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β relaxation near glass transition singularities

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Abstract. Glass transition singularities as obtained by mode-coupling theory are classified within the framework of singularity theory for smooth mappings in parameter spaces. The general equations for the β relaxation process are derived and characterised by sets of a few relevant parameters characteristic for every singularity. The simplest singularity, which is studied in detail, is specified by two relevant coordinates, the separation parameter and the exponent parameter. The scaling laws describing the dynamics and the leading corrections to scaling are discussed. It is shown that a strong asymmetry in the mode-coupling equations leads to a β relaxation peak that can be described asymptotically by a Cole–Cole law. The corresponding dynamics is interpreted within the picture of renewal processes for motion in a high-dimensional potential landscape.

1. Introduction

An outstanding feature of the dynamic behaviour of systems near the liquid–glass transition is the slow time variation of typical relaxation functions. In order to observe the decay of a disturbance from, say 90% of its initial value to 10% of it, one has to cover several decades of time t. Similarly, if one wants to observe the corresponding relaxation peak in a susceptibility spectrum, one has to vary the frequency ω over several orders of magnitude (Wong and Angell 1976). It is conventional to characterise this stretching phenomenon by the statement that the relaxation exhibits a very broad distribution of relaxation rates. For structural glass transitions, as opposed to spin-glass or orientational glass transitions, the mentioned primary or α relaxation often exhibits a simple scaling property: the time–temperature superposition principle. The decay of variable Φ with increasing time t is given by a master function F, which is independent of control parameters like temperature, namely $\Phi(t) = F(t/\tau)$. The changes of temperature merely enter the scale τ (Wong and Angell 1976). Often, but not always, a secondary or β resonance is observed in dielectric loss spectra. The resonance frequency ω_β is located above $1/\tau$, the value for α relaxation. The temperature variation of ω_β is much weaker than that of $1/\tau$. The β resonance also exhibits a very broad distribution of relaxation rates (Johari and Goldstein 1970, 1971).

The mentioned relaxation properties have been derived in recent years within a so-called mode-coupling theory for the idealised glass transition. This theory describes the system by a set of conventionally defined correlation functions $\Phi_q(t)$. Here the label

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q denotes wavevectors of density or spin-density fluctuations. For convenience we normalise the initial conditions: $\Phi_q(t=0)=1$. The Laplace transforms

$$\Phi_q(z) = \mathrm{LT}[\Phi_q(t)](z) = \mathrm{i}\int_0^\infty \mathrm{d}t\, \mathrm{e}^{\mathrm{i}zt}\Phi_q(t) \tag{1.1}$$

are positive analytic functions of complex frequency z. The spectra $\Phi_q''(\omega) = \operatorname{Im}\Phi_q(\omega+\mathrm{i}0)$ are non-negative even functions of ω. They are of direct experimental interest since they determine the cross section for inelastic neutron scattering experiments. The dynamic susceptibilities are trivially related to the correlators, $\chi_q(z) = \chi_q[z\Phi_q(z)+1]$, where χ_q denotes the thermodynamic equilibrium susceptibility. The theory is defined by two equations of motion. One expresses the correlators in terms of a current relaxation kernel or a generalised viscosity $M_q(z)$:

$$\Phi_q(z) = -1/\{z - \Omega_q^2/[z+M_q(z)]\}. \tag{1.2a}$$

The kernel $M_q(z)$ can be written in terms of a stochastic friction term $\nu_q \geqslant 0$ and a non-trivial part $m_q(z)$: $M_q(z) = \mathrm{i}\nu_q + \Omega_q^2 m_q(z)$. Here Ω_q denotes a characteristic microscopic frequency scale. The other equation relates $m_q(t)$ to products of correlation functions:

$$m_q(t) = F_q(\Phi_k(t)). \tag{1.2b}$$

The mode-coupling functional F_q is a polynomial with non-negative coefficients v_1, $v_2, \ldots$, which play a role of mathematical control parameters. Let us combine them into a vector $V=(v_1, v_2, \ldots, v_N)$ of the N-dimensional space R_N of control parameters. The two frequencies ν_q, Ω_q determine the dynamics on microscopic timescales, since equations (1.2) imply

$$\Phi_q(t\to 0) = 1 - \tfrac{1}{2}(\Omega_q t)^2 + \tfrac{1}{6}(\nu_q t)(\Omega_q t)^2 + \mathrm{O}(t^4). \tag{1.3}$$

The equations above were employed originally for supercooled simple liquids (Bengtzelius *et al* 1984) and for a Heisenberg system with symmetric random couplings (Götze and Sjögren 1984). The range of validity of the approximations leading to equations (1.2) is not fully understood. But within an extended theory the preceding one was obtained by ignoring certain relaxation processes, which are due to thermally activated hopping (Götze and Sjögren 1987a). The hopping processes lead to a smearing of the ideal glass transition described by equations (1.2). Since most features of the true transition can be understood by neglecting the smearing (Götze and Sjögren 1988) it is a tolerable simplification to ignore it completely.

The idealised glass transition is characterised by a change in dynamics from ergodic to non-ergodic behaviour if the control parameter vector V crosses some hypersurface S_c in parameter space R_N. On one side of S_c correlations decay to zero for large times: $\Phi_q(t\to\infty)=0$. After perturbation the system returns to equilibrium. The correlator is continuous for low frequencies and the corresponding states V are referred to as liquid. On the other side of S_c correlations do not relax to zero for large times: $\Phi_q(t\to\infty) = f_q > 0$. Perturbations arrest spontaneously, a behaviour which is typical for non-ergodic motion (Kubo 1957). The corresponding states are referred to as glass. For the glass the correlator exhibits a non-ergodicity pole: $\Phi_q(z)\cdot z \to -f_q$ for $z\to 0$. The density spectrum shows an elastic line on top of a continuum: $\Phi_q''(\omega\to 0) = \pi f_q \delta(\omega)$. In addition to the possible pole the correlator $\Phi_q(z)$ exhibits a further singularity for $z\to 0$ if $V\to V_c \in S_c$. This singularity, to be referred to as the glass transition singularity, presents

a new paradigm for many particle dynamics. For structural glass transitions f_q behaves discontinuously at S_c (Bengtzelius *et al* 1984); and one finds asymptotically an α relaxation peak with the mentioned scaling properties (Götze 1984, 1987). In all examples studied so far the peak could be described very well by a Kohlrausch function (DeRaedt and Götze 1986, Bengtzelius 1986, Bosse and Krieger 1986, Krieger and Bosse 1987, Götze and Sjögren 1987b). There is a β relaxation contribution to the spectrum with rather universal features (Götze 1985). Its main signature is a minimum in the susceptibility spectrum (Götze and Sjögren 1988). Under specific circumstances there can be a β peak with the correct experimental signature (Buchalla *et al* 1988). The theory also yielded a number of previously unknown glass transition anomalies, which can be tested by neutron scattering experiments. Recent work shows that some predictions of the theory are in reasonable agreement with the experimental findings (Mezei *et al* 1987a, b, Fujara and Petry 1987, Frick *et al* 1988, Knaak *et al* 1988, Richter *et al* 1988, Frick 1988). Therefore it seems justified to continue with the discussion of equations (1.2).

In this paper some features of β relaxation will be discussed, which are beyond the previously derived leading-order scaling-law results. By introducing natural coordinates in parameter space the range of applicability of scaling laws will be extended. The equations for the evaluation of corrections to scaling are obtained. It will be shown how exponents appear which depend on control parameters like temperature T. Our main result is the derivation of the Cole–Cole law for the β relaxation peak: $\chi(z) \propto 1/[(-\mathrm{i}\, z/\omega_\beta)^a + 1]$.

Most of our results can be understood from a simplified model which deals with one correlation function $\Phi(t)$ only. So we will restrict ourselves mainly to this case and study the equation of motion

$$\Phi(z) = -1/\{z - 1/[(z + \mathrm{i}\nu)/\Omega^2 + \mathrm{LT}[F(\Phi(t))](z)]\}. \tag{1.4a}$$

Here the mode-coupling functional is the polynomial

$$F(f) = \sum_{n=1}^{N} v_n f^n. \tag{1.4b}$$

The case $F(f) = v_1 f$ is trivial from a mathematical point of view and will not be considered here. The model $F(f) = v_2 f^2$ (Leutheusser 1984, Bengtzelius *et al* 1984) is of no interest either, since it does not exhibit stretching for the α relaxation. So the simplest case of interest is the F_{12} model defined with a two-dimensional parameter space $V = (v_1, v_2)$ (Götze 1984). This model was discussed recently in connection with a glass transition of the Pott's model (Kirkpatrick and Thirumalai 1988). We will also be interested in the F_{13} model specified by $F_{13}(f) = v_1 f + v_3 f^3$, since it is relevant for spin-glass transitions (Götze and Sjögren 1984). The simplest model for a two-component system appears if we use (1.4) for one correlator and formulate the following equation for a second correlation function $\Phi_s(t)$:

$$\Phi_s(t) = -1/\{z - 1/[(z + \mathrm{i}\nu_s)/\Omega_s^2 + \lambda_s \mathrm{LT}[\Phi(t)\Phi_s(t)](z)]\}. \tag{1.5}$$

This model was introduced to discuss diffusion of a tagged particle with density correlator $\Phi_s(t)$. It moves in a surrounding medium, whose density correlator is $\Phi(t)$ (Sjögren 1986). The medium may experience a glass transition. The behaviour of $\Phi_s(t)$ depends crucially on the magnitude of the coupling constant λ_s.

