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Integral equation approach to condensed matter relaxation

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Abstract. A model of relaxation in supercooled and entangled polymer liquids is developed starting from an integral equation describing relaxation in liquids near thermal equilibrium and probabilistic modelling of the dynamic heterogeneity presumed to occur in these complex fluids. The treatment of stress relaxation considers two types of dynamic heterogeneity—temporal heterogeneity reflecting the intermittency of particle motion in cooled liquids and spatial heterogeneity or particle clustering governed by Boltzmann's law. Exact solution of the model relaxation integral equation by fractional calculus methods leads to a two parameter family of relaxation functions for which the memory indices (β, ϕ) provide measures of the influence of the temporal and spatial heterogeneity on the relaxation process. The exponent β is related to the geometrical form of the spatial heterogeneity. Relaxation function classes are identified according to the asymptotics of the $\psi(t; \beta, \phi)$ functions at long and short times and their integrability properties. The integral equation model for relaxation provides a framework for understanding the existence of 'universality' in condensed matter relaxation under restricted circumstances.

Recently, it has become appreciated that patterns of relaxation found in polymer materials are observed in a much broader class of substances (glasses, colloids, etc) and this has prompted speculations about the 'universality' of disordered material relaxation [1, 2]. A general model of condensed matter relaxation has been developed to understand these observed regularities [3]. We start from a formally exact integral equation describing relaxation in Hamiltonian dynamical systems (material systems) near thermal equilibrium [4]. Probabilistic reasoning, utilizing Feller's 'fluctuation theory of recurrent events' [5], specifies the functional form of the memory kernel appropriate to describing homogeneous materials where the rate process governing relaxation can be 'regular' or 'intermittent'. The relaxation integral equation obtained involves fractional order differential operators I_t^ϕ where the 'critical exponent' ϕ characterizes the degree of intermittency in the relaxation process. Exact solution of the relaxation function leads to the Cole–Cole function [6] that is commonly reported in empirical descriptions of relaxation in condensed (solid) materials. An extension of the model [3] to include dynamical heterogeneity arising from equilibrium molecular clustering leads to a relaxation integral equation involving a more general class of fractional differential operators. These operators depend on an additional memory parameter β that [3] argues to be related to the geometrical form of the clusters (lines, sheets, compact clumps). Relaxation function 'universality classes' ('strong mixing', 'weak mixing', 'non-ergodic') are defined in terms of the asymptotic time decay and integrability properties of these relaxation functions.

In developing our probabilistic model of condensed matter relaxation we invoke minimal assumptions in order to make the description as general as possible. First, we assume that our material can be described by equilibrium thermodynamics. The existence of equilibrium

implies that correlations arising from small perturbations or spontaneous thermal fluctuations decay with time. Specifically, autocorrelation functions for large scale observable properties of the material, describing the rate of ‘mixing’ of the dynamical system, vanish at long times. Transport properties are defined through integrals of these autocorrelation functions so the integrability of these functions is also a concern in classifying relaxation in condensed materials. Finally, we invoke the condition of stationarity so that results of our measurements do not depend on when they are performed.

Formal calculations based on these general conditions lead to a general functional relation describing autocorrelation functions $\psi(t)$ for long wavelength observable properties A of our condensed material. In particular, if we normalize $A(t)$ so that its average value is zero, then the dimensionless autocorrelation function of $A(t)$,

$$\psi(t) \equiv \langle A(t)A(0) \rangle / \langle A^2(0) \rangle \quad (1)$$

obeys the integral equation [3, 4, 7, 8],

$$d\psi(t)/dt = - \int_0^t d\tau k(|t - \tau|)\psi(\tau) \quad \psi(0) = 1 \quad (2)$$

where $\psi(t) = 0$ for $t < 0$ for a ‘small’ applied perturbation. The symmetric memory kernel ($k(t, \tau) = k(\tau, t)$) is associated with the assumption of constant energy and stationarity, leading to an invariance of equation (2) under time inversion ($t \rightarrow -t$) and time translation ($t \rightarrow t + a$). Although equation (2) has sufficient generality for describing condensed matter relaxation processes, the specification of the memory kernel is difficult from first principles [3, 7]. This situation is helped somewhat from a phenomenological standpoint by the sensitivity of $\psi(t)$ to the form of the memory kernel $k(t)$.

The usual method of modelling $k(t)$ involves an approach patterned after the Langevin model of Brownian motion. A representative particle in the material is subjected to fluctuation forces exerted by its molecular environment and the time averages of these fluctuating forces is related to $k(t)$ by a fluctuation-dissipation theorem. Here we follow a different strategy, since our interest is in studying general classes of relaxation functions appropriate to describing long wavelength condensed matter relaxation.

