

Simple model of the diffusive scattering law in glass-forming liquids

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We found that the decay rate, λ , of the correlation function, G , in glass-forming liquids can be expressed in terms of G itself. A three-parameter function of the form $\lambda = \lambda_0 + \lambda_1 G^k$ leads to an analytic solution for the function G in the time domain. This assumption also allows one to express the function G as an infinite series of Lorentzians in the frequency domain. This model has been applied to Mössbauer absorption spectra of aqueous FeCl_2 solutions in glycerol (14.4-keV line of ^{57}Fe) and higher temperature quasielastic (Rayleigh) scattering data obtained by the scattering of the ^{183}W 46.5-keV Mössbauer line from pure glycerol. The model describes the Mössbauer data as well as the empirical Kohlrausch or Cole-Davidson (CD) laws. Also, the function $\lambda(G)$ can be expressed in a two-parameter form as $\lambda_0 \exp(\alpha G)$. It has been shown, however, that a closed-form expression for the function G does not exist in the time or frequency domain for this latter form. On the other hand, the exponential form gives a two-parameter fit to existing data, suggesting a physical basis to this form and implies that small changes in G are proportional to fractional changes in λ . It has been found that the parameter α has some universal meaning as it remains constant over a significant low-temperature range accessible experimentally, decreasing to the zero value with increasing temperature. Our analysis suggests that the parameter α may change in steps as sample temperature is increased. Such a behavior suggests that some processes (degrees of freedom) are “freezing out” at well-defined temperatures.

I. INTRODUCTION

Recently, noncrystalline systems have attracted considerable attention and many attempts have been undertaken to explain their diffusive properties (for a review see Refs. 1–3) both from the experimental as from the theoretical point of view. Various techniques have been applied to look at diffusive behavior in disordered systems,^{1,2} e.g., dielectric susceptibility studies,^{4–6} differential heat-capacity measurements,^{4,7} nuclear magnetic resonance,⁸ visible light scattering,^{9–11} scattering methods in the wave-vector transfer region comparable to the inverse molecular dimensions, and also “classical” methods such as tracer diffusion and viscosity studies and many other techniques.^{1,2} Scattering methods have the advantage of probing both the spatial and temporal dependence of the appropriate correlation functions, however, they suffer from limited time resolution and limited time-scale range.^{1,12} They can be divided into coherent methods such as quasielastic scattering of Mössbauer radiation,¹³ which in the completely elastic limit is Rayleigh scattering, or coherent neutron scattering, and incoherent ones such as Mössbauer absorption, emission spectroscopy or incoherent neutron scattering. Mössbauer absorption and emission spectroscopies are confined to probing the immediate vicinity of the surface of the Ewald sphere. Coherent methods are sensitive to properties of the pair-correlation functions,¹⁴ while in-

coherent methods measure properties of the self-correlation functions.¹⁴

Noncrystalline systems comprise a variety of different materials, e.g., large biomolecules, polymers of small molecules and viscous, glass-forming liquids.¹ They share many properties but differ in some subtle points. For example, diffusion in glass-forming liquids has long-range character, whereas bounded diffusion is observed in biomolecules.¹ A somewhat special case is the suspension of fine particles in highly viscous liquids.^{15–18} For the latter case, a significant contribution to the local diffusivity may come from rotational motion of the suspended particles.¹⁸

Even for simple glass-forming liquids like glycerol, there is no satisfactory theory explaining the observed dynamic phenomena, particularly in the high viscosity region. There are many empirical laws describing temporal dependence of the correlation function or the superposition of the “partial” correlation functions having usually a simple exponential behavior.^{1,2} The former class contains the widely used Kohlrausch law,¹⁹ while the latter class is well represented by the Cole-Davidson (CD) law,⁶ Cole-Cole,²⁰ and Havriliak-Negami relationships.²¹ Actually, it has been shown that the Kohlrausch and CD laws are almost equivalent approximations as far as the modeling of experimental data in the frequency domain is concerned.²² Recently, Dixon *et al.*⁵ found that a single scaling factor inherent in the Kohlrausch law is unable to explain their dielectric susceptibility data measured over

an extremely wide dynamic range. On the other hand, they found an almost universal scaling transformation,⁵ suggesting a multifractal behavior of the system (for more details, see Refs. 5 and 23). Methods such as dielectric susceptibility or differential heat-capacity measurements tend to average over many processes occurring at different temporal and spatial scales, while scattering methods look at samples microscopically, as their spatial scale is restricted to the appropriate coherence length.