2. Dynamical equations for β relaxation

In the glassy state equation (1.2*b*) implies $m_q(t \to \infty) = F_q(f_k) > 0$, and hence the relaxation kernel exhibits a non-ergodicity pole also, $m_q(z)z \to -F_q(f_k)$ if $z \to 0$. Therefore one expects $m_q(z)$ to be very large for small frequencies for all V near the transition hypersurface S_c. In particular one expects for the specified frequencies and control parameters

$$|(z + i\nu_q)/\Omega_q^2| \ll |\mathrm{LT}[F_q(\Phi_k(t))](z)|. \tag{2.1a}$$

For V near S_c this inequality defines implicitly a microscopic frequency scale Ω_m or a corresponding timescale $t_m = 2\pi/\Omega_m$. For $|z| < \Omega_m$ or $t > t_m$ inequality (2.1*a*) holds and one is allowed to neglect $(z + i\nu_q)/\Omega_q^2$ in comparison with $m_q(z)$. The equations of motion (2.1) then simplify and can be rewritten as:

$$\Phi_q(z)/[1 + z\Phi_q(z)] = \mathrm{LT}[F_q(\Phi_k(t))](z). \tag{2.1b}$$

Equations (1.4) and (1.5) can be simplified in a similar manner. The transition hypersurface S_c, the non-ergodicity parameter f_q, the master functions for α and β relaxation and the like are determined by (2.1*b*). This equation exhibits scale invariance. If $\Phi_q(t)$ is a solution, the same is true for the rescaled correlator

$$\Phi_q^y(t) = \Phi_q(t/y) \qquad \Phi_q^y(z) = y\Phi_q(zy). \tag{2.2}$$

Here $y > 0$ can be any scaling parameter. The term $(z + i\nu_q)/\Omega_q^2$ determines the short-time dynamics as specified by equation (1.3). Dropping this term, one eliminates any detailed connection between short-time dynamics and the behaviour of the correlation functions for small frequencies or long times. The whole influence of the short-time dynamics on the long-time correlators merely concerns the magnitude of the timescale. The latter cannot be derived from equation (2.1*b*). It follows from matching a solution to the correct one for $t \sim t_m$. This can be done by choosing a proper scale factor y. The correct short-time solution for $t \leqslant t_m$ can be found by extension of equation (1.3) to any desired order in t. Another procedure consists of converting equations (1.2) to a set of coupled second-order differential equations, which can then be solved by some standard iteration. Connected with the scale invariance there is another feature of equation (2.1*b*) worth emphasising. The microscopic theory brings out (Bengtzelius *et al* 1984) that the mode-coupling functional F_q depends neither on particle mass nor explicitly on temperature T. It is given solely by pair and triple correlation functions, i.e. by integrals of $\exp[-U(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots)/k_B T]$, where U denotes the interaction potential for particles at positions $r_1, r_2, \ldots$. In this sense one can say that equation (2.1*b*) merely reflects equilibrium properties as given by the potential part of the partition function. The control parameters, which fix functional F_q, depend only on the topology of the potential energy surface defined in the high-dimensional configuration space. This surface has a very complicated structure with many local minima, maxima and saddle points. The mode-coupling theory describes approximately the statistics over all possible paths through the potential landscape. The microscopic details of the dynamics merely enter the timescale for the exploration of the potential landscape. The whole complexity of the potential energy surface is mapped via equation (2.1*b*) onto the time axis. The distribution of possible paths is mapped into distributions of waiting times for the particles which move between metastable states (Sjögren 1989).

It is an obvious simplification of the analysis of the glass phase if one considers $G(t) = \Phi(t) - f$ rather than $\Phi(t)$ itself. The non-ergodicity pole is then eliminated so that $|zG(z)|$

is small for small frequencies. Since $G(t)^{n+1}$ decreases faster to zero than does $G(t)^n$, one can expect also that $|\mathrm{LT}[G(t)^{n+1}](z)/\mathrm{LT}[G(t)^n](z)|$ is small for $z \to 0$. Then the dynamic equations can be simplified by expanding in terms of the identified small parameters. This suggests trying a similar procedure for the whole neighbourhood of S_c. So let us introduce some not yet specified real parameter $\tilde{f}$ and define a function G by

$$\Phi(t) = \tilde{f} + G(t) \qquad z\Phi(z) = -\tilde{f} + zG(z). \tag{2.3}$$

Under the assumptions

$$|zG(z)/(1-\tilde{f})| \ll 1 \tag{2.4a}$$

$$|\mathrm{LT}[G(t)^{n+1}](z)/\mathrm{LT}[G(t)^n](z)| \ll 1 \tag{2.4b}$$

we can expand equation (2.1*b*) as follows:

$$\begin{aligned}&(-\delta_0/z) + \delta_1 G(z)\\ &+ (1+\delta_2)\mathrm{LT}[G(t)^2](z) + zG(z)^2\\ &+ (\gamma_3 + \delta_3)\mathrm{LT}[G(t)^3](z) - \gamma_3 z^2 G(z)^3\\ &+ (\gamma_4 + \delta_4)\mathrm{LT}[G(t)^4](z) + \gamma_4 z^3 G(z)^4 + \ldots = 0.\end{aligned} \tag{2.5}$$

Here the following abbreviations are used: $\gamma_k = 1/(1-\tilde{f})^{k-2}$ and

$$\delta_k(V,\tilde{f}) = [\partial^k \Delta F(V,\tilde{f})/\partial \tilde{f}^k](1-\tilde{f})^3/k! \tag{2.6}$$

$$\Delta F(V,\tilde{f}) = F(V,\tilde{f}) - \tilde{f}(1-\tilde{f})^{-1}. \tag{2.7}$$

These results follow from equation (1.4) for the simplified model. The theory for equations (1.2) yields formula (2.5) also, but the results for δ_k, γ_k are more complicated (Götze 1985, 1987). The mode-coupling functional F and therefore ΔF and δ_k depend smoothly on V and on $\tilde{f}$. For simplicity of notation we will usually not indicate this dependence. We have seen above that the preceding expansion allows for a discussion of the glassy state for all small frequencies if $f = \tilde{f}$ is chosen. For the liquid this is not the case. Expansion (2.5) becomes invalid then if $|z| < 1/\tau$ or $t > \tau$, where τ is the scale for the α relaxation process (Götze 1984, 1985). In this paper the α relaxation will not be discussed explicitly. Expansion (2.5) is the basis of the β relaxation theory. Equations (2.4) define implicitly the range of frequencies or times for the β relaxation process. The task is the solution of (2.5) and the explicit characterisation of the range of validity of the solution.

The equations for the form factors f_q of the glass are obtained by multiplying (2.1*b*) by z and then specialising to $z = 0$ (Bengtzelius *et al* 1984):

$$f_q/(1-f_q) = F_q(v_1, \ldots, v_N; f_1, \ldots, f_M) \qquad q = 1, \ldots, M. \tag{2.8a}$$

Here all variables are indicated explicitly. For the simplified model the result reads

$$\Delta F(V,f) = 0. \tag{2.8b}$$

This equation defines a smooth N-dimensional manifold in the $(N+1)$-dimensional space of vectors $(v_1, v_2, \ldots, v_N, f)$. The projection S of this manifold into the N-dimensional parameter space R_N is the set of possible glass states. The singularities S_c of this mapping are candidates for glass transition singularities. The classification theory of the specified singularities is known from other contexts (Arnold 1986). For every N there is a finite number of generic singularities, i.e. there appear several possibilities of

quite different glass transition scenarios. The simplest singularities are Whitney folds, characterised by such critical values (V_c, f_c) obeying

$$\Delta F(V_c, f_c) = 0 \qquad \partial \Delta F(V_c, f_c)/\partial f = 0. \tag{2.9a}$$

Furthermore the second derivative of ΔF must not vanish. Using the notation (2.6) the fold singularities are specified by

$$\delta_0(V_c, f_c) = 0 \qquad \delta_1(V_c, f_c) = 0 \qquad \delta_2(V_c, f_c) \neq 0. \tag{2.9b}$$

The next more complicated singularities, the Whitney cusps, are found if also $\partial^2 \Delta F/\partial f^2 = 0$ while the third derivative of ΔF is non-zero:

$$\delta_k(V_c, f_c) = 0 \qquad k = 0, 1, 2 \qquad \delta_3(V_c, f_c) \neq 0. \tag{2.10}$$

Higher-order cuspoids are obtained by obvious generalisation. Equation (2.9*b*) defines the hypersurface S_c of the simplest glass transition singularities in parameter space R_N, which will be analysed in detail. Equation (2.10) defines the set of simple endpoints of S_c; the dynamics near these endpoints will be discussed in a subsequent paper. The generic singularities of the full theory do not only depend on the dimensionality N but also on the degeneracy N' of the vanishing eigenvalue of the Jacobian matrix relevant for the set of implicit equations (2.8*a*). The cuspoids are the singularities of simple eigenvalues $N' = 1$, and a one-component model can reproduce this case. This is the topological reason why the two simplest glass transition scenarios, the fold and the cusp singularities, can also be analysed with a simplified model, equation (1.4). For a one-component fluid one can make use of the special form of the mode-coupling functional in order to prove that $N' = 1$ is the only generic possibility (Götze 1987). It is not known at present whether or not mixtures or fluids with internal degrees of freedom require the discussion of singularities with $N' > 1$. In such a case the simplest schematic models would consist of N' coupled equations.