Feller introduced a general theory of ‘return to equilibrium’ in dynamical processes governed by a random evolution [5]. The theory assumes that the relaxation events giving rise to the relaxation process occur as independent random variables in time. This assumption is compatible with our ‘mixing’ and ‘stationarity’ conditions for condensed matter relaxation. A heuristic physical motivation for describing the dynamical evolution of a material composed of interacting particles as a random walk in phase space is discussed by Uhlenbeck [9]. This type of model leads to an intuitive picture of ‘mixing’ in many-body systems and to relaxation event times that occur as independent random variables. The intermittency of these fluctuations has important implications for the character of the relaxation process and general ‘universality classes’ of relaxation naturally emerge from this approach.

We can establish a connection between $\psi(t)$ and ‘renewal theory’ by integrating both sides of equation (2) from 0 to t to obtain the ‘survival renewal equation’,

$$\psi(t) = 1 - \int_0^t d\tau \mathcal{R}(t, \tau)\psi(\tau) \quad \mathcal{R}(t, \tau) = \mathcal{R}(|t - \tau|) \quad (3a)$$

$$\mathcal{R}(t) = \int_0^t d\tau k(\tau). \quad (3b)$$

Equation (3) first arose in the context of describing the decay in the relative number of charter members of an insurance group, where $\mathcal{R}(t)$ describes the rate at which members drop out through death and where new members are added to keep the total number of policy holders

constant. This type of equation can be translated to many contexts (population dynamics, replacement of industrial equipment, etc), but here we should think of $\psi(t)$ as the probability that the initial state of the dynamical system property $A(0)$ persists (i.e., 'survives') up to time t .

The main object of modern 'renewal theory' is the probabilistic modelling of the 'renewal rate' $\mathcal{R}(t)$, taken to be the kernel of equation (3a). The continuum limit of Feller's classical 'fluctuation theory of recurrent events' [5] provides an integral equation for the average rate of 'renewal events' governing the relaxation process,

$$\mathcal{R}(t) = p(t) + \int_0^t d\tau p(|t - \tau|)\mathcal{R}(\tau). \quad (4)$$

$p(t)$ is the probability density describing the (first-passage) time between relaxation increment events. The solution of this equation gives the average rate $\mathcal{R}(t)$ of the random process governing the large scale relaxation process. It is emphasized that the assumption of the independence of the relaxation events restricts the modelling to large scale relaxation processes of equilibrium materials.

The occurrence of universality in $\psi(t)$ and $\mathcal{R}(t)$ in this model of condensed matter relaxation derives from the observation that the solution $\mathcal{R}(t)$ from equation (4) for large t depends only on the existence of $p(t)$ moments,

$$\langle t^n \rangle = \int_0^\infty d\tau p(\tau)\tau^n. \quad (5)$$

There are functional limit theorems governing the classes of $\mathcal{R}(t)$ that arise from this probabilistic model. Three general cases occur, (a) $\langle t^2 \rangle, \langle t \rangle < \infty$, (b) $\langle t^2 \rangle \rightarrow \infty, \langle t \rangle < \infty$ and (c) $\langle t^2 \rangle, \langle t \rangle \rightarrow \infty$, corresponding to different degrees of intensity in the fluctuations governing the relaxation process.

(a) In the case where $\langle t^2 \rangle < \infty$, the relaxation events occur with a well-defined average period $\langle t \rangle < \infty$, leading to a relatively rapid mixing (i.e., $\psi(t \rightarrow \infty) = 0$). If we take, for example, the relaxation process to occur as a Poisson process ($p(t) = e^{-t/\tau_0}/\tau_0$), then equation (4) gives a constant rate [3, 5],

$$\mathcal{R}(t) = 1/\tau_0. \quad (6a)$$

Inserting this result into equation (3) implies an exponential decay, $\psi(t) = e^{-t/\tau_0}$. More generally, $\mathcal{R}(t)$ for any $p(t)$ with a finite second moment has the asymptotic dependence,

$$\mathcal{R}(t) \sim 1/\tau_0 + C_1/t \quad t \rightarrow \infty \quad (6b)$$

where C_1 depends on $\langle t \rangle$ and $\langle t^2 \rangle$. There is then a rapid approach to the constant rate in equation (6a). Exponential decay ('strong mixing') is commonly found in idealized models of condensed matter relaxation.

(b) In the case where $\langle t^2 \rangle \rightarrow \infty$ and $\langle t \rangle < \infty$, corresponding to a more intermittent relaxation process, we still have a finite relaxation rate at long times ($\mathcal{R}(t \rightarrow \infty) \sim 1/\tau_0$), but there is a slower approach of $\mathcal{R}(t)$ to its asymptotic limit [3, 5],

$$\mathcal{R}(t) \sim 1/\tau_0 + C_2 t^{\phi-1} \quad t \rightarrow \infty \quad 0 < \phi < 1 \quad (7)$$

where C_2 depends on the 'critical index' ϕ characterizing the strength of the fluctuations in the relaxation process.

