On the applicability of the mode-coupling theory of glass transitions to good glass formers

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Abstract. Qualitative features of the predictions of the mode-coupling theory of glass transitions are compared with the observed behaviour of good glass formers. In particular, the validity of the idealisation of a sharp glass transition, which is independent of the rate of cooling, is examined critically. A possible extension of the theory is indicated, by which the variability of glass structure on changing the conditions of cooling could be taken into account.

1. Introduction

Recently the study of the glass-transition phenomenon has received new impetus from the development of a mode-coupling theory (Leutheusser 1984, Bengtzelius *et al* 1984, Kirkpatrick 1985, Bengtzelius 1986a, b, Bengtzelius and Sjögren 1986, Jacobs 1986, Krieger and Bosse 1987, Götze and Sjögren 1987). Although the theory is derived for simple liquids, it should, if correct, also apply to the universal properties observed in glass transitions of good glass formers, which have a more complicated molecular structure. Here, a good glass former is defined as a liquid that can be cooled across the glass-transition region sufficiently slowly for thermodynamic measurements and neutron scattering experiments to be made. It is the purpose of this paper to compare some *qualitative* features of the mode-coupling theory of glass transitions with experimental observations for *good glass formers* (for reviews see Angell and Sichina (1976), Brawer (1985) and Jäckle (1986, 1987)). The central question is whether the theoretical idealisation of the glass transition as a sharp transition, which is independent of cooling rates, is valid. It is also pointed out that the theory predicts a certain symmetry of the slowing down near the glass transition, which has not been seen in previous relaxation spectroscopy, and calls for a detailed investigation by neutron scattering. The results of computer simulations of simple liquids are not considered here. A quantitative comparison of the mode-coupling prediction for the viscosity with experiment can be found in a recent review by Angell (1989).

2. A short summary of the mode-coupling theory of glass transitions

The theoretical basis of the mode-coupling theory of glass transitions is the theory of equilibrium fluctuations in simple classical liquids. The space- and time-dependent fluctuations of local quantities, like the particle number density or the energy density, are described by correlation functions for the fluctuations at two different spacetime points. The mode-coupling theory, which is formulated in the framework of the Mori–Zwanzig theory of correlation functions for equilibrium fluctuations, leads to coupled non-linear integral equations for the two-point correlation functions. So far the theory has been worked out only for the (number) density fluctuations. The equation for the density correlation function $F(k, t)$ defined as

$$F(k, t) = \langle n_k(t) n_{-k}(0) \rangle \tag{1}$$

(where n_k is the Fourier transform of the particle number density of wavevector k) can be written as the equation of motion for a harmonic oscillator, generalised by adding a memory term with a memory function $M(k, t)$:

$$\left(\frac{\partial^2}{\partial t^2} + \gamma(k) \frac{\partial}{\partial t} + \omega_0^2(k) \right) F(k, t) + \int_0^t \mathrm{d}t' \, M(k, t - t') \frac{\partial}{\partial t'} F(k, t') = 0. \tag{2}$$

As a result of the mode-coupling approximation, the memory function is expressed as a bi-linear combination of the density correlation function:

$$M(k, t) = \int \frac{\mathrm{d}^3 q}{(2\pi)^3} \, V(k, q) F(|k - q|, t) F(q, t). \tag{2a}$$

This expression contains a vertex function $V(k, q)$ that is determined by static two- and three-particle correlation functions. In the simplified version of the theory (Leutheusser 1984), often referred to as the schematic model, any wavevector dependence is dropped and the vertex function $V(k, q)$ is replaced by a coupling constant λ, which leads to

$$M(t) = 4\lambda \omega_0^2 (F(t))^2. \tag{2b}$$

Equation (2) has to solved for the given vertex function or coupling constant. The fact that the undercooled liquid is only in a metastable equilibrium has no consequences for the structure of the theory. It is to be noted that thermodynamic parameters, like temperature, pressure or density, do not occur explicitly in the theory, but are implicit in the values of the input parameters of the integral equation (2). In the simplified schematic model (Leutheusser 1984), for example, the coupling constant λ is considered as a linearly increasing function of the density. In numerical solutions of equation (2) (Leutheusser 1984, Bengtzelius et al 1984, Bengtzelius 1986a, b, De Raedt and Götze 1986), the predictions of the theory have been worked out mostly as a function of density, rather than of temperature. Nevertheless, they are usually compared with measured temperature dependences, which may only be justified if the glass transition is driven by a reduction in 'free volume'.