In the following two sections it will be shown how equation (2.5) is solved by scaling laws. From equation (2.4*a*) one expects complications if $(1 - \tilde{f})$ is small; this problem will be examined in § 5.

3. Critical relaxation

Let us start the discussion of the equations of motion for parameter points V_c on the transition hypersurface S_c. The dynamic solution for these points shall be referred to as critical relaxation. The value of the glass form factor for $V = V_c$ shall be denoted by f_c and $\delta_k^c = \delta_k(V_c, f_c)$, $\gamma_k^c = \gamma_k(f_c)$. In equation (2.3) we choose $\tilde{f} = f_c$, so that for the transition under consideration equations (2.9) yield $\delta_0^c = \delta_1^c = 0$; $\delta_2^c \neq 0$. The endpoints of S_c are characterised by $\delta_2^c = 0$, equation (2.10). One verifies easily that S_c crosses the nth parameter axis at $v_n^c = n^n/(n-1)^{n-1}$. At this point $f_c = (n-1)/n$ and $\delta_2^c = -\frac{1}{2}$.

Since δ_2 depends on V continuously one then gets $\delta_2^c < 0$ on S_c, as long as endpoints are avoided. Let us introduce the notation $\lambda = 1 + \delta_2^c$, $\mu = -\delta_3^c$, i.e.

$$\lambda = \tfrac{1}{2}(1 - f_c)^3 \sum_n v_n n(n-1) f_c^{n-2} \tag{3.1a}$$

$$\mu = (1 - f_c)^{-1} - \tfrac{1}{6}(1 - f_c)^3 \sum_n v_n n(n-1)(n-2) f_c^{n-3}. \tag{3.1b}$$

The glass transition singularity under study is characterised by

$$0 < \lambda < 1. \tag{3.2}$$

The cusp singularity, to be studied in a following paper, is specified by the condition

$$\lambda = 1 \qquad \mu > 0 \qquad \text{simple endpoints.} \tag{3.3}$$

At the critical points equation (2.5) specialises to

$$\lambda \mathrm{LT}[G(t)^2](z) + zG(z)^2 + (\gamma_3^c - \mu)\mathrm{LT}[G(t)^3](z) - \gamma_3^c z^2 G(z)^3 + \ldots = 0. \tag{3.4}$$

Since $z\mathrm{LT}[t^{-\alpha}](z) = -\Gamma(1-\alpha)(-\mathrm{i}z)^{\alpha}$, with Γ denoting the gamma function, function $G(t) \propto 1/t^a$ makes the first line of equation (3.4) vanish provided

$$\Gamma(1-a)^2/\Gamma(1-2a) = \lambda. \tag{3.5a}$$

If one requires

$$0 < a < \tfrac{1}{2} \tag{3.5b}$$

then the exponent a is determined uniquely, $G(z)$ is positive analytic and inequalities (2.4) are satisfied for small frequencies z or large times t. So the mentioned power function is the relevant critical decay law for $\lambda < 1$, as was noted in all the previous papers on the mode-coupling theory. Equation (3.4) allows for a systematic asymptotic expansion of $G(t)$ in increasing powers of $1/t^a$. We will need the leading and next-to-leading terms:

$$G(t) = (t_0/t)^a + \tfrac{1}{2}c(t_0/t)^{2a} + \ldots. \tag{3.6a}$$

Substitution into equation (3.4) fixes c to

$$c = [\gamma_3^c \Gamma(1-a)^3 + (\mu - \gamma_3^c)\Gamma(1-3a)]/[\lambda\Gamma(1-3a) - \Gamma(1-a)\Gamma(1-2a)]. \tag{3.6b}$$

So for normal transitions the simple power-law decay $G(t) = (t_0/t)^a$ describes the dynamics in the limit $|z| \to 0$ or $t \to \infty$. This power law dominates if t exceeds some critical value t_0^c or if $|z| \ll 1/t_0^c$, where

$$t_0^c = t_0 c^{1/a}. \tag{3.6c}$$

If c is of order unity one can choose $t_0^c \sim t_0 \sim t_m$, and the critical decay is observed as soon as the time exceeds the microscopic one. This situation was exemplified in the preceding papers (DeRaedt and Götze 1986, Götze and Sjögren 1988). However, if λ tends to unity, exponent a decreases to zero:

$$1 - \lambda = \tfrac{1}{6}a^2\pi^2 \qquad a \to 0. \tag{3.7a}$$

In this case coefficient c becomes very large

$$c = 6\mu/(a^2\pi^2) \qquad a \to 0. \tag{3.7b}$$

Consequently, any regular t_0 leads to a diverging t_0^c in equation (3.6c) if $a \to 0$. For small

a the result (3.6*a*) no longer describes the complete relaxation pattern. In a following paper it will be shown that within the time window $t_m < t < t_0^c$ the critical relaxation of the endpoint is dominant, and this is quite different from a simple power law.

4. β Relaxation scaling laws

In this section β relaxation for parameter vector V close to inner points of the transition hypersurface S_c will be considered. From the preceding papers (Bengtzelius *et al* 1984, Götze 1984, 1985) one knows that the dynamics is described by scaling laws. Here we want to extend this work in order to understand the origin of the corrections to scaling laws. For $V \notin S_c$ the two terms of the first line in equation (2.5) appear. Since a fold singularity is generically described by one relevant parameter (Arnold 1986) it must be possible to eliminate one of the terms. This we can achieve by choosing $\tilde{f}$ properly. The condition $\delta_0 = 0$ can be satisfied only on the glass side of S_c but not on the other, and therefore we eliminate δ_1. So $\tilde{f}$ shall be chosen as a function of V obeying:

$$\delta_1(\tilde{f}(V), V) = 0 \qquad \tilde{f}(V_c) = f_c. \tag{4.1}$$

The condition (3.2) for normal transition points implies $\partial\delta_1/\partial f|_c \neq 0$, and equation (4.1) defines $\tilde{f}(V)$ uniquely in a neighbourhood of S_c; it is a smooth function of V. Let us restrict the following discussion to this neighbourhood and introduce additional smooth functions of V:

$$\sigma(V) = \delta_0(\tilde{f}(V), V) \tag{4.2a}$$

$$\lambda(V) = 1 + \delta_2(\tilde{f}(V), V) \tag{4.2b}$$

$$\mu(V) = -\delta_3(\tilde{f}(V), V). \tag{4.2c}$$

On S_c functions $\lambda(V)$, $\mu(V)$ specialise to the corresponding quantities introduced above in (3.1). For $V \in S_c$ function σ vanishes. The set of parameter points $\sigma(V) = \sigma =$ constant is a smooth hypersurface S_σ, which approaches S_c for $\sigma \to 0$. The parameter σ characterises in a natural manner the distance of V from S_c, and therefore it will be referred to as the *separation parameter*. The set of points $\lambda(V) = \lambda =$ constant is also a smooth hypersurface S^λ in R_N. Since λ determines the critical exponents of the theory, equation (3.5*a*), it will be referred to as *exponent parameter*. The construction of the hypersurfaces S_σ and S^λ is trivial for the one-component model. Equations (1.4*b*), (2.6) and (2.7) imply

$$\sigma = (1-\tilde{f})^3 \sum_n v_n \tilde{f}^n - \tilde{f}(1-\tilde{f})^2 \tag{4.3a}$$

$$0 = (1-\tilde{f})^3 \sum_n n v_n \tilde{f}^{n-1} - (1-\tilde{f}) \tag{4.3b}$$

$$\lambda = \tfrac{1}{2}(1-\tilde{f})^3 \sum_n n(n-1) v_n \tilde{f}^{n-2}. \tag{4.3c}$$

One can consider the pair of equations (4.3*a*, *b*) as linear equations for two parameters, (v_1, v_2) say. Solution yields S_σ in a parameter representation; $\tilde{f}$ and v_n for $n \neq 1, 2$ are the hypersurface parameters. Similarly, the pair of equations (4.3*b*, *c*) yield S^λ. The transformation from the N *ad hoc* control parameters $(v_1, \ldots, v_N)$ to $(\sigma, \lambda, v_3, \ldots, v_N)$

can be considered as a coordinate transformation in parameter space. Then σ and λ appear as natural mathematical control parameters of our problem. The other $(N-2)$ parameters $(v_3, \ldots, v_N)$ will be irrelevant for the discussion of the scaling laws. They enter as function μ in the leading corrections to scaling only.

