Spectra of structural relaxation rates in glasses with a continuous distribution of hierarchy levels

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We propose a modified version of the model of Palmer *et al.* [Phys. Rev. Lett. **53**, 958 (1984); **54**, 365 (1985)] for isothermal hierarchically constrained structural relaxation in glasses and glasslike liquids, in which the distribution of hierarchy levels is continuous rather than discrete. On this basis we construct continuous $\varphi(k)$ spectra for the relaxation rates and investigate their shapes, along with the spectral properties of a continuous parameter that measures the degree of structural nonequilibrium character. The results of analytic and numerical calculations agree quite well. We show that within the framework of this approach the difference between glass-forming systems with weak and with strong nonequilibrium behavior arises naturally, and we find criteria for identifying these regimes of relaxational behavior. We establish that from the point of view of statistics, a glass is a non-self-averaging system, i.e., a system in which the first moment and dispersion of the distribution density $\varphi(k)$ differ considerably from the most probable value of the relaxation rate and the width of the spectrum, respectively.

1. INTRODUCTION

A universal characteristic of various types of glassy systems is nonexponential Kohlrausch relaxation.[1-3] The origin of this universal property is associated with the existence of a hierarchy of potential barriers in nonequilibrium strongly interacting condensed systems such as glasses. These randomly distributed potential barriers are present because the structural formation of a glass is a kinetic phase transition of the "solidification without crystallization" type, for which a freezing-in of the structural disorder occurs. Therefore, properties of the glassy state such as the wide spectrum $\varphi(k)$ of rates (k) of structural relaxation (SR) are determined by memory effects and by the disordered nature of the "hot" frozen-in atomic structure, both of which arise in the process of glass formation.[2,3]

It has been shown previously[1,4] that a description of isothermal SR in glasses can be based on the following postulates: (1) the dynamics of nonexponential SR are hierarchically constrained; and (2) structural rearrangement takes place via the mechanism of defect reaction. The model relaxation function $q(t)$ postulated in (4) allows us to (a) describe the three regimes of time evolution of a quasiergodic glassy system, including fractional-exponential Kohlrausch relaxation, in a unified way; (b) obtain a density $\varphi(k)$ of the distribution of relaxation rates that is finite at every instant, and investigate its asymptotic behavior in the ranges of large and small k; (c) connect the parameters of the theoretical model with experimental data on SR; and (d) calculate the activation energy spectrum for atomic reconstruction in the glass.

The fundamental idea of the well-known model of hierarchically constrained glassy relaxation[1] is as follows: from the point of view of nonequilibrium statistical thermodynamics, a glass is an infinite set of weakly interacting subsystems (clusters), in which relaxation takes place simultaneously and independently. The clusters are classified according to levels of a hierarchy labeled by $n = 0,1,2,...$; relaxation in each cluster is successively blocked by taking into account "cooperativeness." This postulate regarding the hierarchical structure of the reservoir of structural degrees of freedom of the glass,[1] by its very nature, is analogous to representations of elementary excitation in solid-state theory. In fact, in a certain sense the hierarchy levels can be treated as elementary relaxational excitations of a system with structural nonequilibrium character.

However, the approach of Ref. 1 fails to incorporate the fact that each atom of a glassy system can participate in an arbitrary number of cooperative processes whose mechanisms mediate the SR; in other words, each atom can belong to several relaxing clusters. Therefore, strictly speaking, the total system cannot be divided up into independent clusters as was implicitly assumed in Ref. 1. Such clusters, which should perhaps correspond to the various levels of the system hierarchy, always overlap. Therefore, we cannot expect discrete clusters and hierarchy levels, since this expectation is tenable only in an approach where n is an integer. In this paper we assert that cooperative SR in glasses takes place not through a denumerable set of paths but rather via a continuum of parallel and independent paths. Thus, it is natural to seek a formulation of the model of hierarchically constrained SR in which the recursion relations for the relaxation rates and occupation are preserved, as postulated in Ref. 1, but to assume that the index n for these relations, which enumerates the various levels of the hierarchy, is a continuous positive quantity.