(c) In the case of strongly intermittent relaxation, where even the first moment diverges $\langle t \rangle \rightarrow \infty$, the relaxation rate approaches zero at long times [3, 5],

$$\mathcal{R}(t) \sim C_3 t^{\phi-1} \quad t \rightarrow \infty \quad 0 < \phi < 1 \quad (8)$$

where C_3 is a known constant [3].

The exponent ϕ , the ‘crossover exponent’, has a geometric interpretation as the Hausdorff (‘fractal’) dimension of the time points τ at which the elementary relaxation (recurrent) events occur. This geometrical interpretation of ϕ can be appreciated by defining a counting function L_t for the ‘local time’ spent by a random walk path at a boundary. In figure 1 we show some realizations of L_t for random walks in two dimensions intersecting a line from which the paths initiate (ϕ generally depends on the spatial dimension, surface dimension and walk dimension). An average over an ensemble of random walk trajectories (128 paths) leads to the solid line in figure 1, consistent with the exact exponent value $\phi = 1/2$. The ‘local time’ variable L_t in figure 1 is a counter for those intermittent ‘renewal events’ having their origin in a random walk path process. For this model we have the average renewal rate, $\mathcal{R}(t) = d\langle L_t \rangle / dt \sim t^{-1/2}$.

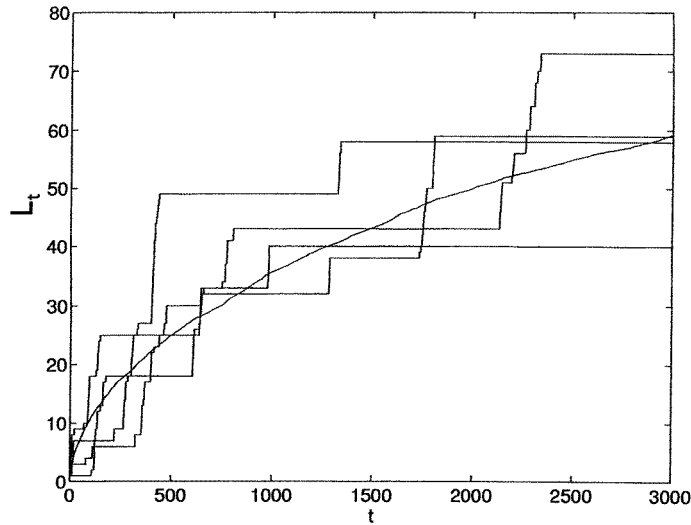


Figure 1. The ‘local time’ L_t of a random walk intersecting a line. Four representative random walk trajectories are considered where the initial step is positioned at the origin and successive returns to an arbitrarily designated line (containing the origin) are counted as L_t . The smooth curve represents an average over 128 path realizations and the $\langle L_t \rangle$ scales as $t^{1/2}$.

The three limiting expressions for $\mathcal{R}(t)$ indicated above are approximated by the expression,

$$\mathcal{R}_\phi(t) \approx \Omega_0 |t|^{\phi-1} / \Gamma(\phi) \quad 0 < \phi \leq 1 \quad (9)$$

where Ω_0 is a relaxation ‘coupling constant’ and $\Gamma(\phi)$ is a normalization factor. Some particular expressions for Ω_0 are discussed by Douglas and Hubbard [3] for models of relaxation in polymeric systems in the $\phi \rightarrow 1$ limit where \mathcal{R}_ϕ reduces to a constant ($\Omega_0 = 1/\tau_0$). Note that the additive constant in equation (6b) is neglected in equation (9).

The integral operator in equation (3) with the kernel defined in equation (9) is a *Riemann–Liouville* (RL) fractional order operator [10],

$$I_x^\alpha f(x) = \int_0^x d\tau [(x - \tau)^{\alpha-1} / \Gamma(\alpha)] f(\tau) \quad (10)$$

where $f(x)$ is multiplied by a Heaviside step-function $\theta(x)$. I_x^α defines a continuous semi-group that forms the basis of a simple operational calculus [10]. The main I_x^α properties are prescribed by the relations [10] ($\alpha, \beta > 0$),

$$I_x^\alpha I_x^\beta f(x) = I_x^{\alpha+\beta} f(x) \quad (11a)$$

$$I_x^\alpha I_x^\beta f(x) = I_x^{\beta} I_x^\alpha f(x) \quad (11b)$$

$$I_x^0 f(x) = I_x^{-\alpha} I_x^\alpha f(x) = f(x) \quad (11c)$$

$$x^{-\alpha} I_x^\alpha x^m = [\Gamma(m+1)/\Gamma(m+1+\alpha)]x^m. \quad (11d)$$

The first identity defines exponent additivity, the second commutativity, the third defines the identity operator and the left-inverse operation, while the fourth defines a useful eigenvalue relation. Note that the kernel $|x-x'|^{\alpha-1}/\Gamma(\alpha)$ becomes a delta-function $\delta(x-x')$ in the limit $\alpha \rightarrow 0^+$, leading to the identity operator in equation (11c). Formal manipulations for negative α must be made with care, and the results often have meaning only in a distributional sense.