Under realistic experimental conditions one cannot vary control parameters like v_n arbitrarily. Rather one can manipulate only a small number of parameters like temperature, density, composition or magnetic field. To study the Whitney fold it is sufficient to consider just one parameter, say the temperature T. Changes of T are then described by a path C in parameter space R_N: $V = V(T)$. Let us assume that C crosses S_c for $T = T_c$. Near the transition point one can approximate C by a straight line, specified by its tangent vector $\boldsymbol{n}$:

$$\boldsymbol{V}(T) = \boldsymbol{V}_c + \varepsilon \boldsymbol{n} + O(\varepsilon^2). \tag{4.4}$$

Here $\varepsilon = (T_c - T)/T_c$ denotes the physical separation parameter. The normal vector $\boldsymbol{n}^c$ of the transition hypersurface S_c at $\boldsymbol{V}_c$ reads:

$$n_l^c = f_c^{l-1}/\alpha \qquad l = 1, \ldots, N. \tag{4.5}$$

Here α is a positive normalisation constant. Vector $\boldsymbol{n}^c$ points in the direction of increasing couplings. Let us anticipate that C crosses S_c transversely so that large T correspond to small couplings: $\boldsymbol{n} \cdot \boldsymbol{n}^c > 0$. Then the strong-coupling side of S_c, the glassy phase, corresponds to $\varepsilon > 0$. The liquid side is characterised by $\varepsilon < 0$ and $\varepsilon = 0$ denotes the critical point. Let us expand equation (4.1) in terms of $\delta\tilde{f} = \tilde{f} - f_c$, $\delta v_l = v_l - v_l^c$. One finds

$$\delta\tilde{f} = \left[\sum_l n_l l f_c^{l-1}\right](1 - f_c)^3[2(1-\lambda)]^{-1} \cdot \varepsilon + O(\varepsilon^2). \tag{4.6}$$

For the expansion of σ one has to distinguish between type A and type B transitions (Götze 1984). The first one occurs at the hypersurface $v_1 = 1$; there $f_c = 0$ and $\lambda = v_2^c$. Thus

$$\sigma = \tfrac{1}{4}[n_1^2/(1 - v_2^c)]\varepsilon^2 + O(\varepsilon^3) \qquad \text{type A.} \tag{4.7}$$

So the separation parameter is positive on both sides of S_c. In leading order in ε, σ is symmetric with respect to changes of ε to $-\varepsilon$. For the second type there holds $f_c > 0$. One obtains

$$\sigma = [f_c(1 - f_c)^3 \alpha \boldsymbol{n} \cdot \boldsymbol{n}^c]\varepsilon + O(\varepsilon^2) \qquad \text{type B.} \tag{4.8}$$

In this case the separation parameter varies linearly across the transition hypersurface S_c. It is positive on the strong-coupling side and negative on the weak-coupling one.

The concepts introduced above are illustrated for the F_{12} model and the F_{13} model in figures 1(*a*) and (*b*). The heavy full curves are the type B transition lines, and the type A transition lines are shown broken. The endpoints are indicated by open circles. It is a non-generic accident of the F_{12} model that the A transition endpoint coincides with the endpoint of the B transition. The coordinate lines S^λ, S_σ are shown by fine full curves. For the F_{13} model the σ lines for the A transition are not shown in order not to overload the figure. The type A transition for the F_{13} model was discussed previously (Götze and Sjögren 1984, Götze and Haussmann 1988) and will not be reconsidered here. The $\lambda = 1$ lines, which mark the boundary of the natural coordinate system, are shown as dotted curves.

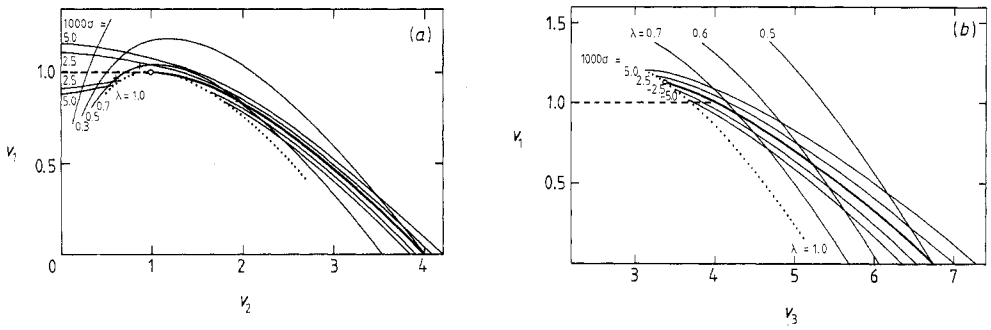

Figure 1. (*a*) Natural coordinate system λ, σ for the F_{12} model. The heavy full curve is the transition line $\sigma = 0$ for type B transition. The broken line is the transition line $\sigma = 0$ for type A transition. The fine full curves denote the constant λ and σ lines for $\lambda = 0.3, 0.5, 0.7$ and $\sigma = \pm 0.0025 \pm 0.0050$ respectively. The dotted curve is the line $\lambda = 1$, and the small circle denotes the endpoint $v_1 = v_2 = 1$. (*b*) Same as (*a*) but for the F_{13} model.

Exploiting the natural coordinates, equation (2.5) reads

$$-(\sigma/z) + \lambda \mathrm{LT}[G(t)^2](z) + zG(z)^2 + (\gamma_3 - \mu)\mathrm{LT}[G(t)^3](z) - \gamma_3 z^2 G(z)^3 + \ldots = 0. \tag{4.9}$$

From the discussion of the critical behaviour in the preceding section one expects that the first line determines the leading contribution $G_0(t)$ to the correlator $G(t)$, while the second line yields the first correction. One gets

$$G_0(t) = c_\sigma g_\pm(t\omega_\sigma) \qquad c_\sigma = (|\sigma|)^{1/2} \qquad \sigma \gtrless 0 \tag{4.10a}$$

where functions $g_\pm$ obey the equation

$$\mp \hat{z}^{-1} + \lambda \mathrm{LT}[g_\pm(\hat{t})^2](\hat{z}) + \hat{z} g_\pm(\hat{z})^2 = 0 \tag{4.10b}$$

and $\hat{t} = t\omega_\sigma, \hat{z} = z/\omega_\sigma$. Function $G_0(t)$ is given by a scaling law. Changes of the separation parameter σ merely enter via changes of the correlation scale c_σ and the frequency scale ω_σ. The master functions $g_\pm$, to be determined from the scaling equation (4.10*b*), do not depend on σ; but notice that they depend on the exponent parameter λ. Because of the scale invariance of (4.9) or (4.10*b*), ω_σ cannot be derived from those equations. To fix it we notice that for large rescaled frequencies $|\hat{z}| = |z/\omega_\sigma| \gg 1$ or short rescaled times $\hat{t} = t\omega_\sigma \ll 1$ the first term in (4.10*b*) can be neglected and thus one comes back to (3.4): $g_\pm(\hat{t}) \propto 1/\hat{t}^a$. Imposing the normalisation

$$g_\pm(\hat{t})\hat{t}^a \to 1 \qquad \hat{t} \to 0 \tag{4.10c}$$

solution (4.10*a*) is compatible with result (3.6*a*) if and only if

$$\omega_\sigma = |\sigma|^{1/2a}/t_0. \tag{4.10d}$$

The solution of equation (4.10*b*) can be studied by series expansion (Götze 1984). The scaling equation (4.10*b*) exhibits a $1/\hat{z}$ singularity. For $\sigma > 0$ it can be eliminated by the substitution

$$g_+(\hat{t}) = (1 - \lambda)^{-1/2} + 2(1 - \lambda)^{1/2} g(\hat{t}). \tag{4.11a}$$

The first term leads to a $\sigma^{1/2}$ variation of the form factor at the glass instability point:

$f = \tilde{f} + c_\sigma(1-\lambda)^{-1/2}$, $\sigma \to +0$. The new master function then obeys the modified scaling equation

$$-g(\hat{z}) + \lambda \mathrm{LT}[g(\hat{t})^2](z) + \hat{z}g(\hat{z})^2 = 0. \tag{4.11b}$$

In particular one finds for the zero-frequency spectrum

$$g''(\hat{\omega} = 0) = \lambda \int_0^\infty \mathrm{d}\hat{t}\, g(\hat{t})^2. \tag{4.11c}$$

This result indicates that $g(\hat{z})$ is regular for small $\hat{z}$ implying exponential decay of $g(\hat{t})$ for large $\hat{t}$. The $1/\hat{z}$ singularity in equation (4.10*b*) for $g_-(\hat{t})$ implies an even stronger singularity for the correlator (Götze 1984) which is equivalent to the von Schweidler law

$$g_-(\hat{t} \gg 1) = -B\hat{t}^b \tag{4.12a}$$

$$g_-(|\hat{z}| \ll 1) = (B/\hat{z})\Gamma(1+b)/(-\mathrm{i}\hat{z})^b. \tag{4.12b}$$

The von Schweidler exponent b is also determined by the exponent parameter: $\lambda = \Gamma(1+b)^2/\Gamma(1+b)$, $0 < b \leqslant 1$. If one replaces σ and $\tilde{f}$ by the leading asymptotic expressions near the transition, equations (4.6), (4.7) and (4.8), the preceding results reduce to the ones discussed in the previous papers (Götze 1984, 1985). To get an understanding of the relevance of $G_0(t)$ we write $G(t) = G_0(t) + \delta G(t)$ and reformulate equation (4.9) as an equation for δG. Obviously, $\delta G(t)$ is proportional to $c_\sigma^2 = |\sigma|$ and one can write

$$G(t) = c_\sigma[g_\pm(t\omega_\sigma) + c_\sigma f_\pm(t\omega_\sigma) + \ldots]. \tag{4.13}$$