In this paper we propose a modification of the model of hierarchically constrained glass relaxation dynamics[1] that is characterized by a continuous (not discrete, as in Ref. 1) distribution of relaxation probabilities. This allows us to investigate the properties of this distribution and its evolution in cases where the system is weakly or strongly out of equilibrium. In Sec. 2 we discuss our interpretation of the model of glass relaxation with a discrete set of hierarchy levels; in Sec. 3 we justify the transition to a continuous hierarchical distribution. In Sec. 4, we investigate the shape of the spectrum $\varphi(k)$ in an exactly-soluble model of correlated isother-

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mal SR with a continuous distribution of hierarchy levels. In Sec. 5 we find the asymmetry parameters of the spectrum $\varphi(k)$ for the cases of weak and strong structural nonequilibrium character. In Sec. 6 we attempt to associate the parameters of the "nonequilibrium character" of this model of correlated SR with the fundamental concept of a glass structural temperature. The interpolation model we construct in this paper, with a continuous distribution of hierarchy levels, can serve as a basis for analysis and processing of experimental data on frozen-in nonexponential relaxation in condensed systems.

2. INTERPRETATION OF A MODEL OF COOPERATIVE RELAXATION WITH A DISCRETE SET OF HIERARCHY LEVELS

In what follows, we investigate SR in a temperature region for glass formation that is somewhat higher than the liquid-glass transition point. The discrete model of hierarchically constrained glass relaxation[1] is based on the following recursion relations:

1) Relaxation that is correlated in character (barrier scaling for the kinetics):

$$k_{n+1}=k_n \exp(-\mu_{n+1}) \quad (n=0,\,1,\,2,\ldots) \tag{1}$$

implying that the system of the $(n+1)$th hierarchy level must overcome a certain characteristic potential barrier [the exponential factor in (1) is the barrier transmittivity], after which its relaxation proceeds in the same way as the system for the nth level; the relaxation rate k_n corresponds to the latter in Eq. (1).

2) A hierarchy of reduced potential barriers μ_n for cooperative glass relaxation that separate subsystems of adjacent levels with labels n and $n-1$ and have the form

$$\mu_n=\mu/n^s, \quad s\geqslant 1, \quad 0<\mu<\infty. \tag{2}$$

The quantity μ is referred to as the "cooperativeness" parameter. The case $\mu=0$ corresponds to neglecting cooperative effects in overcoming the barriers to structural relaxation, while the case $\mu\to\infty$ is for completely frozen-in SR.

3) A statistical distribution w_n $(n=0,1,2,\ldots)$ of the subsystems with respect to hierarchy level that acts as the measure of the structural nonequilibrium character of the total glass-forming system. We can expect that a "narrow" distribution w_n corresponds to "weak" nonequilibrium character, while a "wide" distribution reflects "strong" nonequilibrium character. In order to describe the scaling of the occupations w_n, it is useful to introduce a representation of a certain averaged glass defect; this allows us to describe the statistical behavior of the disorder on the average at the hierarchy level in the glass. Then the system for the nth level contains n independent glassy defects. The probability of annihilating one of these defects for the nth level equals $\exp(-\mu_n)$ [see (1) and (2)]. The atomic reconstruction in the glass is cooperative, i.e., it is arranged in such a way that in order to annihilate a single glass defect in the system for the $(n+1)$th level we need to overcome a smaller potential barrier than we do in the system for the nth level [see (2)]. The occupation of a level with n glassy defects is determined by the probability $p=1/\lambda$ $(1<\lambda<\infty)$ of its formation in the nonequilibrium cooling process (multiplicative scaling of the occupation):

$$w_n\propto p^n, \quad 0<p<1. \tag{3}$$

From this, based on the recursion relations (1)–(3), the isothermal structural relaxation function in the glass is described by the weighted average over all the levels of the hierarchy:

$$q(t)=\sum_{n=0}^{\infty} w_n \exp(-k_n t), \tag{4}$$

$$k_n=k_0 \exp[-\mu\zeta(s,n)], \qquad \zeta(s,n)=\sum_{j=1}^{n} j^{-s}, \tag{5}$$

where $s=1+\varepsilon$, $\varepsilon\ll 1$ (the strong inequality guarantees the existence of the Kohlrausch regime at intermediate times[1]). The incomplete Riemann zeta function $\zeta(s,n)$ should be supplemented in its definition by $\zeta(s,0)=0$, i.e., for $n=0$.

This model of correlated glass relaxation can also be viewed as a specific realization of the distribution function for the heights of the potential barriers in the glassy system; therefore the parameter μ in (2) is the effectiveness of the barrier, independent of how the latter is overcome, i.e., whether by thermal activation or tunnelling. We can expect that the quantity p corresponds to the probability of appearance of weakened or broken bonds in the atomic lattice of a structural glass, while the quantity $\exp(-\mu_n)$ is the transmittivity of the effective barrier corresponding to cooperative processes of annihilation of such a defect at the nth hierarchical level.

The spectral density of the distribution $\varphi(k)$ of relaxation rates for the model proposed in Ref. 1 is a discrete set of delta functions:

$$q(t)=\int_0^\infty dk \exp(-kt)\varphi(k), \quad q(0)=\sum_{n=0}^{\infty} w_n=\int_0^\infty dk\, \varphi(k)=1,$$

$$\varphi(k)=\sum_{n=0}^{\infty} w_n\delta(k-k_n). \tag{6}$$

It is known that a weakly nonequilibrium system is characterized by a single relaxation time, i.e., for such a system the relaxation-time approximation is exact. In this case, the many-particle system described in the discrete model by relations (1)–(6) is found in the zeroth level of the hierarchy $(w_n=\delta_{n0}, p=0)$; in other words, the relaxation of this system occurs without participation of the structural degrees of freedom (the value of the parameter μ is insignificant). For a glassy system with strong nonequilibrium character, levels with large values of n $[0<n<\bar{n}$, where $\bar{n}\approx(\ln\lambda)^{-1}]$ contribute substantially to the spectrum $\varphi(k)$ [see (6)], where the quantity n is the width of the distribution w_n. Thus, in terms of this model of correlated (or cooperative) SR, the structural nonequilibrium character is characterized by the inequalities $\bar{n}>1$, $\ln\lambda<1$, and the scale parameter p is determined according to (3).

In what follows, we present the results of our investigation of the shape of the SR spectrum in glasses, both for fixed values of the fractional exponent α [i.e., the case $\mu=\text{const}$ in (2)] and for variable μ; in this case, it turns out that the regimes of strong and weak structural nonequilibrium character of the many-particle systems are distinguished precisely by their values of the parameters p (more precisely, the parameter $\ln \lambda$).

3. TRANSITION TO A CONTINUOUS HIERARCHICAL DISTRIBUTION

In this section we construct generalized models[1] such that the spectral density $\varphi(k)$ is a continuous normalized distribution of relaxation rates, each moment of which is finite (see also Ref. 4). The well-known postulates of the hierarchically constrained model of glass relaxation dynamics (Sec. 2) are satisfied in this case as well. The advantage of this generalization is the fact that it allows us to investigate the shape of the spectrum $\varphi(k)$ and compare it with other models and approximations (Sec. 4).