   The non-linear integral equation (2) has a remarkable property. It was discovered that, when the strength of the non-linear coupling is increased, a point is reached beyond which the intensity of the space-dependent fluctuations is partly frozen as a function of time. Since the irregular liquid-like structure is not changed at this point, the freezing of fluctuations is interpreted as a transition to a glassy state. For this transition the intensity

of the frozen part of the density fluctuations of different wavevectors plays the role of a (wavevector-dependent) order parameter (Geszti 1983). It determines the intensity of elastic scattering by x-rays or neutrons.

As the transition is approached from the side of the undercooled liquid, the temporal variation of part of the fluctuations slows down more and more, causing an unlimited increase in bulk and shear viscosity. In the simplified version of the theory (Leutheusser 1984) the asymptotic behaviour of the density correlation function at long times is exponential. The numerical solution for the complete theory (Bengtzelius (1986b); see also De Raedt and Götze (1986)) for long times can be fitted by the Kohlrausch formula, and is in good qualitative agreement with experiment (Mezei *et al* 1987b). This behaviour is interpreted as the result of a slowing down of the primary relaxation near the glass transition. The slow part of the fluctuations finally freezes when the transition is reached. Therefore the order parameter is discontinuous, assuming a non-zero value at the transition. The order parameter increases further inside the glass domain, where it is predicted to follow a $\sqrt{\lambda - \lambda_c}$ behaviour close to the transition. Since there is neither a discontinuity of structure nor a singularity of static thermodynamic quantities like specific heat or compressibility, the term 'dynamical phase transition' has been proposed for the transition. The partial freezing of fluctuations implies that on the glass side of the transition the liquid is not longer ergodic. Therefore, the intensity of the frozen part of the density fluctuations of different wavevectors is also called the (wavevector-dependent) 'non-ergodicity parameter'. The non-ergodicity of a glass state inevitably leads to the question of how such a state is macroscopically defined and how it is determined by the history of a particular glass sample. At this point one is faced with the problem that a proper thermodynamic description of glass transitions does not exist. In the mode-coupling theory of glass transitions, both on the liquid and the glass side of the transition, a state is characterised by the input parameters of the non-linear integral equation, such as the coupling parameter λ or the parameters determining the vertex function $V(k, q)$. A particular process, of cooling for example, corresponds to a trajectory in the space of these parameters. The problem of how, in the non-ergodic glass state, these parameters depend on the present and past values of thermodynamic variables like (ambient) temperature and pressure is, however, not addressed in this theory.

Another result of the theory is the following. Although the slowest part of equilibrium fluctuations freezes at the transition point, there are still slow fluctuations in the glass. However, these fluctuations do not slow down further when one moves deeper into the glass region, as one would expect for processes of secondary relaxation. On the contrary, they slow down more and more in the opposite direction, as the transition is approached from the glass side! This slowing down leads to a divergence at the transition of the shear (η) and bulk (η_v) viscosity coefficients that can be defined for an isotropic solid (Landau and Lifshitz 1970). In the simplified version of the theory one obtains

$$\eta \sim (1 - \lambda)^{-1.765} \qquad \eta_v \sim (\lambda - 1)^{-0.765} \qquad (3)$$

where λ is the coupling parameter, which has a critical value $\lambda_c = 1$ at the transition. It does not matter for our qualitative discussion whether the exponents given in (3) are exact or not. The fluctuation spectra and the half-widths both above and below the transition were calculated by Bengtzelius (1986b) for a Lennard-Jones liquid using the complete version of the theory (see figures 6 and 7 of his paper).