It is, of course, possible to develop a dynamical model of a complex system. Even for relatively simple cases, however, such models depend on a variety of adjustable parameters.²⁴ An approximation to such an approach is the mode-coupling theory^{25,26} describing phenomena in the low viscosity region relatively well, where the dynamic observables such as dielectric susceptibility tend to approach gradually a simple Debye behavior.

Another possible approach is to reformulate the problem as an eigenvalue problem.²⁷⁻²⁹ Such an approach is particularly simple in the case of pure diffusivity in the quasielastic limit, as in this case we may always transform to a Hermitian problem.^{29,30} The dimensionality of the problem is usually finite in solids, where diffusion occurs between (and within) well-defined Bravais lattices.^{30,31} In the case of noncrystalline systems, however, an eigenvalue problem has to be defined in terms of differential operators and continuous partition functions.²⁹ These operators contain the Fokker-Planck potential,²⁹ characteristic of the particular system (except for the rotation of the Brownian particle Ref. 18), and hence, one always obtains an elastic contribution (also in the case of Brownian rotation). A special case of this approach is the overdamped Brownian oscillator which has been applied to some spectra of biomolecules.³²⁻³⁴ Glass-forming liquids, however, do not exhibit any significant elastic contribution, indicating that the ensemble average Fokker-Planck potential is almost constant over the space.²⁹ Such a situation is consistent with the temperature dependence of the correlation functions, as the latter obey a Vogel-Fulcher-Tammann or power law rather than an Arrhenius law.²

Summarizing the present situation, it can be stated that fragile glass-forming liquids are still best described by the empirical Kohlrausch law at least over the limited dynamic range currently accessible to experiment. The Kohlrausch law, however, contains unphysical, i.e., infinitely fast relaxation processes. On the other hand, it indicates clearly that the time evolution of a given relaxation "slows down" with the passage of time more rapidly than expected for purely exponential behavior with a single relaxation time. Such a time behavior can be crudely modeled assuming a sequence of events blocking each other (see, e.g., Refs. 35 and 36). A real system is much more complex than such crude models, and thus, realistic models would be expected to contain many adjustable parameters for a precise description of the observations. It is possible to incorporate formally a spatial behavior of the correlation function into the CD approximation,¹² and into the Kohlrausch law as well, however, the CD approximation contains infinitely fast relaxation processes which cannot be physically meaningful.

II. SIMPLE MODEL APPLICABLE TO SCATTERING METHODS

A. Basic model

Properly designed scattering and transmission experiments measure either the self-correlation function of the diffusing entity (incoherent methods) or pair-correlation functions of the system (coherent methods) in the frequency wave-vector domain, provided other degrees of freedom can be neglected.^{30,37} For systems obeying the Kohlrausch law, a single scalar correlation function suffices to describe the scattering law in the quasielastic limit. For unbounded diffusion, the time dependence of the correlation function describing the system close to equilibrium takes on the form³⁸

$$dG/dt + \lambda G = 0, \quad (1)$$

where $t \geq 0$ stands for the time, and G denotes either a self-correlation function (incoherent methods) or ensemble averaged configuration probability (coherent methods) related directly to the pair-correlation function. Hence, the function G has the following properties: $G(t=0) \equiv 1$, $\lim_{t \rightarrow \infty} [G(t)] = 0$, and $dG/dt < 0$ for any time $t \geq 0$. For a simple linear (Debye) system the rate parameter $\lambda > 0$ does not depend upon time, and hence, the function G has a simple exponential time dependence. However, for a nonlinear system, the parameter λ might depend upon time, as pointed out by Dattagupta.³⁸ In fact, it seems more physical to introduce the time dependence implicitly $\lambda = \lambda(G)$, where the parameter λ does not depend explicitly upon time, as the time scale is in effect defined by G . One can approximate λ by an expansion into a Taylor series in G , however, such an approach generates inevitably an infinite set of adjustable parameters having strong correlations when fitted to real data. On the other hand, it seems likely that the unperturbed system ($G=0$) approaches a linear limit, while the perturbed system is "more nonlinear." Hence, we take the first-order approximation to λ to have the following form:

$$\lambda = \lambda_0 + \lambda_1 G^k, \quad (2)$$

where $\lambda_0 > 0$ denotes a decay constant in the linear regime, and $\lambda_1 G^k$ represents the nonlinear enhancement of relaxation rate associated with large displacements from equilibrium ($\lambda_1 \geq 0$). For systems that are rather well described by the Kohlrausch law, the exponent $k \geq 1$ (in general, it is required that $k > 0$). Taking $k = 1$ would give the lowest order expansion of the Maclaurin series and only two adjustable parameters, like the Kohlrausch and CD approaches, but this assumption will not suffice over a broad temperature range.

Substitution of the relationship (2) into Eq. (1) leads to the Bernoulli differential equation, with the following solution in our case [$G(t=0) \equiv 1$]:

$$G(t) = [\lambda_0 / (\lambda_0 + \lambda_1)]^{(1/k)} \exp(-\lambda_0 t) \times \{1 - [\lambda_1 / (\lambda_0 + \lambda_1)] \exp(-k \lambda_0 t)\}^{-1/k}. \quad (3)$$

A frequency domain function $G(\omega)$ can be obtained by

Fourier transformation of Eq. (3) and, hence

$$\begin{aligned} G(\omega) &= (1/\pi) \int_0^\infty dt G(t) e^{-i\omega t} \\ &= (1/\pi) [\lambda_0/(\lambda_0 + \lambda_1)]^{(1/k)} \\ &\quad \times \sum_{n=0}^\infty C_n [(\beta_n - i\omega)/(\beta_n^2 + \omega^2)], \end{aligned} \quad (4)$$

where

$$\beta_n = \lambda_0(1 + kn), \quad C_0 = 1,$$

and the recursion relation between successive C_n values is

$$C_{n+1}/C_n = (n+1)^{-1} [n + (1/k)] [\lambda_1/(\lambda_0 + \lambda_1)].$$

The scattering law then takes on the usual form

$$S(\omega) = \text{Re}[G(\omega)], \quad (5)$$

which is a sum of simple Lorentzian functions. This result is particularly appealing and gives the solution in a form that indicates the distribution of relevant relaxation times.

A spatial (wave-vector) dependence of the scattering law (5) can be introduced in the simplest way by scaling the constants λ_0 and λ_1 in the following way:^{39,40}

$$\lambda_0 = \Lambda_0 [1 - \alpha_0(\bar{q})] \quad \text{and} \quad \lambda_1 = \Lambda_1 [1 - \alpha_0(\bar{q})], \quad (6)$$

where Λ_0 and Λ_1 represent the appropriate unscaled effective frequencies of the diffusive events, while

$$\alpha_0(\bar{q}) = \int_{-\infty}^\infty d^3r \rho(\bar{r}) e^{i\bar{q}\cdot\bar{r}}, \quad (7)$$

where \bar{q} denotes the wave-vector transfer to the system, while $\rho(\bar{r})$ stands for either the corresponding spatial self-correlation function or for the instantaneous pair-correlation function normalized to a single scattering particle.¹⁴ Hence, the distribution function $\rho(\bar{r})$ can, in principle, be calculated as (for details see Ref. 14):

$$\begin{aligned} G(\omega) &= (1/\pi) [\lambda_0/(\lambda_0 + \lambda_1)]^{(1/k)} \\ &\quad \times \left[\sum_{n=0}^N C_n [(\beta_n - i\omega)/(\beta_n^2 + \omega^2)] + \int_N^\infty dx C(x) \{ [\lambda_0(1 + kx) - i\omega]/[\lambda_0^2(1 + kx)^2 + \omega^2] \} \right] \end{aligned} \quad (12)$$

where $C(x)$ is obtained from Eq. (11) and the integral gives an approximation to the sum above N . For such a case, it is expected that $\lambda_0 \rightarrow 0$ and $\lambda_1 > 0$. Hence, the following approximations can be made: $\lambda_0/(\lambda_0 + \lambda_1) \cong \lambda_0/\lambda_1$ and $\beta_N = \lambda_0[1 + kN] \cong k\lambda_0 N$, provided $kN \gg 1$. Therefore, the "continuous" part of the function $G(\omega)$ takes on the form

$$\begin{aligned} G_1(\omega) &= \pi^{-1} \lambda_1^{-(1/k)} \Gamma^{-1}(1/k) \\ &\quad \times \int_{\beta_N}^\infty d\beta [\lambda_1/(\lambda_0 + \lambda_1)]^{[\beta/(k\lambda_0)]} \\ &\quad \times \beta^{[(1/k)-1]} [(\beta - i\omega)/(\beta^2 + \omega^2)]. \end{aligned} \quad (13)$$