Insertion of equation (9) into equation (3) and utilizing the definition of the *Riemann–Liouville* operator I_t^ϕ yields a ‘fractional differential equation’ for $\psi(t)$,

$$\psi(t) = 1 - \Omega_0 I_t^\phi \psi(t) \quad (12)$$

that can be formally rearranged and expanded for small Ω_0 as

$$\psi(t) = 1/[1 + \Omega_0 I_t^\phi] = \sum_{k=0}^{\infty} [-\Omega_0 I_t^\phi]^k. \quad (13)$$

Since $I_x^{k\phi} = x^{k\phi}/\Gamma(1+k\phi)$, we obtain ($0 < \phi \leq 1$),

$$\psi(t) = \sum_{k=0}^{\infty} [-z_\Omega]^k / \Gamma(1+k\phi) \quad z_\Omega = \Omega_0 t^\phi \quad (14)$$

and this expansion can be identified [3] as a *Mittag–Leffler* function E_ϕ ,

$$\psi(t) = E_\phi(-z_\Omega) \quad z_\Omega = (t/\tau_0)^\phi \quad \tau_0 = (\Omega_0)^{-1/\phi}. \quad (15)$$

$E_\phi(-\Delta_s)$ is plotted for a range of ϕ values in figure 2(a).

The Mittag–Leffler function is a natural generalization of the exponential relaxation function observed in ‘strongly mixing’ dynamical systems at equilibrium. Cole and Cole [6] introduced this function to phenomenologically describe dielectric relaxation in a broad range of condensed materials. This function is commonly discussed in the frequency domain where it is known as the ‘Cole–Cole function’.

Yonezawa and coworkers [11] have recently performed some interesting simulation studies that give insight into the physical significance of the intermittency index ϕ . Constraining the relaxation process to occur on a fractal space or the particle motion to occur as a continuous time random walk with a long pausing distribution leads to variations in ϕ in the resulting Mittag–Leffler (Cole–Cole) relaxation functions [11]. This finding is natural since the probability of recurrence of particle motion to a previously visited point is altered in these models, thereby changing ϕ (see figure 1). The problem of the return probability of a lattice random walk to the original point at $t = 0$ is exactly described by the renewal equations above [12]. In this context $\psi(t)$ describes the probability that a random walk does not return to the origin (‘survives’) up to time t (see equations (A.3) and (A.4) of [12]) where the rate of return to the origin of the random walk $\mathcal{R}(t)$ obeys an integral equation of the form of equation (3) (see equation (8.25b) of [12]).

A realistic model of condensed matter relaxation in cooled liquids must address the changes in phase space structure of the dynamical system describing the material that accompanies temperature changes. It has been suggested that diffusion in an ultrametric space should mimic this kind of complex phase space evolution [13], and temperature can be incorporated into this model by making the hopping process thermally activated. This model allows exact calculation of the random walk recurrence properties. Notably this model exhibits a variable intermittency index and an ergodic to non-ergodic transition at a well defined characteristic