From a theory of time-dependent fluctuations in stable or metastable thermal equilibrium one can derive the values of thermodynamic derivatives of second order (or 'susceptibilities'), like the isothermal compressibility κ_T, the specific heat C_p at constant

pressure, the thermal expansion coefficient α and, for a glass, the shear modulus G. For example, as is well known, the intensity of long-wavelength fluctuations of the particle number density is determined by the isothermal compressibility in a liquid, and by the isothermal longitudinal elastic compliance $S_{1,T}$, given by

$$1/S_{1,T} = 1/\kappa_T + \tfrac{4}{3}G \tag{4}$$

in a glass. Since only fluctuations varying with time count in the corresponding fluctuation formulae, the partial freezing of fluctuations, which is described by the mode-coupling theory, leads to discontinuous jumps in the thermodynamic quantities at the transition (Jäckle 1983, 1986, Bengtzelius and Sjögren 1986).

In the past, the discontinuities of the thermodynamic quantities have been widely discussed in comparison with the Ehrenfest relations (Davies and Jones 1953, Rehage and Borchard 1973). If the glass transition could be treated as a thermodynamic phase transition of second order, these discontinuities would be directly related to the slope of the liquid–glass coexistence curve in the P–T diagram. For the discontinuities $\Delta \kappa_T$ and $\Delta \alpha$ of the isothermal compressibility and thermal expansion coefficient, for example, the Ehrenfest relation reads (see, e.g., Callen 1960)

$$\Delta \kappa_T/\Delta \alpha = \mathrm{d}T_\mathrm{g}/\mathrm{d}P. \tag{5}$$

A dimensionless combination of the discontinuities of κ_T, C_p and α, known as the Prigogine–Defay ratio Π, is of particular interest. Π is defined by

$$\Pi = \Delta \kappa_T \Delta C_p/T_\mathrm{g}V(\Delta \alpha)^2. \tag{6}$$

Π would be equal to one if the Ehrenfest relations were fulfilled. It has been shown (Jäckle 1983) that in this case the correlation between the frozen fluctuations of enthalpy and volume of small glass samples would be strictly linear. Experimental values of Π are significantly larger than unity. The mode-coupling theory predicts that at the glass transition about 50% of the intensity of long-wavelength density fluctuations freezes (Leutheusser 1984, Bengtzelius *et al* 1984, Bengtzelius 1986b). Accordingly, the isothermal longitudinal elastic compliance is reduced by 50% at the transition. If the shear modulus of a glass is small compared with its bulk modulus, this prediction implies that the relative jump of the isothermal compressibility is also close to 50% ($\Delta \kappa_T \kappa_T^{(1)} \lesssim \tfrac{1}{2}$). This result is in approximate agreement with experimental values for good glass formers (Gupta and Moynihan 1976). Since the calculation of correlation functions involving energy fluctuations is a formidable problem that has not been tackled so far, the results of the mode-coupling theory for the discontinuities of C_p and α are not known. However, Bengtzelius and Sjögren (1986) have estimated the value of these discontinuities, using ideas of the mode-coupling theory. Their estimate implies that Π should be proportional to $(\gamma^{(1)} - 1)^{-1}$, where $\gamma^{(1)}$ is the specific heat ratio C_p/C_v on the liquid side of the transition. This result is compatible with the small number of experimental data available.

3. The nature of the transition

The mode-coupling theory describes the glass transition as a sharp transition (Leutheusser 1984, Bengtzelius *et al* 1984, Kirkpatrick 1985). In a more recent paper Götze and Sjögren (1987) have proposed a modified version of the theory, which is capable of describing both a sharp and a gradual transition. In view of the fact that in reality glass

transitions always occur gradually, it is desirable to ask first how the result of the original theory may be reconciled with the experimental observations. A discussion of Götze and Sjögren's scenario of a gradual transition is given at the end of this section.