For the limiting case $\lambda_0 \rightarrow 0$, the first term of the expression (12) makes a negligible contribution and hence

$$\rho(\bar{r}) = \rho_0^{-1} \langle \rho_l(\bar{r}_1, t=0) \rho_l(\bar{r}_1 + \bar{r}, t=0) \rangle_{\bar{r}_1, t} \quad (8)$$

in the case of incoherent scattering or as

$$\rho(\bar{r}) = (N_0^{-1} \rho_0^{-1}) \sum_l \langle \rho_l(\bar{r}_1, t=0) \rho_l(\bar{r}_1 + \bar{r}, t=0) \rangle_{\bar{r}_1, t} \quad (9)$$

in the case of coherent scattering. Here, $\langle \dots \rangle$ denotes an ensemble average, ρ_0 stands for the average density, and N_0 denotes a number of coherently scattering particles; $\rho_l(\bar{r}, t)$ represents the density of the l th particle at time t . For spherically symmetrical distribution functions, e.g., for the glycerol case, one obtains $\rho(\bar{r}) = \rho(r)$, where $\rho(r)$ stands for the appropriate radial distribution function and, hence

$$\alpha_0(\bar{q}) = \alpha_0(q) = (4\pi) \int_0^\infty dr r^2 \rho(r) J_0(qr), \quad (10)$$

where $J_0(qr)$ denotes the *zeroth-order* cylindrical Bessel function of the first kind. Such an approach is consistent with the scaling rules described by Zabel¹⁴ and with the incorporation of the spatial behavior into the CD law.¹²

It is interesting to note that in our case successive linewidths correspond exactly to the harmonic Fokker-Planck potential,²⁹ except for the absence of the elastic component in our model, while the corresponding intensities fall much more slowly with increasing linewidths.

The coefficients C_n can be approximated by the following expression, provided $n \gg 1$:

$$C_n = \Gamma^{-1}(1/k) [\lambda_1/(\lambda_0 + \lambda_1)]^n n^{[(1/k)-1]}, \quad (11)$$

where $\Gamma(1/k)$ stands for the Euler-gamma function. On the other hand, expression (4) can be approximated in the following way provided one has a very broad distribution of Lorentzians, i.e., the system is close to the glass "transition" temperature, where $N \gg 1$:

$$\begin{aligned} G(\omega) &= \pi^{-1} (\beta_N/\lambda_1)^{(1/k)} \Gamma^{-1}(1/k) \\ &\quad \times \int_1^\infty dz z^{[(1/k)-1]} [(\beta_N z - i\omega)/(\beta_N^2 z^2 + \omega^2)], \end{aligned} \quad (14)$$

where $z = \beta/\beta_N$, with $\beta_N > 0$ and $k > 1$. The latter expression cannot be normalized in the absolute sense, i.e., the integral over the whole frequency domain is divergent, however, there is no need for the function $G(\omega)$ to be normalizable as it represents a scattering law and hence, it has to be convoluted with the "instrumental" function which is always normalizable. Hence, it is practical to use the following function instead of expression (14) (particularly for the scattering case):

$$g(\omega) \equiv (1/\beta_N)[G(\omega)/G(\omega=0)] ,$$

where

$$g(\omega=0) = (1/\beta_N) .$$

Hence, an almost closed-form expression for the function $g(\omega)$ can be found that depends only upon two parameters: the scaling factor β_N and the exponent k . The function $g(\omega)$ takes on the form

$$g(\omega) = [1 - (1/k)] \times \int_1^\infty dz z^{[(1/k)-1]} [(\beta_N z - i\omega)/(\beta_N^2 z^2 + \omega^2)] . \quad (16)$$

Expression (16) is characterized by a significant contribution from very broad components characteristic of fractal or multifractal behavior.⁴¹ The scaling factor β_N is likely to depend upon the wave-vector transfer in the same manner as parameters λ_0 and λ_1 . It is clear that all moments of the expression (16) are divergent. For relatively narrow distributions, however, expression (4) holds which allows one to calculate moments of arbitrary order, particularly an average width $\langle \beta \rangle$. The average decay constant as well as higher moments can be alternatively and more reliably calculated using directly the $\lambda(G)$ dependence.