Functions $f_\pm$ are again independent of the separation parameter. They describe the leading correction to the scaling law and are to be obtained from the linear equation:

$$2\lambda \mathrm{LT}[g_\pm(\hat{t})f_\pm(\hat{t})](\hat{z}) + 2\hat{z}g_\pm(\hat{z})f_\pm(\hat{z}) = \gamma_3\hat{z}^2 g_\pm(\hat{z})^3 - (\gamma_3 - \mu)\mathrm{LT}[g_\pm(\hat{t})^3](\hat{z}). \tag{4.14}$$

Higher-order contributions to equation (4.13) can be derived similarly. The result for $G(t)$ implies

$$\lim_{\sigma \to \pm 0} \hat{G}(\hat{t}) = g_\pm(\hat{t}) \qquad \hat{G} = G/c_\sigma \qquad \hat{t} = t\omega_\sigma. \tag{4.15}$$

In the scaling limit, $\sigma \to 0$ and $t \to \infty$, $z \to 0$ such that the rescaled time $\hat{t} = t\omega_\sigma$ and rescaled frequency $\hat{z} = z/\omega_\sigma$ are fixed, the rescaled correlator $\hat{G} = G/c_\sigma$ approaches the master function $g_\pm$. One checks easily that for the specified limit the ratios on the left-hand side of inequalities (2.4) vanish. Hence on scale ω_σ the scaling law $G_0(t)$ solves the dynamic equation (2.5) for β relaxation in the limit $\sigma \to 0$. Furthermore the ratio of the left-hand side to the right-hand side of equation (2.1*a*) vanishes so that equation (2.5) is equivalent to the original equation of motion (1.4).

The scaling law is a good approximation to the solution of the mode-coupling equations if the second contribution in the brackets of equation (4.13) can be neglected in comparison to the first one. For short rescaled times equation (4.14) can be solved easily after substitution of equation (4.10*c*):

$$f_\pm(\hat{t})\hat{t}^{2a} \to \tfrac{1}{2}c \qquad \hat{t} \to 0. \tag{4.16}$$

Constant c is given by equation (3.6*b*) and so $f_\pm$ reproduces for $t\omega_\sigma \gg 1$ the leading correction to the critical decay, equation (3.6*a*). Because of equation (4.11*a*) function g_+ exhibits a non-ergodicity pole: $g_+(\hat{z})\hat{z} \to -(1-\lambda)^{-1/2}$ for $\hat{z} \to 0$. This pole implies a

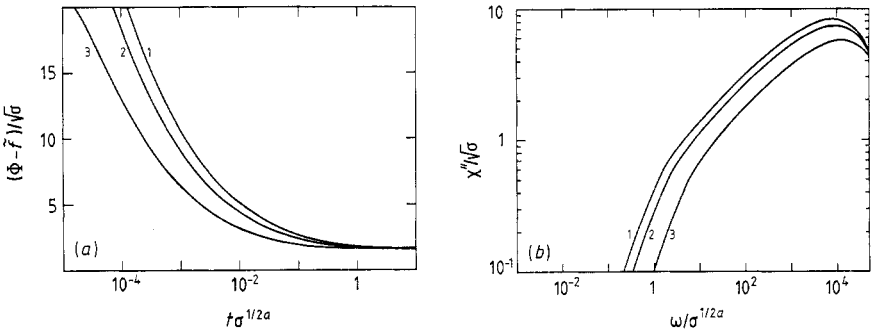

Figure 2. (*a*) Plot of $(\Phi - \tilde{f})/\sigma^{1/2}$ as a function of rescaled time $t\sigma^{1/2a}$ of the F_{12} model for $\sigma = 0.001, \lambda = 0.7$. The curves 1, 2, 3 correspond to $(v_1, v_2) = (0.965, 0.600), (1.033, 0.857), (0.856, 1.939)$, $\nu = 5\Omega$. (*b*) Plot of $\chi''/\sigma^{1/2}$ as a function of $\omega/\sigma^{1/2a}$ for the same data as in (*a*).

similar one for f_+, which can easily be evaluated from equation (4.14). As a result one gets in analogy to equation (4.11*a*):

$$f_+(\hat{t}) = -\tfrac{1}{2}\mu(1-\lambda)^{-2} + f(\hat{t}) \tag{4.17}$$

where $f(\hat{z})$ is regular for small frequencies. Because of equation (4.13) the non-ergodicity contribution from f_+ yields a contribution to the glass form factor f which is proportional to σ. Similarly to the reasoning of § 3 we conclude: if the neighbourhood of the endpoint is avoided the scaling law result (4.10*a*) describes the solution for $\sigma > 0$, provided $t \gg t_m$, $|z| \ll 1/t_m$ and $|\sigma| < 0.01$ so that the relevant correction term c_σ in equation (4.13) is smaller than 10%. In the specified region $G(t)$ is determined completely by the two cordinates σ and λ. On the whole hypersurface S^λ the solution is fixed by σ, and changes of σ merely enter via changes of scales. This holds except that t_0 in equation (4.10*b*) will vary somewhat with V. The scaling property is exemplified in figures 2(*a*) and (*b*) for the F_{12} model for $\lambda = 0.7$ and $\sigma = 0.001$. Shown are the rescaled correlators $[\Phi(t) - \tilde{f}]/\sigma^{1/2}$ and the rescaled susceptibility spectra $\chi''/\sigma^{1/2}$ as functions of the rescaled time $t\sigma^{1/2a}$ or rescaled frequency $\omega/\sigma^{1/2a}$, respectively. The three curves correspond respectively to parameters on the liquid side of the type A transition, on the glass side of the type A transition, and on the glass side of the type B transition. The corresponding parameter vectors (v_1, v_2) are indicated in figure 1(*a*) by crosses. If $G(t)$ obeyed the scaling law exactly, the three curves shown in the figures would coincide. The regular variations of t_0 with V imply that the curves exhibit a parallel shift. Redoing this shift the curves of figure 2(*a*) coincide completely. This holds also for the curves of figure 2(*b*) for $\omega/\sigma^{1/2a} < 10^4$. For large frequencies the susceptibility spectra show a peak. It reflects the motion on microscopic scales which is outside the range of validity of the β relaxation theory. The von Schweidler divergence of $g_-(\hat{z})$ for $\hat{z} \to 0$ implies an even stronger low-frequency divergence for $f_-(\hat{z})$. Substitution of equations (4.12) into (4.14) yields

$$f_-(\hat{t} \gg 1) = \tfrac{1}{2}B_1\hat{t}^{2b} \tag{4.18a}$$

where B_1/B^2 is given by equation (3.6*b*) with a replaced by $-b$. Substitution of these results into equation (4.13) leads to

$$G(t\omega_\sigma \gg 1) = -B(t/\tau)^b + \tfrac{1}{2}B_1(t/\tau)^{2b}. \tag{4.18b}$$

Here $1/\tau = \omega_\sigma|\sigma|^{1/2b} = |\sigma|^\gamma/t_0$, with $\gamma = 1/(2a) + 1/(2b)$, is a new frequency scale. The β relaxation scaling law for $\sigma < 0$ is thus restricted to $|z\tau| \gg 1$ or $t/\tau \ll 1$. This restriction

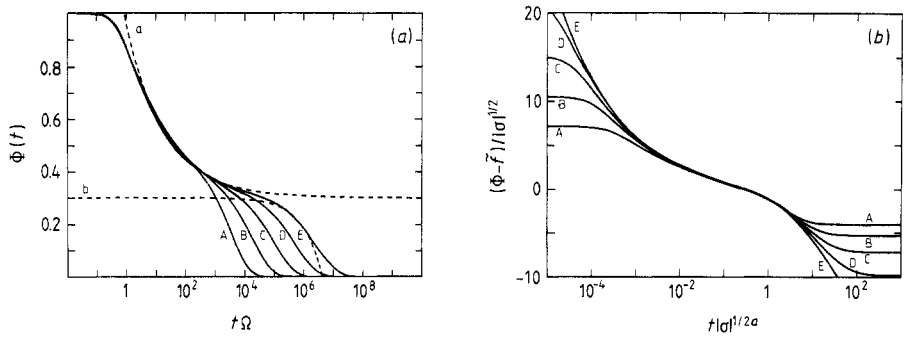

Figure 3. (*a*) The function $\Phi(t)$ versus $\log_{10}(t\Omega)$ for the F_{12} model for $\lambda = 0.7$, $\nu = 5\,\Omega$ and $-\sigma = 0.008, 0.004, 0.002, 0.001, 0.0005$ (full curves A–E). The broken curve labelled a gives the function $f_c + A/t^a$ with $A = 0.65$ and the broken curve labelled b gives the function $f_c - B(t/\tau)^b$ with $B = 1.30$. (*b*) Plot of $(\Phi - \tilde{f})/|\sigma|^{1/2}$ as a function of $t|\sigma|^{1/2a}$ for the data of (*a*).

holds in addition to the ones derived above for $\sigma > 0$. The restriction is due to the α relaxation process, whose scale is $1/\tau$. What appears as leading correction to β scaling for large $t\omega_\sigma$ in equation (4.18*b*) is identical to the next-to-leading term in the short-time expansion of the α relaxation process, discussed in our previous work (Götze 1984, Götze and Sjögren 1987b). In figure 3(*a*) the relaxation curves $\Phi(t)$ for the F_{12} model are shown for parameter points on the line $\lambda = 0.7$. The separation parameters are $-\sigma = 0.008/2^n$ for $n = 0$–4. An initial microscopic variation according to equation (1.3) ($\nu = 5\Omega$) is observed for $\log_{10}(t\Omega) < 0.5$. Then all curves follow the critical decay law $f_c + A/(t\Omega)^a$ with $A = 0.65$, which is given as the broken curve in the figure with label a. This holds until the von Schweidler law $f_c - B(t/\tau)^b$ with $B = 1.3$ takes over. The latter is shown for $\sigma = -0.0005$ by the broken curve with label b. In figure 3(*b*) the results are replotted as $[\Phi(t) - \tilde{f}]/|\sigma|^{1/2}$ versus $t|\sigma|^{1/2a}$ in order to demonstrate the β relaxation scaling property.