I first briefly review the experimental situation. It is well known that an undercooled liquid, when it is cooled to low temperatures at a constant cooling rate $R = |\dot{T}|$, transforms into a glass within a transition region of finite width ΔT. In this 'transformation range' the state of the material is time dependent, and thermodynamics cannot be applied. The centre of the transition region is defined as the glass-transition temperature T_g. Typical values of the relative width $\Delta T/T_g$ as observed for good glass formers are of the order of several per cent. Since the glass transition occurs when the relaxation time τ for viscous flow becomes comparable with the experimental timescale, which is inversely proportional to the cooling rate, the glass-transition temperature is lowered when the cooling is done more slowly. It follows from this condition that the dependence of T_g on the cooling rate R is logarithmic as described by the formula

$$T_g = (A/k_B)/\ln(C/R) \tag{7}$$

where A is the activation energy of viscous flow near T_g and C is a positive constant. The formula is in agreement with the observed variation of T_g in the experimentally accessible range of cooling rates $R \geqslant 10^{-5}$ K s^{-1}. For example, the glass-transition temperature of a borosilicate is lowered by 8% when the cooling rate is reduced from 3×10^{-2} to 10^{-4} K s^{-1} (Ritland 1954). I refrain from speculating about the significance equation (7) might have for even smaller rates of cooling and only note that no limit for the lowering of the transition temperature is found experimentally. In addition to lowering the glass-transition temperature, slower cooling also leads to a narrowing of the transformation range and a sharpening of the glass transition according to

$$\Delta T/T_g \propto 1/\ln(C/R). \tag{8}$$

These experimental facts contrast with the results for the mode-coupling theory, according to which the glass transition is both sharp and independent of any cooling conditions. (The theory just does not take account of any cooling conditions). Which conclusions must be drawn in view of these discrepancies? In the following two paragraphs I discuss separately the problems concerning the sharpness of the transition and of its dependence on cooling.

(i) It is clear that any theoretical predictions of sharp features of the glass transition are not confirmed by experiment. For example, the square-root behaviour of the order parameter, which is predicted by the theory, is not observed. The temperature dependence of the elastic-neutron scattering intensity across the transition has been measured for two molecular liquids by Frick *et al* (1988) and by Fujara and Petry (1987). In neither case do we find a vertical slope as a function of temperature, such as would correspond to a square-root singularity. (The absence of a vertical slope is most obvious in figures 1 and 3 of Frick *et al* (1988); their figure 6 only obscures this fact.)

On the other hand, the existence of a finite width of the transition region is not of primary importance regarding the values of the discontinuities of the thermodynamic quantities C_p, κ_T and α. In particular, the observed violation of one of the Ehrenfest relations can be accounted for by the dependence of the glass state on the conditions of glass formation, neglecting the finite width of the transition region. Experimentally, the magnitude of the discontinuity of C_p, for example, is obtained by extrapolating the specific heat curves of liquid and glass to the glass-transition temperature T_g in the middle
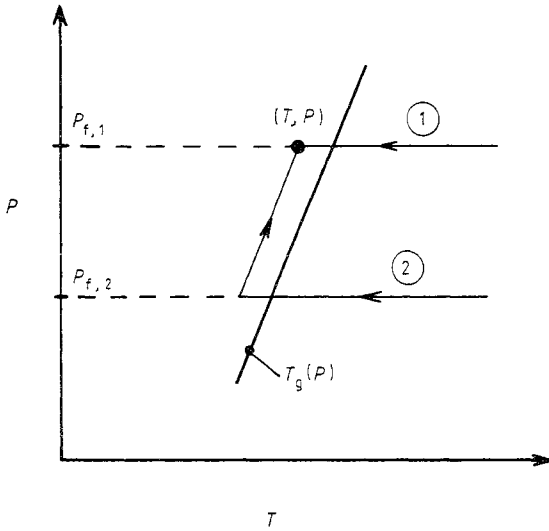
Figure 1. On the two paths 1 and 2 (with pressures of formation $P_{f,1}$ and $P_{f,2}$) different glass states are reached at temperature T and pressure P below the glass-transition line, which is denoted by $T_g(P)$.