Expression (2) can be fairly well approximated by the form

$$\lambda_0 \exp(\alpha G) , \quad (17)$$

where $\alpha \geq 0$ and λ_0 are the only adjustable parameters. Unfortunately, this parametrization does not lead to a suitable closed-form solution of Eq. (1). The parameter α , however, can be obtained by minimizing the residuals between the two forms of $\lambda(G)$ given by expressions (2) and (17). Optimization of the exponential form is ob-

tained by minimizing

$$I = \int_0^1 dG [(\lambda/\lambda_0) - \exp(\alpha G)]^2 , \quad (18)$$

where the λ used is from the best fit given by Eq. (2). The latter constraint leads to the condition $(\partial I/\partial \alpha) = 0$, and hence, one obtains the following relationship for the parameter α in terms of (λ_1/λ_0) and k :

$$3 + 4e^{\alpha}(\alpha - 1) + e^{2\alpha}(1 - 2\alpha) + 4(\lambda_1/\lambda_0) \sum_{m=0}^{\infty} \{\alpha^{(m+2)}/[(k+m+1)m!]\} = 0 . \quad (19)$$

The last equation has a unique solution for $\alpha \geq 0$ and can be solved numerically. For a linear (Debye) system one obtains $\alpha = 0$, which represents the limiting single relaxation time case.

B. Application to Mössbauer transmission and scattering experiments

Mössbauer spectra have rather limited dynamic range, and hence, expression (4) can be used in most cases. For a transmission or nonresonant quasielastic scattering (Rayleigh) experiment, data treatment is particularly simple provided a source emits an unbroadened Lorentzian line, scatterer (if present) is optically thin for the radiation used (see, e.g., Ref. 30) and the absorber is resonantly thin as well. We require a negligible broadening of the intrinsic absorber line and negligible interference contributions as well.⁴² If the number of counts far-off resonance does not depend upon velocity (proper alignment), and the Doppler velocity (to first order here) is well defined, the spectral shape $P(\omega)$ is approximately given by

$$P(\omega) = B_0 \left[1 - A_L \left[\sum_{n=0}^{\infty} [(\frac{1}{2}\Gamma_0)/(\beta_n + \frac{1}{2}\Gamma_0)] C_n \times \{(\beta_n + \frac{1}{2}\Gamma_0)^2 / [(\beta_n + \frac{1}{2}\Gamma_0)^2 + (\omega - \omega_0)^2]\} / \sum_{n=0}^{\infty} [(\frac{1}{2}\Gamma_0)/(\beta_n + \frac{1}{2}\Gamma_0)] C_n \right] \right] , \quad (20)$$

where B_0 stands for the number of counts far-off resonance, A_L is the relative spectrum amplitude, ω_0 denotes the resonance velocity (frequency), while Γ_0 represents the unbroadened linewidth obtainable at temperatures low enough that all the relevant dynamic degrees of freedom are frozen within the resolution of the experimental setup.

C. Approximate treatment of the electric quadrupole relaxation

An acidic aqueous FeCl_2 solution dissolved in glycerol exhibits Fe^{2+} ions in the high spin state subject to the

electric quadrupole interaction due mostly to the local asymmetry in the molecular wave functions.⁴³ There is no indication of any preferential orientation and/or Goldanskii-Karyagin effect.⁴³ This interaction is practically uniquely defined, but it is hard to estimate an asymmetry parameter due to the complex coordination of the iron ion ($\frac{1}{2} \rightarrow \frac{3}{2}$, practically pure $M1$ Mössbauer transition in ^{57}Fe -14.4 keV). An inspection of the relatively low-temperature data of Abras and Mullen⁴³ indicates that the quadrupole splitting Δ decreases with increasing temperature, independently of the relaxation process itself. Such a decrease seems to be almost halted at higher temperatures (note, that crystal-field levels responsible for