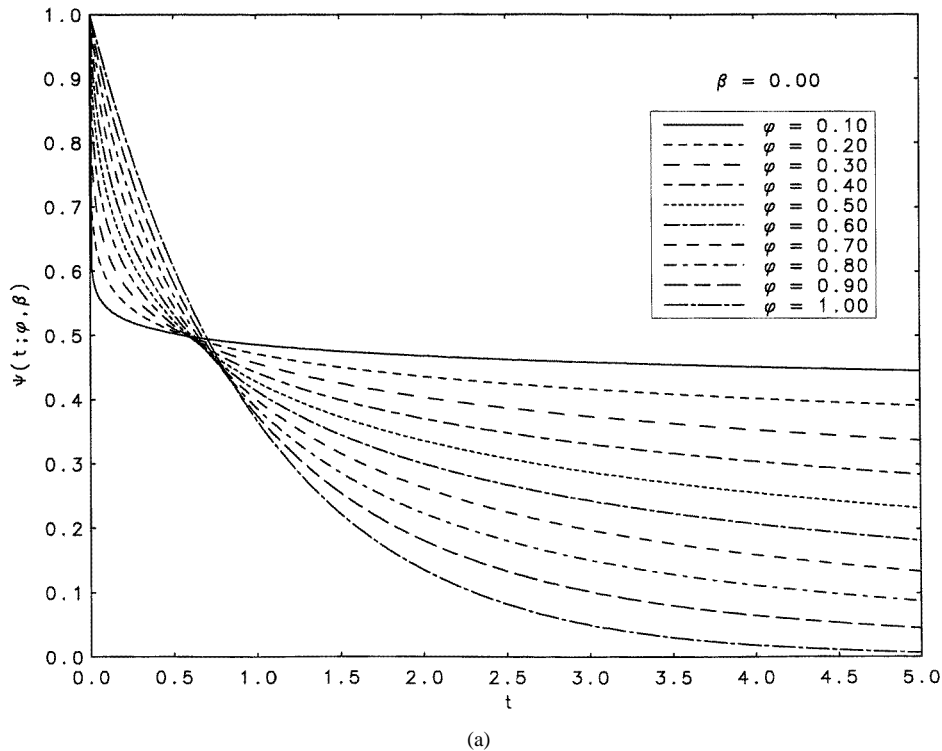


Figure 2. Relaxation function $\psi(t; \phi, \beta)$ for a range of ϕ and β values. The indices ϕ and β model heterogeneity in time and space, respectively. (a) Stretched exponential ($\phi = 1$); (b) Mittag–Leffler ($\beta = 0$); (c) generalized relaxation function of Douglas and Hubbard [3] ($\phi = 0.6, 0.7, 0.8, 0.9, 1.0$; $\beta = 0.5$). The time constant τ^* in equation (29) is taken to equal 1.

temperature where fluctuations in the random walk recurrences become strongly heterogeneous in time [3, 13]. Odagaki has argued that the glass transition corresponds to such an intermittency transition [14] (see also [3]).

It should be appreciated from this discussion that the general limit theorem leading to the $\psi(t; \phi)$ relaxation functions occurs for a multitude of microscopic models that are ‘attracted’ to the same ‘universality class’ of relaxation functions. The mathematical origin of this regularity is the same as in equilibrium critical phenomena, except we do not have a mechanism to select out particular values of the ‘critical index’ ϕ . Instead, we can expect ϕ to reflect the geometry of the material’s phase space. This structure depends on system parameters such as temperature. The occurrence of fractal phase space geometry (due perhaps to the ‘fracture’ of islands of stability into sticky Cantori structures as in model dynamical systems [15]) should be sufficient to give rise to this pattern of relaxation. Probably, the best we can hope to achieve in understanding this type of phenomenon (i.e., ϕ variation) is the construction of exactly solvable models where this phase space geometry change can be calculated numerically and the relaxation processes accompanying these changes can be monitored.

There are some particular properties of this Mittag–Leffler function worth emphasizing in connection with relaxation processes in condensed materials. First, we observe that $E_\phi(-z_\Omega)$ is an absolutely monotone function for $0 < \phi \leq 1$ and $z_\Omega > 0$ so that $\psi(t)$ decays uniformly. This is a characteristic feature of *large scale* relaxation in condensed materials. We also observe that by changing temperature (and thus the magnitude of the coupling constant Ω_0

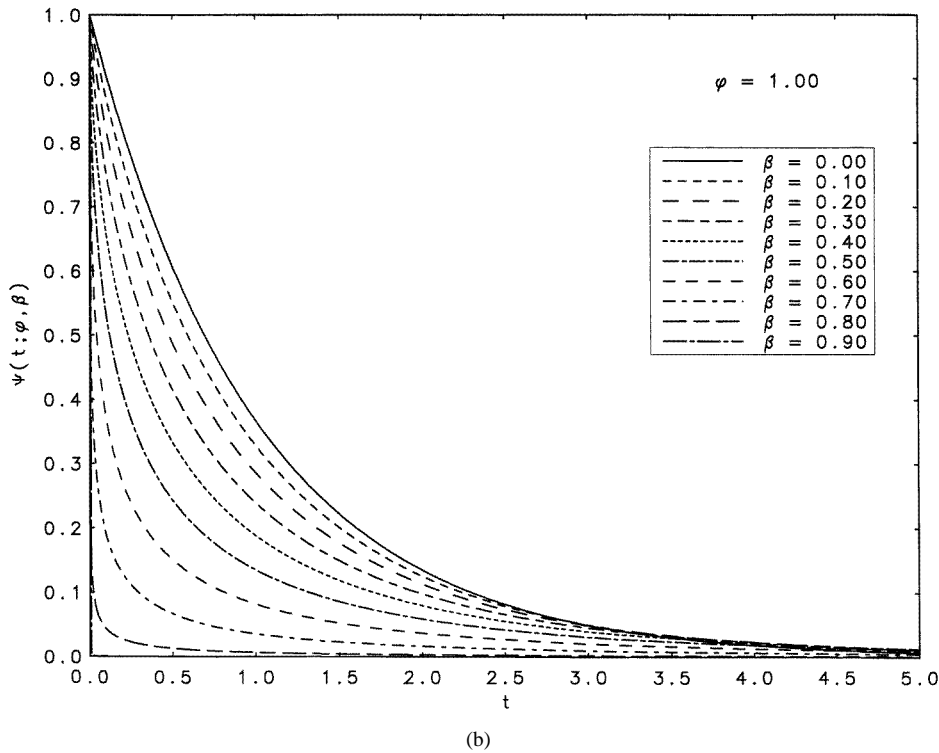


Figure 2. (Continued)

in equation (9)) the functional form of the relaxation function is *invariant* (provided ϕ does not change in this temperature interval). This ‘time–temperature superposition’ property is a mathematical consequence of the homogeneous form of the memory kernel,

$$k(t; \phi) = d\mathcal{R}(t)/dt \sim \Omega_0 |t|^{\phi-2} / \Gamma(\phi - 1) \quad 0 < \phi \leq 1 \quad (16a)$$

$$k(\lambda t; \phi) = \lambda^{\phi-2} k(t; \phi). \quad (16b)$$

This analytic symmetry reflects the existence of the probabilistic limit theorems discussed above, again as in critical phenomena.