of the transformation range. Therefore, the accuracy of the value obtained depends on the width ΔT of the transition region. This accuracy is of particular importance for the testing of the Ehrenfest relations for these quantities. It has been found that usually one of the two Ehrenfest relations is violated, and consequently the Prigogine–Defay ratio exceeds unity. Owing to the relative narrowness of the transition region, the margin of error due to the extrapolation procedure is much smaller than the observed deviations. What then is wrong with the derivation of the Ehrenfest relations, if the finite width of the transition region does not matter? This question has been answered by Goldstein (1973). Goldstein pointed out that the volume, although continuous across the glass-transition line $T_g(P)$, on the glass side of the transition also depends on the pressure of formation P_f (figure 1). Of course, the specific volume of a glass, like any other physical property, to some extent also depends on the rate of cooling in the transformation range. In the limit of infinitely slow cooling the pressure of formation may be expected to be the only additional parameter to characterise the non-ergodic glass state. Goldstein's argument can be formulated mathematically by taking into account the dependence of the glass volume $V^{(g)}$ on P_f in the derivation of one of the Ehrenfest relations. This dependence leads to an additional contribution proportional to the derivative of $V^{(g)}$ with respect to P_f. The modified Ehrenfest relation reads

$$\mathrm{d}T_g/\mathrm{d}P = (\Delta\kappa_T + \partial \ln V^{(g)}/\partial P_f)/\Delta\alpha. \tag{9}$$

The additional term is responsible for the Prigogine–Defay ratio being larger than unity. We obtain the following new formula for Π:

$$\Pi = [1 + (\partial \ln V^{(g)}/\partial P_f)/\Delta\kappa_T]^{-1}. \tag{10}$$

Equations (9) and (10) are the formal expression of Goldstein's reasoning.

(ii) The discrepancy concerning the dependence of the glass-transition temperature on the rate of cooling would be removed if the ideal theoretical glass transition could be interpreted as corresponding to the limit of infinitely slow cooling. This interpretation would imply that, for each glass-forming material, the theoretical glass transition occurs at a lower temperature (and/or a higher pressure) than is observed on the longest experimental timescales. However, a fit of mode-coupling predictions to experimental

data leads to values of the glass-transition temperature that are typically 30 K higher than those observed in caloric measurements (Mezei *et al* 1987a, b, Fujara and Petry 1987, Frick *et al* 1988, Angell 1989). According to Angell (1989), the mode-coupling result for the viscosity fits the experimental data only in the low-viscosity regime. At still lower temperatures, the theoretical viscosity curve rises much more steeply than is observed experimentally, leading to a glass-transition temperature considerably above the caloric value. We conclude that the discrepancy regarding the dependence of the glass transition on cooling cannot be removed by suitable interpretation.

We now comment on a modification of the mode-coupling theory of glass transitions that was proposed recently by Götze and Sjögren (1987). These authors add a second memory term to the integral equation for the time-dependent density correlation function with a memory function that is linear rather than quadratic in the correlation function. For the schematic model they write

$$M(t) = \lambda_1 F(t) + \lambda_2 (F(t))^2 \tag{11}$$

with two independent coupling parameters λ_1 and λ_2. In the extended theory, in which the dependence on wavevectors is taken into account, the coupling constants are replaced by vertex functions $V_1(k)$ and $V_2(k, q)$. According to Götze and Sjögren, the vertex functions or coupling parameters are determined by the metastable equilibrium of the liquid. The authors argue that, in the extended space of input parameters of the modified theory, trajectories for glass-formation processes exist that avoid a sharp transition. It is assumed that these are the trajectories that are explored under realistic conditions. The modified theory may at first sight appear to be an improvement on the original theory, since the idealisation of a sharp glass transition may be avoided. It leads, however, to a scenario in which an essential feature of glass transitions is missing.