Let us come back to the changes of the dynamics due to those more realistic parameter variations discussed above in connection with equation (4.4). Projection of the path C in the hyperplanes S^λ, S_σ gives smooth functions $\lambda(T)$ and $\sigma(T)$. For $T \simeq T_c$ the correlator is given by the scaling law (4.10). But not only is the separation parameter a complicated function of temperature but so is the exponent parameter. In particular the exponents themselves will depend on the control parameter: $a = a(T)$, $b = b(T)$. If the model is defined, all these functions can be evaluated. However, for realistic systems this is not possible at present, since the connection of the physical control parameter T with the mathematical ones, σ and λ, is determined by all microscopic details. Nevertheless, our theory yields results beyond a qualitative discussion. For given T two measurements can yield $\lambda(T)$, $\sigma(T)$. For example, the detection of the critical spectrum, $\chi''(\omega) \propto \omega^a$, equation (3.6*a*) yields $a(T)$ and from equation (3.5*a*) $\lambda(T)$ follows. Determining the crossover frequency of $\chi''(\omega)$ from the von Schweidler law $\chi''(\omega) \propto (\omega/\omega_\sigma)^{-b}$ to the critical law for $\sigma < 0$ or from the linear low-frequency increase $\chi''(\omega) \propto (\omega/\omega_\sigma)$ to the sublinear critical increase for $\sigma > 0$ yields ω_σ. Equation (4.10*a*) then determines σ itself up to an irrelevant scale t_0. Then the complete β spectrum is given for this temperature by our formulae. This implies, for example, that the von Schweidler exponent $b(T)$ should be related to $a(T)$ by $\Gamma(1+b)^2/\Gamma(1+2b) = \Gamma(1-a)^2/\Gamma(1-a)$. The ratio $\chi''(\omega = \omega_\sigma)/\omega_\sigma^a$ should be a constant. Near the transition one gets for type B transitions from equation (4.8), $\sigma(T)/\varepsilon \to \sigma_0 > 0$, $\lambda(T) \to \lambda < 1$. This implies simple power-law

results $c_\sigma \propto |\varepsilon|^{1/2}$, $\omega_\sigma \propto |\varepsilon|^{1/2a}$. The range of validity of these results is smaller than the one of the general theory. The asymptotic formula

$$G(t) \sim (\sigma_0|\varepsilon|)^{1/2} g_\pm(t(\sigma_0|\varepsilon|)^{1/2a}/t_0) \tag{4.19}$$

which was studied in the preceding papers, does not work as well as our more general expression, equation (4.10*a*). This is evident from the results shown in figure 3 in comparison with similar ones shown for the same model and $\lambda = 0.7$ in Götze and Sjögren (1988). In the latter case the transition line was crossed on a perpendicular path C. The deviations of $G(t)$ from the asymptotic law in this case are not really deviations from the scaling law. Rather they reflect variations of $\lambda(T) - \lambda(T_c)$. If for $\lambda < 1$ serious deviations from scaling laws are found, they reflect interesting phenomena, which cannot be described properly by a one-component model. An example will be discussed in the next section.

5. β relaxation peak

In the previous section it was shown that β relaxation of a one-component model can be described well by a scaling law, equation (4.10), provided proper coordinates (σ, λ) are introduced. One can show quite generally (Götze 1985) that for $\sigma \to 0$ in a multi-component model $\Phi_q(t) = f_q + h_q G_0(t)$. In this sense β relaxation is universal. However, the range of validity of the scaling law does not exhibit the same kind of universality. The corrections to scaling depend on f_q, h_q. So new parameters enter and new features of the spectra may occur. In this section an example will be discussed for the model defined in connection with equation (1.5). Let us start by identifying the problem more explicitly. Near the glass transition the dynamic equation is simplified by dropping $(z + i\nu_s)/\Omega_s^2$, as discussed in § 2. One can also express the correlator Φ in terms of $\tilde{f}$ and $G(t)$, equation (2.3). As a result one gets with $v_1 = \lambda_s \tilde{f}$:

$$\Phi_s(z)/[1 + z\Phi_s(z)] = v_1 \Phi_s(z) + N(z) \tag{5.1a}$$

$$N(z) = \lambda_s \mathrm{LT}[\Phi_s(t)G(t)]. \tag{5.1b}$$

Introducing a parameter $\tilde{f}_s$ as before in order to write $\Phi_s(t) = \tilde{f}_s + G_s(t)$, one can simplify the equations under the assumption

$$|zG_s(z)/(1 - \tilde{f}_s)| \ll 1. \tag{5.2a}$$

The result, which is the analogue to equation (2.5), reads:

$$\begin{aligned}(-1/z)[\tilde{f}_s(1 - \tilde{f}_s)^{-1} - \tilde{f}_s v_1] \\ + G_s(z)[(1 - \tilde{f}_s)^{-2} - v_1] - G(z)\lambda_s \tilde{f}_s \\ -\lambda_s \mathrm{LT}[G(t)G_s(t)](z) - (1 - \tilde{f}_s)^{-3} z G_s(z)^2 + \ldots = 0.\end{aligned} \tag{5.2b}$$

The pole term can be eliminated by choosing $\tilde{f}_s = 1 - v_1^{-1}$. In leading order G_s is then found by substituting the leading result, equation (4.10), for G and requiring the second line to vanish:

$$G_s^0(t) = G_0(t)/(\lambda_s \tilde{f}^2). \tag{5.3}$$

So the correlator G_s follows the same scaling law as $G(t)$, except for a trivial scale factor. One can show easily that in the scaling limit, explained in connection with equation

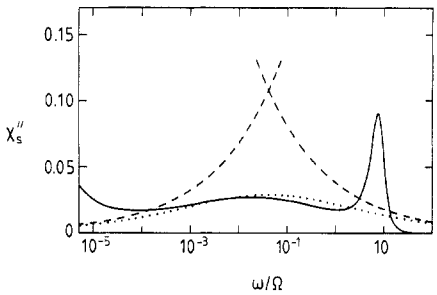

Figure 4. Plot of $\chi_s''(\omega)$ versus $\log_{10}(\omega/\Omega)$ for $\lambda_s = 15$, $\Omega_s = 2\Omega$, $\nu_s = 5\Omega$, $\sigma = -0.0005$, $\lambda = 0.7$, $\nu = 5\Omega$ (full curve). The broken curves show the asymptotic laws proportional to ω^a and ω^{-a} respectively. The dotted curve is the Cole–Cole law in equation (5.9*b*).

(4.15), the result G_s^0 provides a solution of our problem. In this limit, for example, the last line in equation (5.2*b*) drops out. Let us recall the critical correlator, equation (3.6*a*):

$$G_0(z) = A(-1/z)\Gamma(1-a)(-iz/\Omega)^a \qquad |z| \gg \omega_\sigma. \tag{5.4a}$$

Hence the critical susceptibility spectrum reads:

$$\chi_s^{0''}(\omega) = A\Gamma(1-a)\sin(\tfrac{1}{2}\pi a)(\omega/\Omega)^a/\lambda_s f_c^2. \tag{5.4b}$$

In figure 4 the full curve reproduces part of our previous result for χ_s'' for $\lambda_s = 15$, $\nu_s = 5\Omega$, $\Omega_s = 2\Omega$, $\lambda = 0.7$ close to the transition point (Buchalla *et al* 1988). The parameters λ_s and Ω_s were chosen to illustrate a strong-coupling situation. The increasing broken curve is the expected critical spectrum, equation (5.4*b*). In this case the large λ_s yields a small $(1 - \tilde{f}_s)$ and therefore one comes in conflict with inequality (5.2*a*) for $\log_{10}(\omega/\Omega) \geqslant -4$. One can work out the leading correction to the critical spectrum of χ_s from equation (5.2*b*) as done in § 3. It is negative and dominates for $\omega/\Omega > 10^{-4}$. In conclusion, if $(1 - \tilde{f}_s)^{-1}$ becomes large a frequency window opens between ω_σ and Ω, where the scaling law (5.3) does not describe the relaxation of Φ_s. Figure 4 shows that $\chi_s''(\omega)$ is indeed quite different from the critical spectrum. It exhibits a resonance whose width is larger than five decades. Thus it describes a relaxation process with a distribution of relaxation rates extending over more than four decades. This is the β peak, often observed in dielectric loss experiments (Johari and Goldstein 1970, 1971). It can be analysed within our theory, because it is located in a frequency region where $G(t)$, the relevant input in equations (5.1), has the simple critical form of equation (5.4*a*).