The probabilistic model of condensed matter relaxation naturally leads to a classification scheme for $\psi(t)$ functions depending on the character of the fluctuations governing the relaxation process. The simplest case corresponds to the ‘strong mixing’ case where $\mathcal{R}(t)$ rapidly approaches a constant value so that $\psi(t)$ obeys the limits

$$\lim_{t \rightarrow 0^+} \psi(t) = 1 \quad - \lim_{t \rightarrow \infty} [\log \psi(t)/t] = \Omega_0 = \mathcal{R}(t \rightarrow \infty). \quad (17)$$

The long time limit in equation (17) reflects the existence of a limit theorem governing the rate of physical events giving rise to relaxation. Specifically, if $N(t)$ is a random variable which counts these random (and presumably independent) events, then ‘strong mixing’ implies the ergodic theorem,

$$\mathcal{R}(t \rightarrow \infty) = \lim_{t \rightarrow \infty} \langle N(t) \rangle / t \quad (18)$$

where $\mathcal{R}(t \rightarrow \infty)$ is positive finite constant characterizing the rate of mixing of the dynamical system (i.e., material).

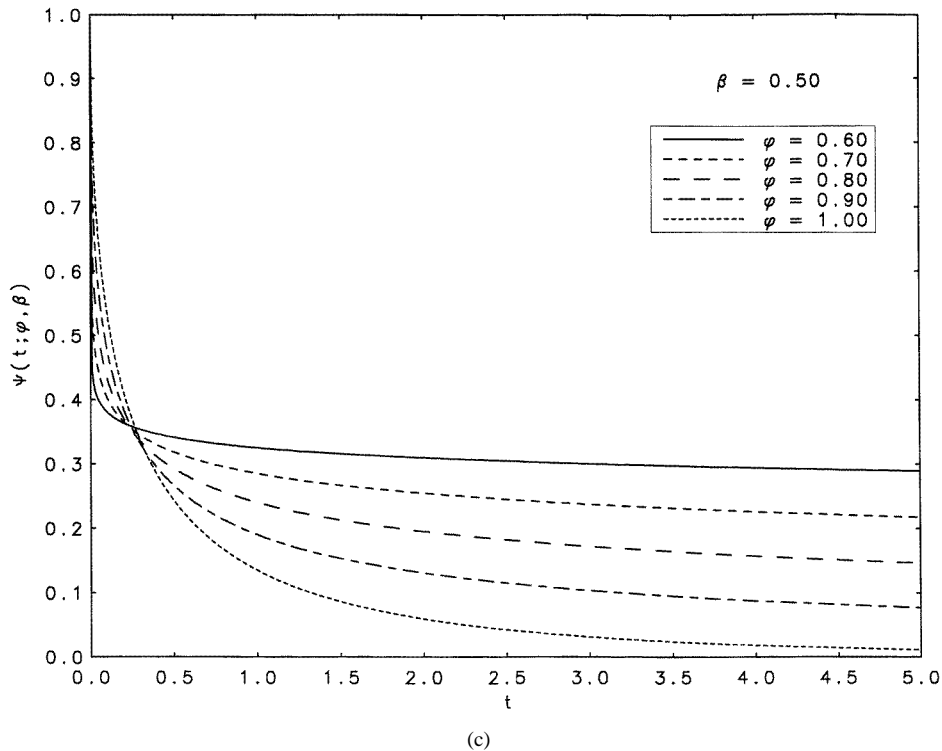


Figure 2. (Continued)

If the relaxation process occurs more sporadically we have the ‘weak ergodic theorem’,

$$\lim_{t \rightarrow \infty} \langle N(t) \rangle / t^\phi = \Omega_0 / \Gamma(\phi) \quad (19)$$

where Ω_0 is a positive constant and ϕ lies in the range $0 < \phi < 1$. This gives rise to the limiting behaviour,

$$\lim_{t \rightarrow 0^+} \psi(t) = 1 \quad - \quad \lim_{t \rightarrow \infty} [\log \psi(t) / t] = 0 \quad (20)$$

characteristic of the ‘weak mixing’ relaxation functions. Finally, we note that if $N(t)$ decays fast (e.g., exponentially fast) for large t so that the integral of $\mathcal{R}(t)$ over $(0, \infty)$ is finite, then $\psi(t)$ no longer decays to zero at long times. This ‘non-ergodic’ limiting behaviour corresponds to a material that is not in equilibrium, a commonly observed behaviour in ‘glassy’ materials.