On trajectories for which no sharp transition occurs, the correlation function for the density fluctuations always decays to zero asymptotically for long times. In this case ergodicity is never broken. One might argue that the correlation function can be measured only on finite experimental timescales and that the behaviour at longer times and in the mathematical limit $t \to \infty$ is of no interest. This, however, is not quite true. The point is as follows. The mode-coupling theory is essentially a theory for small fluctuations around a reference state. If no sharp transition occurs, it is natural to assume that the reference state is the state of metastable equilibrium of the liquid, even if the average relaxation time is longer than any experimental time. Under this assumption all coupling parameters are equilibrium quantities, as is indeed assumed by Götze and Sjögren. In the real process of glass formation, on the other hand, the undercooled liquid moves further and further away from (metastable) equilibrium. For this reason, additional thermodynamic parameters, like the pressure of formation P_f and—in a phenomenological theory—the fictive temperature T_f, need to be introduced in order to characterise the state of a glass. Although the variations in structure between different glass states may seem to be almost negligibly small, they strongly affect the dynamical properties. For example, the viscosity of vitreous silica near the glass-transition temperature varies by several orders of magnitude depending on the fictive temperature T_f at which it has been equilibrated for a sufficiently long period of time (figure 2; see also Hetherington *et al* 1964, De Bast and Gilard 1963). A similar variation in atomic self-diffusion coefficients may be expected. The theoretical problem raised by these observations is not solved by referring to a formal framework of linear response theory. It should be clear that a kinetic theory of relaxation far from the metastable equilibrium of the undercooled liquid is needed in order to describe the observed behaviour (see,
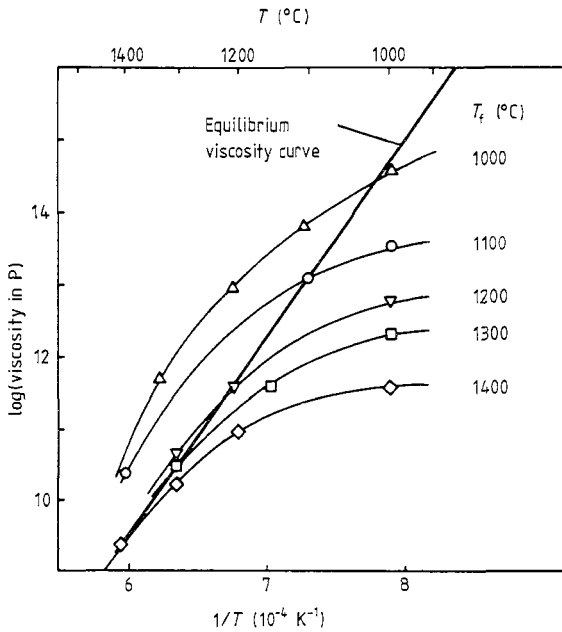
Figure 2. The variation of the viscosity of fused quartz (O. G. Vitreosil with 0.04 wt% hydroxyl) with temperature for different fictive temperatures T_f (from Hetherington *et al* 1964).

for example, the discussion in § 6 of Jäckle (1986)). So far, such a theory exists only at a phenomenological level.

The phenomenological theory (Brawer 1985) is based on the concept of the 'fictive temperature'. The fictive temperature of a glass is that temperature at which the equilibrium liquid has, if equilibrium can be reached, approximately the same molecular structure. As a phenomenological concept, the fictive temperature needs to be defined with respect to a particular physical property, the density for example. A microscopic definition has not been given so far. All the effects that can be described phenomenologically in terms of a relaxing fictive temperature (Moynihan *et al* 1976) are missing in Götze and Sjögren's scenario of continuous glass transitions. To overcome this deficiency, an *ad hoc* dependence of the coupling parameters on a fictive temperature could possibly be included in the theory in a phenomenological manner, although this would be contrary to the authors' original intention of developing a microscopic theory. For 'computer glass transitions' of simple liquids an alternative possibility is to obtain the vertex functions from computer simulation. The vertex functions can be expressed in terms of two- and three-body correlation functions, which can be calculated on the computer. In this way, for example, the dependence of the glass state on the cooling rate could be incorporated into the theory.