Central to this proposed generalization of the glass SR model is an interpolation of the incomplete Riemann zeta function, which is given in the form of the discrete sum (5) for $n = 1,2,3,...$, over the entire range of positive real n. For $n > 1$ this continuation is trivial, and follows from the well-known properties of the incomplete zeta function:

$$\zeta(s,n) \approx C + \frac{1-n^{-\varepsilon}}{\varepsilon} + \frac{1}{2n^s}, \quad n>1, \tag{7}$$

where $C \approx 0.5772$ is the Euler constant. The error in approximation (7) at the point $n = 1$, where $\zeta(s,1) = 1$, is about 7.7%, and decreases rapidly as n increases. In order to construct the continuation into the region $n < 1$, in this paper we propose an interpolation procedure for the function $\zeta(s,n)$ when the distribution of hierarchy levels in relations (4)–(6) is continuous by matching the analytic expression (7), which is valid for $n > 1$, to a certain model function with the following properties for $0 \leqslant n < a$ (where a is the matching point; see below): (a) the function should increase monotonically with increasing n; (b) the function and its first and second derivatives should equal the corresponding values that follow from Eq. (7) at the matching point; and (c) the function $(\zeta')^{-1} = (d\zeta/dn)^{-1}$ should reduce to zero at the point $n = 0$. As we will show below (Sec. 4), this latter condition guarantees continuous behavior of the distribution density $\varphi(k)$ at the upper boundary of the spectrum ($k \to k_0$).

The requirements we have formulated lead to the following form of the function $\zeta(s,n)$ for $n < a$:

$$\zeta(s,n) = b_1 n^{0.5} + b_2 n + b_3 n^{1.5}, \tag{8}$$

where the coefficients b_i are specified by condition (b). The choice of the matching point for Eqs. (7) and (8) is determined by the following additional condition on the resulting spectrum (compare with (6); $0 < N = \ln \lambda < \infty$):

$$\varphi(k) \approx N \int_0^\infty dn\, \lambda^{-n} \delta(k-k_n) = N \frac{\lambda^{-n}}{\mu k \zeta'(s,n)} \tag{9}$$

should not have singularities of the point-of-inflection type, i.e., points where the second derivative ζ'' changes sign. The value $a = 1$ is not appropriate as a matching point, because according to (7) the derivative $\zeta''(s,1) \approx \varepsilon/2$ is close to zero. In what follows, we use the point $a = 2$ as a matching point, at which this latter problem does not arise. Then for $\varepsilon = 0.01$, we find the following numerical values for the coefficients in (8): $b_1 = 0.936$, $b_2 = 0.208$, $b_3 = -0.079$.

In contrast to the discrete model (Sec. 2), in this case the hierarchy has no structureless (zero) level. That is, in this model of cooperative relaxation with a continuous label n, rapid elastic relaxation can be described only by including additional degrees of freedom in the many-particle system. This is especially important when we take the limit $\mu \to \infty$, which models the complete freezing-in of the SR. In the discrete model this corresponds to

$$q(t) = (1-p)\exp(-k_0 t) + p,$$

i.e., the relaxation takes place without participation of the structural degrees of freedom corresponding to the labels $n = 1,2,3,...$, and is incomplete: $q(t\to\infty) = p \neq 0$.

Two facts must be emphasized. First of all, the direct transition in the recursion relations (1)–(3) to a continuous label n [in particular, the transition to differential equations for the rates k_n in (1)] is unsatisfactory. Actually, according to (1) and (2), the function

$$\frac{d(\ln k_n)}{dn} = -\frac{\mu}{(n+1)^s}, \qquad \mu^{-1} \ln \frac{k_0}{k_n} = \frac{1-(n+1)^{-\varepsilon}}{\varepsilon} \tag{10}$$

does not coincide with (7) for any n. Secondly, the function (8) is not the analytic continuation of the discrete sum (5). In fact, the exact analytic continuation of the sum (5) is implemented by using the integral representation for the incomplete Riemann zeta function:

$$\zeta(s,n) = \frac{1}{\Gamma(s)} \int_0^\infty dx\, x^{s-1} \frac{1-e^{-nx}}{e^x - 1}, \tag{11}$$

where $\Gamma(s)$ is the gamma function. For small n ($0 < n < 1$) the following expansion is valid:

$$\zeta(s,n) = n \sum_{m=0}^\infty (-1)^m \zeta(m+2) n^m, \tag{12}$$

where $\zeta(s)$ is the standard Riemann zeta function. According to (11) and (12), the value of the derivative at $n = 0$ is $\zeta'(s,n) \approx \zeta(2) = (1/6)\pi^2$. Therefore, in using (11) the spectrum $\varphi(k)$ would have a discontinuity at $k = k_0$ [see (9)].