Weak mixing type relaxation leads to non-trivial constitutive equations and forms of matter intermediate between the conventional defined solids and liquids. The Mittag–Leffler function approaches a power law (von Schweidler relaxation) for long times,

$$\psi(t; \phi) \sim (t/\tau_0)^{-\phi} \quad t \rightarrow \infty. \quad (21)$$

Next, if we insert this approximation for the shear relaxation function into the functional relating stress $\sigma(t)$ in strain rate $\dot{\gamma}(t)$ in the limit of linear response, then we obtain the *fractional order* constitutive equation relating these quantities,

$$\sigma(t) \propto I_t^{1-\phi} \dot{\gamma}. \quad (22)$$

Equation (22) reduces to the Newtonian constitutive relation for liquids and to a Hookean solid for ϕ equal to 1 and 0, respectively. Equation (22) has been shown to provide a good approximation of polymer gels and a variety of real (commercial) materials [16].

A shortcoming of our probabilistic approach to modelling condensed matter relaxation is that it does not account for transient *spatial* heterogeneities that develop through interparticle interaction. It is now recognized that cooled liquids develop large scale dynamic heterogeneities [18] and dynamic light scattering studies have also provided evidence for spatial heterogeneity in entangled polymer solutions [19]. Douglas and Hubbard [3] suggested that this clustering phenomenon, having its origin in topological interchain interactions, is responsible for the universal ‘entanglement’ phenomena observed in high molecular weight and concentrated polymer solutions and for characteristic features of stress relaxation in glass-forming liquids where the clustering arises from interparticle attractions. Douglas and Hubbard [3] extended the probabilistic model of condensed matter relaxation by introducing probabilistic arguments for the form of this clustering process, based on the assumption of thermodynamic equilibrium (Boltzmann’s law assumed to govern the cluster size distribution). According to this model the average energy of the transient clusters is extensive in their size where the geometry of these structures can be string-, sheet- or clump-like depending on the particulars of the interparticle interactions. String-like structures were suggested to form in ‘fragile’ glass forming liquids, sheets in ‘strong’ glasses, while clumps were suggested for ‘entangled’ polymer solutions.

The Douglas–Hubbard model indicated that spatial heterogeneity arising from particle clustering at equilibrium should give rise to a stretched exponential stress relaxation [3],

$$\psi(t) \approx \exp[-\Omega_0 t^{1-\beta}/(1-\beta)] \quad t \rightarrow \infty. \quad (23)$$

This form of relaxation arises from the averaging over cluster size distribution and in this model β depends on the geometry of the spatial heterogeneity involved,

$$\beta(\text{line}) = 2/3 \quad \beta(\text{sheet}) = 1/2 \quad \beta(\text{clump}) = 2/5. \quad (24)$$

The relaxation function $\psi(t)$ corresponds to a memory kernel in equation (3) having the form

$$k(t, \tau) = \Omega_0 \tau^{-\beta} \delta(t - \tau) \quad (25)$$

where δ is a delta-function.

Rigorous calculations [17] of the survival probability of a random walk in a medium with randomly placed absorbing obstructions exactly leads to relaxation functions of the form equation (23) where d is the spatial dimension rather than the cluster dimension, as in the present modelling. The calculations of Donsker and Varadhan [17] clearly indicate that material disorder can lead to stretched exponential relaxation and the cluster model of Douglas and Hubbard [3] is patterned about this same conceptual idea. Notably, the inhomogeneities in the stress-relaxation model are assumed to persist to timescales greater than the relaxation process, but still finite so the fluid can remain in equilibrium.

An interesting implication of stretched exponential relaxation is the breaking of the time-translation symmetry of the memory kernel in equation (3) (see equation (15)). This analytical symmetry is linked to conservation of energy in the derivation of equation (3). Of course, this is only an apparent symmetry breaking that derives from the disorder average [3]. There is no paradox if we consider our material to be composed of an *ensemble* of dynamical systems comprised of different local environments on the timescale of the relaxation process under discussion (this is nothing but the classical ‘distribution of relaxation times’ idea). The wide occurrence of stretched exponential relaxation in condensed materials suggests that material heterogeneity arising from long-lived particle clustering is a rather widespread phenomenon in condensed materials.