such a behavior are very broad in the disordered systems) and a genuine relaxation is clearly observable. It is likely that the main reason for the relaxation is the rotation of the iron complexes during diffusive events (at least at moderate temperatures). It is a significant rotation effect as compared to the similar situation in the Brownian particle due to the compactness of the complexes.¹⁸ It is, of course, impossible to write down the exact relaxation operator in any form due to the complexities of the motion and poorly understood symmetry of the electric-field gradient. However, the exact operator can be approximated by a simple Hermitian 2×2 operator acting on the distinct eigenvalues of the hyperfine Hamiltonian (note that the nuclear ground state does not participate in the relaxation). Such an approach is equivalent to a pure rotation leading to a maximum possible mixing of the distinctly different eigenvalues. Hence, the total super-operator \hat{R} takes on the form⁴⁴

$$\hat{R} = \begin{pmatrix} -i\varepsilon - w & w \\ w & i\varepsilon - w \end{pmatrix}, \quad (21)$$

where $\varepsilon = \frac{1}{2}\Delta \geq 0$ and $w \geq 0$ stands for the effective relaxation rate of the electric-field gradient. The eigenvalues and eigenvectors of the super-operator \hat{R} can be readily calculated leading to the following line intensities c (relative areas), contributions to the linewidths $\Delta\Gamma$, and corrections to the line positions $\Delta\omega$:

$$c_1 = \frac{1}{2}, \quad \Delta\Gamma_1 = 2w, \quad \Delta\omega_1 = -[\varepsilon^2 - w^2]^{1/2},$$

$$c_2 = \frac{1}{2}, \quad \Delta\Gamma_2 = 2w, \quad \Delta\omega_2 = [\varepsilon^2 - w^2]^{1/2}$$

for $w \leq \varepsilon$ and

$$c_1 = \frac{1}{2}[1 + (w^2 - \varepsilon^2)^{1/2}/w],$$

$$\Delta\Gamma_1 = 2[w - (w^2 - \varepsilon^2)^{1/2}], \quad \Delta\omega_1 = 0, \quad (22)$$

$$c_2 = \frac{1}{2}[1 - (w^2 - \varepsilon^2)^{1/2}/w],$$

$$\Delta\Gamma_2 = 2[w + (w^2 - \varepsilon^2)^{1/2}], \quad \Delta\omega_2 = 0$$

for $w > \varepsilon$.

These corrections are to be incorporated appropriately into expression (20), where each of the above shown components is transformed in accordance with the diffusive scattering law (4). A quadrupolar relaxation causes an additional broadening, of course. In principle, the relaxation rate w is weakly correlated to the diffusive time scales. We found, however, that for the experimentally accessible range the approximation $w \cong \lambda_0$ holds. It has to be realized, that the latter approximation is rather crude as there is no reason for the rate constant w to depend upon the wave-vector transfer. On the other hand, the validity of the relationship $w \cong \lambda_0$ indicates that the fast processes remain rather decoupled from the charge relaxation within the ferrous complex.

III. APPLICATION TO EXPERIMENTAL DATA AND CONCLUSIONS

The model has been applied to the Mössbauer absorption data obtained for acidic (pH=2) aqueous FeCl_2 solution in glycerol (14.4-keV Mössbauer line of ^{57}Fe) and to the nonresonant quasielastic scattering data obtained upon scattering of the 46.5-keV Mössbauer line of ^{183}W from pure glycerol. The scattering data have been obtained at a constant wave-vector transfer, being set close to the first "diffraction" maximum (the smallest coherent broadening, Ref. 14) at 1.36 \AA^{-1} . Experimental details of the iron spectroscopy can be found in Ref. 12, while details of the scattering experiment are described in Ref. 45 (for a description of the experimental setup see also Refs. 46 and 47). A summary of results found from this model by fitting to the data are collected in Table I, while the corresponding spectra are shown in Figs. 1 and 2.

It can be clearly seen that the system becomes quite rapidly linear (Debye-like) with the temperature T increasing far away from the glass "transition" point. Such a finding means that our system is only approximately scale invariant (a necessary symmetry of the "orthodox"

TABLE I. Essential results of the model fitting to the experimental data. See text for details. For a simple Debye behavior $\langle\beta\rangle = \lambda_0$. χ^2 denotes a mean variance of the fitted data—per degree of freedom. RSMR stands for the Rayleigh scattering of the Mössbauer radiation.