Solving equation (5.1*a*) for Φ_s in terms of N yields:

$$\Phi_s(z) = (1/2zv_1)[-zN(z) + 1 - v_1 + W_-(z)W_+(z)]. \tag{5.5a}$$

Here the abbreviations are used

$$W_\pm(z) = [zN(z) - \alpha_\pm]^{1/2} \qquad \alpha_\pm = 1 + v_1 \pm 2v_1^{1/2}. \tag{5.5b}$$

This is equivalent to the expression for $\chi_s(z) = 1 + z\Phi_s(z)$:

$$\chi_s(z) = -2/[zN(z) - 1 - v_1 + W_-(z)W_+(z)]. \tag{5.5c}$$

In the limit of small $zN(z)$ we expand the roots in equation (5.5*a*) and obtain

$$\Phi_s(z) = (-\tilde{f}_s/z) + N(z)/[v_1(v_1 - 1)] \qquad |zN(z)| \ll \alpha_\pm. \tag{5.6a}$$

The leading contribution to $N(z)$ is then found by substituting $\Phi_s(t) = \tilde{f}_s$ into equation

(5.1*b*): $N(z) = \lambda_s \tilde{f}_s G(z)$. With equation (5.4*a*) one arrives at the desired low-frequency expression for the β peak:

$$\chi_s(z) = (-iz/\Omega)^a A\Gamma(1-a)/\lambda_s f_c^2 \qquad |zN(z)| \ll \alpha_\pm . \tag{5.6b}$$

The formula is equivalent to equation (5.4*b*) and the result is the increasing broken curve in figure 4. In the opposite limit for large $|zN(z)|$, we expand the roots in equation (5.5*c*) in order to get

$$\chi_s(z) = -1/[zN(z)] \qquad |zN(z)| \gg \alpha_\pm . \tag{5.7a}$$

This implies the substitution $\Phi_s(t) = 1$ in equation (5.1*b*), so that $N(z) = \lambda_s G(z)$. With equation (5.4*a*) one obtains the high-frequency expression for the β peak:

$$\chi_s(z) = (-iz/\Omega)^{-a}/[\lambda_s A\Gamma(1-a)] \qquad |zN(z)| \gg \alpha_\pm . \tag{5.7b}$$

Hence $\chi_s''(\omega)$ decreases with increasing frequency. The result is shown as the decreasing broken curve in figure 4. In conclusion, if $|z/(1-\tilde{f}_s)|$ is so large that condition (5.2*a*) is violated, the susceptibility spectrum crosses over from the sublinear critical increase $\chi_s'' \propto \omega^a$ to a decreasing power-law spectrum $\chi_s'' \propto 1/\omega^a$. The crossover causes the β peak and the power-law wings cause the broad distribution of relaxation rates. The two asymptotes intersect at a frequency

$$\omega_\beta = \Omega\{f_c/[A\Gamma(1-a)]\}^{1/a} \tag{5.8}$$

which gives an estimation of the position of the β peak. For our model the number in the curly braces is about 0.34. Since $1/a \sim 3$ one finds ω_β to be about 1.4 decades below Ω. We notice that for a larger value of the exponent parameter λ the exponent a would be smaller, and thus the β peak would be shifted to even lower frequencies.

To proceed beyond the evaluation of asymptotes for large and small frequencies, we want to solve the equations of motion for large v_1. One notices from equation (5.5*b*) that $W_+W_-/v_1 = [zN(z)/v_1 - 1] + O(1/v_1^{1/2})$. From equation (5.5*c*) one gets therefore $\chi_s(z)/v_1 = -1/[zN(z)/v_1 - 1] + O(1/v_1^{1/2})$. From equation (5.5*a*) one concludes that $\Phi_s(t) = 1 + O(1/v_1^{1/2})$ and thus equation (5.1*b*) yields $N(z) = \lambda_s[G(z) + O(1/v_1^{1/2})]$. Remembering $v_1 = \lambda_s \tilde{f}$ one arrives at the result:

$$\lim_{\lambda_s \to \infty} \chi_s(z)(\lambda_\beta \tilde{f}) = -1/\{[zG_0(z)/\tilde{f}] - 1\}. \tag{5.9a}$$

This formula yields the β relaxation dynamics for strong coupling for all frequencies and separation parameters σ, where the scaling law result, equation (4.10), is valid for Φ. Specialising to the region of critical dynamics one can substitute equation (5.4*a*) to get

$$\chi_s(z) = (1/\lambda_s \tilde{f})/[(-iz/\omega_\beta)^a + 1] \qquad \lambda_s \gg 1 \qquad \omega_\sigma \ll |z| \ll \Omega. \tag{5.9b}$$

This is the Cole–Cole susceptibility formula. It is thus found as an exact asymptotic implication of the mode-coupling theory. The range of validity is specified precisely. This formula shows that the β peak does not vary sensitively for T near the transition value. It exists on the glassy side $\sigma > 0$ as long as the critical spectrum for $\Phi(t)$ can be observed. It also exists for small σ on the liquid side of the transition. However with increasing $(T - T_c)/T_c$ it disappears soon, since the strong von Schweidler tail of the α relaxation peak will cover the β peak. Notice that formula (5.9*a*) describes this phenomenon completely as well. The dotted curve in figure 4 represents the Cole–Cole spectrum. The small discrepancies between the numerical solution and the analytical result (5.9*b*) are due to the corrections to the asymptotic expansion, which are pro-

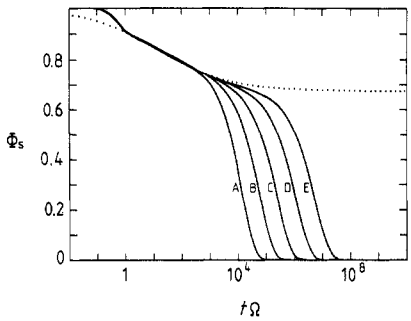

Figure 5. Plot of $\Phi_s(t\Omega)$ versus $\log_{10}(t\Omega)$ for $\lambda_s = 10$, $\Omega_s = \Omega$, $\nu_s = 5\Omega$. The parameters (λ, σ) are the same as used in figure 3. The dotted curve is the Mittag–Leffler function, equation (5.9*c*).

portional to $1/v_1^{1/2}$. The Laplace back-transform of the correlator corresponding to the Cole–Cole law is given by the Mittag–Leffler function $M_a[x] = \Sigma_n x^n/\Gamma(1 + na)$:

$$\Phi_s(t) = \tilde{f}_s + (1/\lambda_s \tilde{f}) M_a[-(t\omega_\beta)^a] \qquad \lambda_s \gg 1 \qquad t_m \ll t \ll \omega_\sigma^{-1}. \tag{5.9c}$$

This result is shown as a dotted curve in figure 5 for our model in comparison with the numerical solutions for $\Phi_s(t)$. The parameters for σ and λ are the same as those used in figure 3. For times exceeding the initial decay interval, $\Omega t \leqslant 1$, formula (5.9*c*) describes the correlators perfectly till the von Schweidler decay signals the start of the α relaxation process. The result in (5.9*b*) implies an interesting scaling property for the β peak. Plotting $\chi_s''(\omega)/\chi_s''(\omega_\beta)$ versus ω/ω_β all curves are predicted to fall on one master curve. Such a scaling behaviour has been observed experimentally for several substances with very symmetric master curves (Ishida *et al* 1962, 1965).

The universality features of the β relaxation allow the reduction of the general equations of motion (1.2) to the ones for schematic models (Götze 1985, 1987). So our results are valid for the most general cases studied so far for the dynamics of glass transitions within mode-coupling theories. They imply the existence of the β peak whenever $(1 - f_q)$ for one set of q values is much smaller than $(1 - f_q)$ for the other q values, as explained by Buchalla *et al* (1988). This holds in particular for the Bosse–Krieger model (Bosse and Krieger 1986) of a symmetric molten salt, as was also illustrated recently by numerical work (Bosse *et al* 1988). Our present formulae show how for this and similar cases $\Phi_q''(\omega)$ can be determined analytically. None of the models mentioned is realistic enough to evaluate the dielectric loss $\varepsilon''(\omega)$ for those glass formers for which β peaks have actually been measured. But at least for the representative class of experiments, where $\varepsilon''(\omega)$ is caused by polar molecules solved in non-polar glass formers, one can understand qualitatively that $\varepsilon''(\omega)$ is given by the tagged particle density susceptibility $\chi_s''(\omega)$. Therefore our formulae are of direct relevance for the experiment. In the specified case $\varepsilon''(\omega)\omega$ is given by the tagged particle transverse current relaxation spectrum for vanishing wavevector $\Phi_s^{\perp\,''}(\omega)$ (Forster 1975 p 303). The simplest pair modes having an overlap with the relevant variables are $j_s(\boldsymbol{q})\rho(-\boldsymbol{q})$, where j_s is the longitudinal tagged particle current and $\rho(q)$ is the coherent density fluctuation. Hence the mode-coupling approximation yields $\omega\varepsilon''(\omega) = \Sigma_q V(q)\mathrm{FT}[\ddot{\Phi}_{sq}(t)\Phi_q(t)]$. Here $V(q)$ is some vertex; as usual it weights most strongly the contribution from wavevectors q corresponding to short distances (Bengtzelius *et al* 1984). The dominant dipole relaxation is due to nearest-neighbour fluctuations. Within the β regime the leading con-

tribution to the specified mode-coupling integral is found by substituting $\Phi_q(t) \sim f_q^c$, $(\Phi_q^s(t) - f_q^s) = h_q^s G^s(t)$. As a result one indeed gets $\varepsilon''(\omega) = (\Sigma_q V(q) f_q^c h_q)\chi_s''(\omega)$, as anticipated above.