It is natural to consider relaxation in condensed materials to involve *both* intermittency in the rate of the relaxation process (arising from collective particle motions in dense

environments) and material heterogeneity. These effects are modelled by the more general relaxation kernel which generalizes equations (9) and (25),

$$\mathcal{R}(t, \tau) = \Omega_0 |t - \tau|^{\phi-1} \tau^{-\beta} / \Gamma(\phi) \quad 0 < \phi, \beta \leq 1. \quad (26)$$

Inserting $\mathcal{R}(t, \tau)$ into the relaxation integral equation (3) yields,

$$\psi(t; \phi, \beta) = 1 - \Omega_0 \int_0^t d\tau [|t - \tau|^{\phi-1} \tau^{-\beta} / \Gamma(\phi)] \psi(\tau; \phi, \beta). \quad (27)$$

This integral equation involves the replacement of the *Riemann–Liouville* operator of equation (10) by the more general *Erdélyi–Kober* fractional order operator [10],

$$I_t^{\delta, \phi} f(t) = t^{-(\phi+\delta)} \int_0^t d\tau [|t - \tau|^{\phi-1} \tau^\delta / \Gamma(\phi)] f(\tau). \quad (28)$$

Exact solution of the integral equation by fractional calculus methods gives [3]

$$\psi(t; \phi, \beta) = \sum_{k=0}^{\infty} a_k(\phi, \beta) [z_{\Omega}(\phi, \beta)]^k \quad (29a)$$

$$a_0(\phi, \beta) = 1 \quad a_k(\phi, \beta) = \prod_{m=1}^k \Gamma(1 + m\hat{\phi} - \phi) / \Gamma(1 + m\hat{\phi}) \quad (29b)$$

$$\hat{\phi} = \phi - \beta \quad 0 < \hat{\phi}, \phi, \beta \leq 1 \quad (29c)$$

$$z_{\Omega}(\phi, \beta) = \Omega_0 t^{\hat{\phi}} = (t/\tau^*)^{\hat{\phi}} \quad \tau^*(\phi, \beta) = \Omega_0^{-1/\hat{\phi}}. \quad (29d)$$

$\psi(t; \phi, \beta)$ reduces to a Mittag–Leffler function for $\beta = 0$ and a stretched exponential function for $\phi = 1$, but otherwise $\psi(t; \phi, \beta)$ becomes a hybrid form of these functions. Some representative plots of these relaxation curves are given in figure 2. $\psi(t; \phi, \beta)$ arises in an electrochemistry context in the description of the dropping mercury electrode [20] and in this context the function $\psi(t, \phi, \beta)$ for $\hat{\phi} = 3/14$ is known as the Koutecky function [3, 10, 20].

The Havriliak–Negami function [21] is widely used to correlate frequency domain relaxation data for condensed materials. This function depends on two parameters that are similar to ϕ and β of $\psi(t; \phi, \beta)$. Indeed, the two classes of functions should provide rather close approximations to each other. It would be interesting to test this new class of relaxation functions against accurate measurements (stress relaxation and dielectric data) to determine the system dependence of ϕ and β parameters.

Although the limiting stretched exponential ($\phi = 1$; $0 < \beta < 1$) relaxation functions obey the conditions of ‘weak mixing’ given in equation (20), the integral of $\psi(t; \phi = 1, \beta)$ from 0 to ∞ is finite for this class of functions,

$$\int_0^{\infty} d\tau \psi(\tau; \phi = 1, \beta) < \infty \quad (30)$$

making this class of functions suitable for modelling liquid relaxation (i.e., viscosity is finite if $\psi(t)$ is a shear relaxation function).

The slow decay of the $\psi(t; \phi, \beta)$ for $\phi \neq 1$ and $\beta \neq 0$ requires a refinement of the relaxation function classification introduced above. We observe that the integral of $\psi(t; \phi; \beta)$ over $[0, \infty)$ diverges,

$$\int_0^{\infty} d\tau \psi(\tau; \phi, \beta = 0) \rightarrow \infty \quad 0 < \phi < 1 \quad (31)$$

while the integral of $\psi(t, \phi = 1, \beta)$ over $[0, \infty)$ is finite,

$$0 < \int_0^{\infty} d\tau \psi(\tau; \phi = 1, \beta) < \infty \quad 0 < \beta < 1 \quad (32)$$

Thus, we further divide the ‘weak mixing’ class of relaxation functions into ‘homogeneous weak mixing’ and ‘inhomogeneous weak mixing’ subclasses, according to whether the integral of $\psi(t; \phi, \beta)$ over $[0, \infty)$ is finite or not. This provides a useful classification scheme for condensed matter relaxation functions.

The complexity in the configurational dynamics of polymer materials and supercooled liquids is reflected in the intermittency in particle motion and in the tendency for the particles to cluster and move in a collective fashion. The integral equation model of relaxation in conjunction with renewal theory provides a basis for understanding regularities in (long wavelength) relaxation processes in condensed materials. Basic properties of condensed matter relaxation (time–temperature superposition, monotonic decay of relaxation functions etc) become apparent from a consideration of the types of ‘mixing’ which should occur for statistical mechanical systems at equilibrium and from simple modelling of particle clustering based on Boltzmann’s law. A general class of relaxation functions depending on temporal and spatial heterogeneity indices (ϕ, β) is determined and a classification scheme for relaxation functions is introduced as a byproduct of this investigation. It would be interesting to test this new class of relaxation functions against accurate dielectric data to determine the system dependence of ϕ and β parameters.

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