T (K)	λ_0 (mm/s)	λ_1/λ_0	$1/k$	$\langle\beta\rangle$ (mm/s)	α	χ^2	Comments
250	0.187(3)	22(16)	0.09(1)	0.5(2)	2.3(5)	0.96	Fe
255	0.294(6)	11(3)	0.17(2)	0.8(1)	2.1(2)	0.95	Fe
260	0.46(2)	9(2)	0.34(4)	1.6(2)	2.4(1)	0.74	Fe
265	0.54(3)	7.8(6)	1.0(—)	2.6(1)	2.6(1)	0.93	Fe
270	3.2(2)	2.1(3)	1.0(—)	6.6(4)	1.5(1)	0.76	Fe
275	6.0(4)	2.4(4)	1.0(—)	13(1)	1.6(1)	0.88	Fe
308	3.39(6) ^a	0	(—)	(—)	0	2.26 ^b	RSMR
330	16(1)	0	(—)	(—)	0	1.14	RSMR
361	56(6)	0	(—)	(—)	0	1.20	RSMR
386	158(36)	0	(—)	(—)	0	0.53	RSMR

^aThe apparent decrease seen here is due to a change in wave-vector transfer to the system and a change from incoherent to coherent scattering. This results in this and subsequent numbers in this column being scaled down by roughly a factor of 60.

^bAs seen in Fig. 2 one point is responsible for the exceptionally high χ^2 .

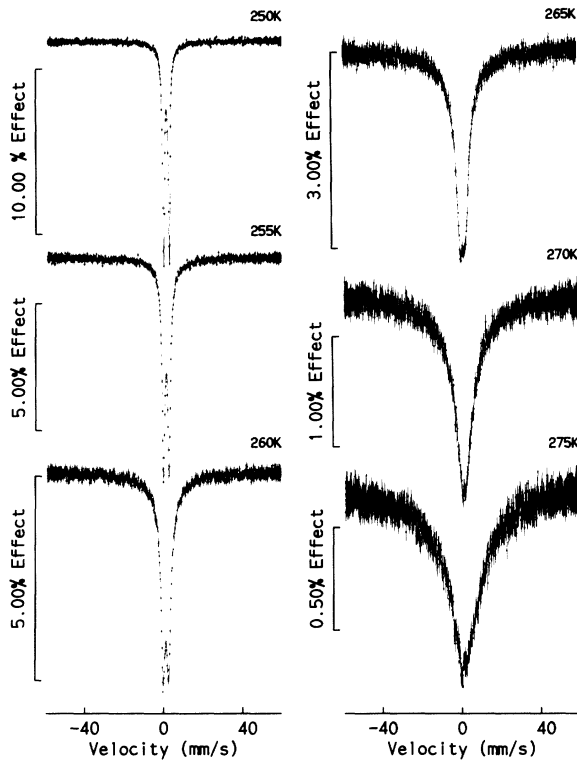


FIG. 1. Mössbauer spectra of FeCl_2 solution in glycerol (about 5% water) versus temperature (taken from Ref. 12).

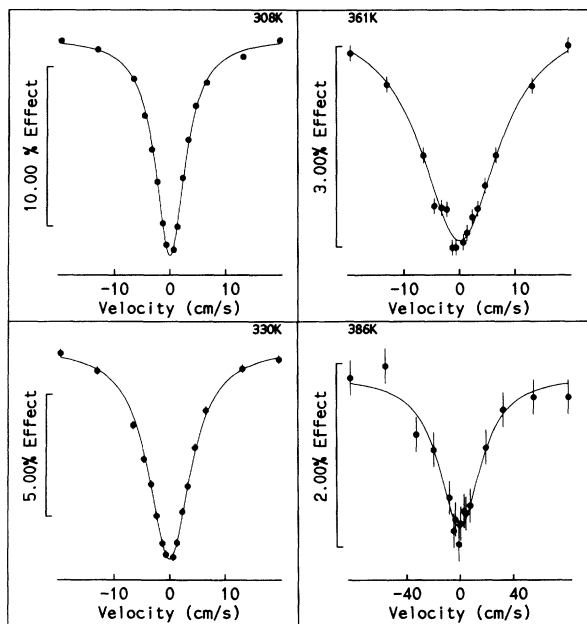


FIG. 2. Quasielastic scattering spectra of Mössbauer radiation (^{183}W , 46.5 keV) obtained upon scattering off pure glycerol at various temperatures (taken from Ref. 45). The wave-vector transfer is $q = 1.36 \text{ \AA}^{-1}$ for all spectra shown.

