynamics of Irreversible Processes* 3rd edn (New York: Interscience) p 114
- [38] Beiner M, Kahle S, Hempel E, Schröter K and Donth E 1998 *Europhys. Lett.* **44** 321
- [39] Kahle S 1999 Private communication (Jülich)
- [40] Kahle S, Schröter K, Hempel E and Donth E 1999 *J. Chem. Phys.* **111** 6462
- [41] Arbe A, Richter D, Colmenero J and Farago B 1996 *Phys. Rev. E* **54** 3853
- [42] Donth E, Schröter K and Kahle S 1999 *Phys. Rev. E* **60** 1099
- [43] Arbe A, Colmenero J, Gomez D, Richter D and Farago B 1999 *Phys. Rev. E* **60** 1103
- [44] Schröter K, Unger R, Reissig S, Garwe F, Kahle S, Beiner M and Donth E 1998 *Macromolecules* **31** 8966
- [45] Kahle S, Schulz M and Donth E 1998 *J. Non-Cryst. Solids* **238** 234
Schulz M and Donth E 1994 *J. Non-Cryst. Solids* **168** 186
- [46] Doliwa B and Heuer A 2000 *Phys. Rev. E* **61** 6898
- [47] Cugliandolo L F and Kurchan J 1993 *Phys. Rev. Lett.* **71** 173
- [48] Parisi G 1997 *Phys. Rev. Lett.* **79** 3660
- [49] Sastry S, Debenedetti P G, Stillinger F H, Schröder T B, Dyre J C and Glotzer S C 1999 *Physica A* **270** 301
- [50] Grigera T S and Israeloff N E 1999 *Phys. Rev. Lett.* **83** 5038
- [51] Mézard M and Parisi G 1996 *J. Phys. A: Math. Gen.* **29** 6515