4. Symmetry of slowing down on both sides of the transition

According to the mode-coupling theory of glass transitions, there is a certain symmetry in the slowing down of density fluctuations on either side of the transition. In addition to the fluctuation component which freezes at the transition, there is a second slow component of the correlation function, which decays according to a power law (in the schematic model proportional to $t^{-0.395}$) right at the transition. The decay of this

component speeds up in the same way on both sides of the transition as one moves away from it. This result is reminiscent of the behaviour observed near phase transitions of the second kind. The result is surprising since relaxation spectroscopy (ultrasonic, dielectric, NMR) for good glass formers always shows a monotonic decrease in relaxation times with increasing temperature, both for the primary (α) and the secondary (β, γ) relaxations (Wong and Angell 1976). A consequence of the predicted behaviour would be a contribution to ultrasonic absorption in glass proportional to $\omega^2 \eta_v$, which depends *quadratically* on frequency and at the same time *increases* with increasing temperature towards the glass-transition point. Such a term contrasts with the usual contribution from a relaxation mechanism, which on the low-temperature side of the absorption peak is frequency independent. As for the spectrum of density fluctuations, it is conceivable that, in cases where different relaxation processes produce overlapping relaxation peaks, in a limited temperature interval the measured total spectrum of density fluctuations gives the impression of a slowing down of relaxation with *increasing* temperature. A different mechanism may occur if slow vibrational motions exist, the frequencies of which overlap with the relaxation spectrum. If in the glass region close to the transition such slow vibrational modes become softer, the quasi-elastic component of the fluctuation spectrum may become narrower as the transition is approached. (The observation of a minimum in the relaxation rate of a microemulsion as a function of concentration (Chen and Huang 1985) may have a similar origin. Increasing the concentration towards the limit of close packing leads to stronger repulsive forces and, therefore, higher frequencies of the oscillatory motions.) A second slow component of the density-fluctuation spectrum has in fact been discovered recently by inelastic neutron scattering from polybutadiene (Frick *et al* 1988, Frick 1988) and from 1,3,5-tri-α-naphtyl-benzene (Fujara and Petry 1987) near the respective glass transitions. The spectral width of this component seems to be independent of temperature. This disagrees both with the mode-coupling prediction and with the result of an ordinary relaxation process. It has to be seen whether a more detailed neutron scattering study will lead to better agreement with the prediction of the mode-coupling theory.

To summarise, several problems arising from a qualitative comparison of the mode-coupling theory of glass transitions with experimental facts have been pointed out. Problems related to the finite width of the transformation range, the dependence on the timescale of cooling and the ambiguity of the non-ergodic glass state have been emphasised. It is argued that the prediction of a sharp glass transition by the theory should be interpreted as corresponding to the limit of infinitely slow cooling, but that fits of experimental data are not consistent with such an interpretation. It is shown that the theoretical prediction of a sharp glass transition is compatible with the observed violation of one of the Ehrenfest relations, and with the fact that the Prigogine–Defay ratio is larger than unity, only if the glassy state depends on the pressure P_f of glass formation as an additional thermodynamic variable (figure 1). Reformulating an argument of Goldstein, a new formula (10) for the Prigogine–Defay ratio is derived that contains the derivative of the glass volume with respect to the pressure P_f of formation. Possible ways of extending the modified theory due to Götze and Sjögren (1987), which leads to a smooth rather than a sharp glass transition, have been indicated. The need for such an extension arises from the fact that an undercooled liquid leaves the path of metastable equilibrium when it is cooled into the glass-transition region (figure 2). As a consequence, the vertex functions (or coupling constants) occurring in the integral equation for the density correlation function are no longer equilibrium quantities. It is suggested that the extra dependence of these quantities on additional non-equilibrium

parameters may either be described in a phenomenological way, or may, for simple liquids, be obtained from computer simulation. The usefulness of such an extension depends on the validity of the mode-coupling theory in the regime of high viscosity (with $\eta > 10^5$ P, say), where glass transitions of good glass formers are usually observed. In view of the discrepancies between measured and fitted viscosity curves and glass-transition temperatures, and the unconfirmed prediction of a symmetrical slowing down around the glass transition, however, the reliability of the theory in this domain remains uncertain (see also Angell (1989) and Fredrickson (1989)).

Acknowledgments

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