This comparison shows that while the function (7), (8) we have constructed agrees with the postulates of the model given in Ref. 1 (see also Ref. 3), and also with the requirement of continuity of the distribution density $\varphi(k)$ over the entire region of allowed values of the relaxation rate k, it is not the approximation (11). Introduction of the modified function (7) and (8) lets us successfully avoid a deficiency of the discrete model of Ref. 1, i.e., nonergodicity as $\mu \to \infty$, connected with the fact that the zero level of the hierarchy $n = 0$ does not contain the cooperative effects. However, in this case the approximation still has some arbitrariness, connected with the value of the exponent in the expansion (8). Our analysis shows that the expansion proposed here in half-integer powers is satisfactory.

Thus, we have obtained an interpolation function for the modified incomplete Riemann function entering into Eq. (5) for the relaxation rates, in which the label n now runs over all positive values; this function is shown in Fig. 1 for

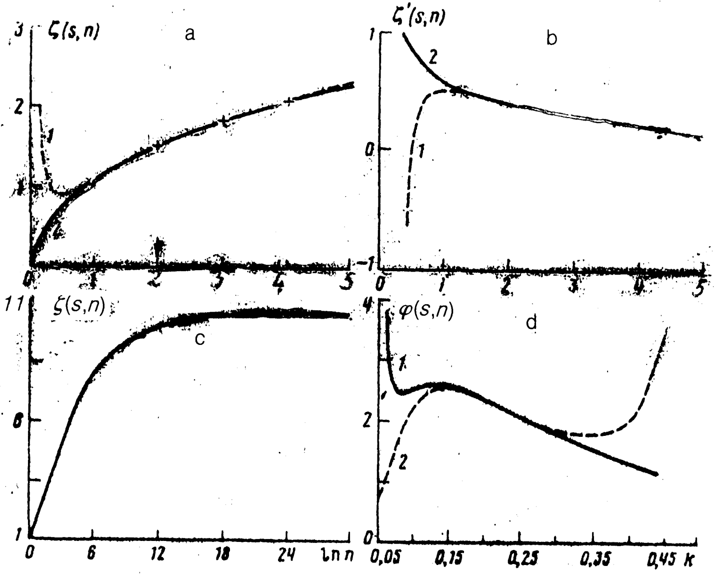

FIG. 1. Continuous interpolation of the incomplete Riemann zeta function $\zeta(s,n)$ (a) and its derivative $\zeta'(s,n)$ (b) based on Eqs. (7) and (8) for $\varepsilon = 0.01$ and a matching point $a = 2$ ($\zeta(s,1) = 1.065$): *1*) approximation (7), *2*) approximation (8); the dots are the discrete representation (5). (c) shows the behavior of the function $\zeta(s,n)$ over a logarithmically wide region of variation of n ($n_1 = 2.203\cdot 10^4$, $\varepsilon = 0.1$); (d) shows results of matching for the spectrum $\varphi(k)$ (9) ($\ln\lambda = 10$, $\mu = 1$): *1*) approximation (7), *2*) approximation (8).

$a = 2$. We should note: (1) the high quality of this interpolation, i.e., its agreement with the discrete sum (5) at the corresponding points; (2) the existence of a linear region $\zeta \propto \ln n$ for $1 \ll n \ll n_1 = \exp \varepsilon^{-1}$ [this is the condition that expression (7) be expandable in a series: $\varepsilon \ln n \gg 1$]; (3) saturation of the function $\zeta(s,n)$ for $n \gg n_1$:

$$\zeta(s) = \lim_{n\to\infty} \zeta(s,n) = \zeta(s,\infty) \approx C + \varepsilon^{-1}, \quad \zeta(1) = \infty. \qquad (13)$$