The Cole–Cole law is related to an exact limit distribution in renewal theory (Feller 1971). This observation as well as the connection of our general theory with path averagings in a potential landscape, discussed in § 2, allows us to give a probabilistic interpretation of our β relaxation result. Consider a tagged particle. Most of the time it will sit in a local potential minimum; it is trapped in some cage. Occasionally, spontaneous fluctuations will yield a rearrangement of the particle surroundings and thereby induce a jump to a different cage. Let us denote the time the particle spends in a particular configuration, the waiting time, by T. This time can also be viewed as the lifetime of the considered metastable state. It is a random variable with a certain distribution function $P(x) = \Pr[T \leq x]$. The number of jumps or renewals up to time t, N_t, is also a random variable with the distribution function $\Pr[N_t > r] = \Pr[T_1 + \ldots T_r < t] = P^{r*}(t)$, where P^{r*} denotes the convolution of $P(t)$ with itself r times. For large times $P^{r*}(t)$ will tend to a limit distribution, whose properties depend on $P(x)$. Let us consider the case where $P(x)$ exhibits a power-law decrease for large x, specified by an exponent $0 < a < 1$:

$$1 - P(x) \sim x^{-a}. \tag{5.10a}$$

Then one gets (Feller 1971, p 373)

$$\Pr[N_t > (2-a)(t/x)^a/a] \to F_a(x). \tag{5.10b}$$

Here $F_a(x)$ is a one-sided stable distribution, defined as the spectral density of a Kohlrausch decay process (Feller 1971, ch 13):

$$\exp(-t^a) = \int_0^\infty e^{-tx} F_a'(x)\, dx. \tag{5.10c}$$

So from (5.10*b*) one finds for large times

$$\Pr[(a/(2-a))N_t < x] =: G(t,x) = 1 - F_a(tx^{-1/a}). \tag{5.11a}$$

Function $G(t,x)$ is related to the Mittag–Leffler function (Feller 1971, p 453):

$$\int_0^\infty e^{-px}\, \partial_x G(t,x)\, dx = M_a(-pt^a). \tag{5.11b}$$

So our result (5.9*c*) is given as average over the number of renewals up to time t, N_t:

$$\Phi_s(t) = \tilde{f}_s + (1/\lambda_s \tilde{f}) E[\exp(-p_a N_t)]. \tag{5.12}$$

Here $p_a = \tilde{f}a/[A\Gamma(1-a)(2-a)]$ and $E[\ldots]$ denotes an expectation value with respect to the distribution defined in equation (5.11*a*). Hence the result for the β relaxation peak is equivalent to a distribution of waiting times characterised by equation (5.10*a*). This distribution function has no finite moments. In particular the expectation of the waiting time itself diverges: $E[T] = \infty$. The particle can be trapped for an arbitrarily long time. The renewal periods make up a Cantor-like set Z_a with Hausdorff dimension a. Imagining the renewal periods to trigger a clock which runs on the set Z_a, one can define a stochastic time $\Theta_a(t)$ with the same distribution as N_t (Karlin and Taylor 1981 ch 15, Sjögren 1989). So alternatively one can say that the β peak reflects relaxation but with the stochastic time $\Theta_a(t)$ replacing real time.

6. Conclusions

The phase transitions obtained from the non-linear mode-coupling equation for the dynamics of strongly coupled particles can be related to certain singularities defined in parameter space (Götze and Haussmann 1988). The simplest of those singularities, the Whitney folds, are studied in this paper. They lead to a picture where the dynamics is ruled by two power laws and by two corresponding frequency scales, given by two exponents a and b. We have introduced a system of natural coordinates. Two of them, the exponent parameter λ and the separation parameter σ, are the relevant ones for the discussion of the β relaxation dynamics. It is possible to define hyperplanes S^λ in parameter space where the exponents a, b are fixed. Owing to the variation of a physical control parameter like temperature T, the system will move on a path C in control parameter space, which intersects the transition hypersurface S_c for $T = T_c$. The path will in general not be located on S^λ and this implies that the exponent parameter will depend on temperature $\lambda = \lambda(T)$, and so will the exponents $a = a(T)$, $b = b(T)$. In practice this will introduce large corrections to the asymptotic scaling laws, which refer to $\lambda(T_c)$. This was demonstrated in previous calculations (Götze and Sjögren 1988). In a two-component system the β relaxation spectra for the charge, say, may be quite different from the ones for the density. It may exhibit a β peak above the α peak (Buchalla *et al* 1988, Bosse *et al* 1988). In the limit of strong coupling between charge and mass fluctuations, we found that the β peak is exactly described by a Cole–Cole law. This result holds also when all wavevector dependences are taken into account. Since the Cole–Cole law results as a limit distribution in renewal theory, our result is consistent with a picture of particle motion in an energy landscape. The stochastic lifetimes of the metastable states, visited by the tagged particle, are found to have an algebraic long-time tail x^{-a}. Since $a \leqslant \frac{1}{2}$ the distribution of waiting times does not have finite moments and so there exist many low-lying almost degenerate metastable states. The renewal periods where the system jumps between different metastable states define a Cantor-like set on the time axis with fractal dimensionality a. In previous work the α relaxation was also described by a Cole–Cole law but with the von Schweidler exponent b replacing a (Götze and Sjögren 1987b). Thus there is a large time region covering the whole β relaxation process and a major part of the α relaxation, which is described by the renewal processes. Since the α and β processes overlap in the von Schweidler region, the two renewal processes are closely related. The crossover of the spectral exponents from a to b implies a change of the fractal dimensionality for the renewal processes.

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References

Arnold V I 1986 *Catastrophe Theory* 2nd edn (Berlin: Springer)
Bengtzelius U 1986 *Phys. Rev.* A **34** 5059

Bengtzelius U, Götze W and Sjölander A 1984 *J. Phys. C: Solid State Phys.* **17** 5915
Bosse J and Krieger U 1986 *J. Phys. C: Solid State Phys.* **19** L609
Bosse J, Krieger U and Thakur J S 1988 Preprint
Buchalla G, Dersch U, Götze W and Sjögren L 1988 *J. Phys. C: Solid State Phys.* **21** 4239
DeRaedt H and Götze W 1986 *J. Phys. C: Solid State Phys.* **19** 2607
Feller W 1971 *An Introduction to Probability Theory and its Applications* 2nd edn, vol II (New York: Wiley)
Forster D 1975 *Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions* (Reading, MA: Benjamin)
Frick B 1988 *Polymer Motion in Dense Systems* Springer Tracts in Modern Physics, in press (Berlin: Springer)
Frick B, Richter D, Petry W and Buchenau U 1988 *Z. Phys.* B **70** 73
Fujara F and Petry W 1987 *Europhys. Lett.* **4** 921
Götze W 1984 *Z. Phys.* B **56** 139
—— 1985 *Z. Phys.* B **60** 195
—— 1987 *Amorphous and Liquid Materials* ed. E Lüscher, G Fritsch and G Jaccuci (Dordrecht: Martinus Nijhoff)
Götze W and Haussmann R 1988 *Z. Phys.* B **72** 403
Götze W and Sjögren L 1984 *J. Phys. C: Solid State Phys.* **17** 5759
—— 1987a *Z. Phys.* B **65** 415
—— 1987b *J. Phys. C: Solid State Phys.* **20** 879
—— 1988 *J. Phys. C: Solid State Phys.* **21** 3407
Ishida Y, Matsuo M and Yamafuji K 1962 *Kolloid Z.* **180** 108
Ishida Y, Yamafuji K and Shimada K 1965 *Kolloid Z.* **200** 49
Johari G P and Goldstein M 1970 *J. Chem. Phys.* **53** 2372
—— 1971 *J. Chem. Phys.* **55** 4245
Karlin S and Taylor H M 1981 *A Second Course in Stochastic Processes* (New York: Academic)
Kirkpatrick T R and Thirumalai D 1988 *Phys. Rev.* B **37** 5342
Knaak W, Mezei F and Farago B 1988 *Europhys. Lett.* **7** 529
Krieger U and Bosse J 1987 *Phys. Rev. Lett.* **59** 1601
Kubo R 1957 *J. Phys. Soc. Japan* **12** 570
Leutheusser E 1984 *Phys. Rev.* A **29** 2765
Mezei F, Knaak W and Farago B 1987a *Phys. Rev. Lett.* **58** 571
—— 1987b *Phys. Scr.* T **19** 363
Richter D, Frick B and Farago B 1988 *Phys. Rev. Lett.* **61** 2465
Sjögren L 1986 *Phys. Rev.* A **33** 1254
—— 1989 *Z. Phys.* B **74** 353
Wong J and Angell C A 1976 *Glass Structure by Spectroscopy* (New York: Dekker)