fractal system). However, very broad contributions are clearly discernible upon lowering the temperature towards the glass region. The latter behavior is reflected by a progressively increasing role of the nonlinear term with decreasing temperature. It is interesting to note that the exponent k seems to “diverge” upon approaching the “frozen” state. Due to the fact that $1/k$ is related to the fractal (multifractal) dimensionality, the overall picture is consistent (in a very broad sense) with the hypothesis of the system fractality (multifractality) in the almost glassy state. We would like to comment as well that the shift ω_0 (iron data) starts to drop much more rapidly than expected from the Dulong-Petit rule in the region of already fast diffusivity indicating some significant changes in the electron density experienced by the iron ion in this temperature range.

It is interesting to note, that the parameter α responsible for a deviation from the simple liquidlike behavior remains practically constant from the lowest accessible experimentally temperature up to slightly above 265 K. We find for the weighted average $\langle \alpha \rangle_1 = 2.53(6)$ in this region (see Fig. 3). For higher temperatures the parameter α decreases to the zero value, e.g., the weighted average of the data points measured at 270 and 275 K equals $\langle \alpha \rangle_2 = 1.52(7)$, while the scattering data obtained at 308 K and above can be evaluated taking $\langle \alpha \rangle_3 = 0$. The critical exponent of the CD law can be uniquely related to the parameter α by assuming that the average relaxation times are the same for both laws. From Fig. 3 this implies that the CD critical exponent equals 0.33 below 265 K and is 0.55 in the 270 to 275 K temperature region.

The temperature where the collapse to the Debye behavior starts seems to be somewhat lower than reported for pure glycerol by measuring the dielectric susceptibility⁴⁸ and evaluating data within the CD law. Such a

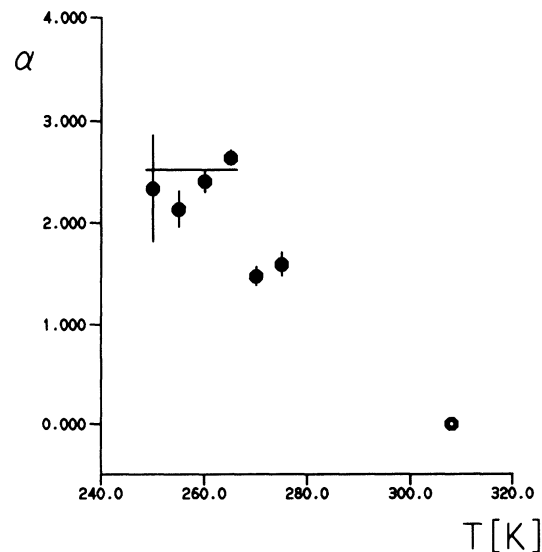


FIG. 3. Parameter α plotted versus temperature. Solid horizontal line represents weighted average over the low-temperature region.

behavior could be due to the water coordination of the iron complex in the acidic environment. Our results, shown in Fig. 3, suggest that the decrease of the parameter α versus increasing temperature may well occur in steps in accordance with the "hierarchical" model by Palmer *et al.*,³⁵ where one can speculate that successive degrees of freedom come into play at relatively well-defined temperatures. One cannot exclude the possibility that the observed steps are caused by the coupling between the ferrous complex and the host. Scaling of the corresponding broadenings observed by the absorption spectroscopy and scattering, respectively, indicates that the majority of diffusive events occurs at distances short compared to the ⁵⁷Fe length scale of 0.86 Å. It can then be concluded that diffusive displacements are mainly due to the collective motion within glycerol.

The question remains open how the parameter α (or the parameter k) depends upon the wave-vector transfer to the system q . Any such dependence is indicative of the

correlation between temporal and spatial scales. In order to investigate such a correlation a Rayleigh scattering of the Mössbauer radiation experiment has to be performed at different wave-vector transfers and at sufficiently low temperature, i.e., with a good enough energy resolution (provided one is looking at a pair-correlation function). It seems that such an experiment might be feasible with the Mössbauer beams obtained from synchrotron-radiation sources.

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