The latter property is equivalent to the existence of a minimum relaxation rate in the system $[\tilde{k} \approx k_0 \exp(-\mu C) < k_0]$:

$$k_{min} = \lim_{n\to\infty} k_n = k_0 \exp[-\mu\zeta(s)]$$

$$= \begin{cases} \tilde{k}\exp(-\mu/\varepsilon) = \tilde{k} n_1^{-\mu}, & s>1 \\ 0, & s=1 \end{cases}, \qquad (14)$$

which is the lower bound of the spectrum $\varphi(k)$. Consequently, the integration in the first relation (6) is in practice carried out from $k_{\min}$ to k_0 ($k_{\min} \leqslant k \leqslant k_0$).

This procedure for going to a continuum of hierarchy levels leads to the following expression for the relaxation rates:

$$k_n \approx \begin{cases} k_0 \exp[-\mu(b_1 n^{0,5} + b_2 n + b_3 n^{1,5})], \quad 0 \leqslant n < a & (15a) \\ k_0 \exp[-\mu(C + \ln n + 1/2n)] \approx \tilde{k} n^{-\mu}, \quad a \leqslant n \leqslant n_1. & (15b) \\ k_{min} \exp(\mu n^{-\varepsilon}/\varepsilon), \quad n \gg n_1 & (15c) \end{cases}$$

Thus, the approach discussed in the next sections for describing glassy SR based on Eqs. (4), (9), and (15) is an interpolation scheme, which can be used over the entire region of variation of the relaxation rate.

4. SHAPE OF THE RATE SPECTRUM FOR STRUCTURAL RELAXATION IN A MODEL WITH A CONTINUOUS DISTRIBUTION OF HIERARCHY LEVELS

We note several distinctive features of the resulting spectral density $\varphi(k)$. First of all, near the upper boundary of this spectrum ($k \to k_0, n \ll 1$) the function $\varphi(k)$ continuously goes to zero $[\varphi(k = k_0) = 0]$ according to the following law:

$$\varphi(k) = N \frac{2n^{0,5}}{\mu k_0 b_1}, \qquad n = \left[(b_1\mu)^{-1} \ln \frac{k_0}{k}\right]^2. \qquad (16)$$

Second, we have $\varphi(k = k_2) \approx 2.67 N(\lambda^2 k_2 \mu)^{-1}$ at the matching point $n = 2$. Third, for $k_{n_1} < k \ll k_1$ ($1 \ll n < n_1$) the spectrum is well approximated by the expression

$$\varphi(k) \approx N(\tilde{k}\mu)^{-1} \lambda^{-n} n^{1+\mu} = N\lambda^{-n} n/\mu k_n. \qquad (17)$$

Fourth, near the accumulation point $k = k_{\min}$ the spectral distribution $\varphi(k)$ goes smoothly to zero (see below).

Because of its method of construction, the modified model of SR given in this paper does not contain any structureless hierarchical level, i.e., relaxation in which very small n contribute ($n \ll 1$, $\ln\lambda \to \infty$) remains structural and cooperative.

These properties are illustrated by the results of a calculation of the spectra $\varphi(k)$ of rates of cooperative relaxation based on relations (9) and (15) as a function of the model parameters $\ln\lambda$ and μ (Fig. 2). Obviously, the quantity $\ln\lambda$, which is uniquely linked with the probability p for forming an average glassy defect (Sec. 2), plays the role of a characteristic parameter for a glassy many-particle system with structural nonequilibrium properties. Then since a wide (narrow) statistical distribution w_n (3) corresponds to small (large) values of the parameter $\ln\lambda$, we can conclude that the spectra in Fig. 2a correspond to a regime of weak structural nonequilibrium character, while those in Fig. 2b correspond to a regime of strong structural nonequilibrium character. By changing the cooperativeness parameter μ for these plots, we change the fractional exponent $\alpha = 1/(1+\mu)$ defined in Ref. 1.

The transition from a regime of weak to one of strong nonequilibrium character is shown in Fig. 2c, from which we conclude that in the first case the spectral density $\varphi(k)$ is essentially different from zero in a region of values $k \approx k_0$, and is symmetric in the limit $\ln\lambda \to \infty$ (Fig. 2a), while for

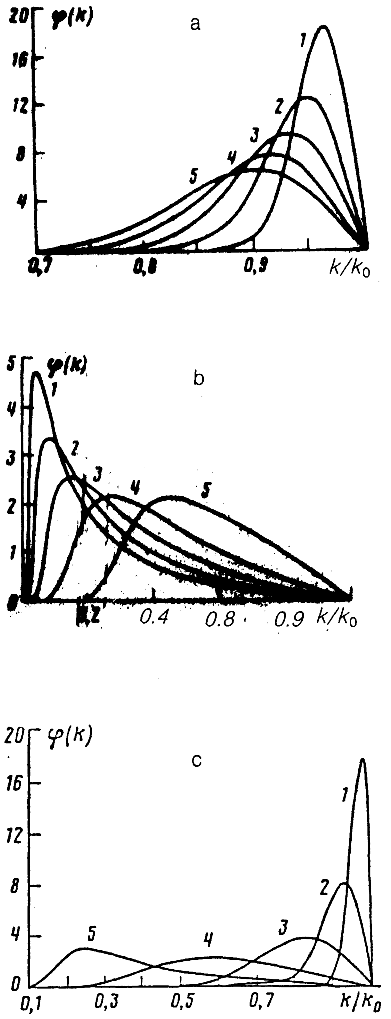

FIG. 2. Normalized calculated spectra $\varphi(k)$ [Eqs. (9) and (15)] for $\varepsilon = 0.01$ and various values of the parameters: a) $\ln\lambda = 100, \mu = 0.5$ (*1*), 0.75 (*2*), 1.0 (*3*), 1.25 (*4*), 1.5 (*5*); b) $\ln\lambda = 0.5, \mu = 0.5$ (*1*), 1.75 (*2*), 1.0 (*3*), 0.75 (*4*), 0.5 (*5*); c) $\mu = 0.5$, $\ln\lambda = 100$ (*1*), 20 (*2*), 4 (*3*), 0.8 (*4*), 0.16 (*5*).

the case of a strongly nonequilibrium system the spectrum is concentrated near values of $k \gtrsim k_{\min}$ and is always strongly asymmetric (Fig. 2b). Thus, in this model of cooperative glassy relaxation, representations with weak and strong nonequilibrium character arise naturally, and the corresponding regimes of relaxation admit a further quantitative analysis (see Sec. 5 and below).

Rather than discussing the nonequilibrium character at the quantitative level, it is useful to compare the results shown in Fig. 2 with model $\varphi(k)$ distributions found in the literature: the Kohlrausch law[5] ($\alpha = 0.5, \mu = 1$)

$$\varphi_K(k) = \frac{\tau}{2[\pi(k\tau)^3]^{0,5}} \exp\left(-\frac{1}{4k\tau}\right), \tag{18}$$

the Davidson–Cole distribution[6]

$$\varphi_{DC}(k) = \begin{cases} \dfrac{\sin(\pi\alpha)}{\pi k}(k\tau-1)^{-\alpha}, & k\tau>1 \\ 0, & k\tau\leqslant 1 \end{cases} \tag{19}$$

and the distribution function for relaxation rates in two-level systems (TLS) in glasses[7]

$$\varphi_{\mathrm{TLS}}(k) = {}^3/_4 k\tau^2 (1-k\tau)^{-0,5}. \tag{20}$$

The quantity τ coincides with the fractional-exponential relaxation introduced in Ref. 1 (here we have corrected a misprint that appears there):

$$\frac{1}{\tau} = \tilde{k}(1+\mu)^{1+\mu}\left(\frac{\ln\lambda}{\mu}\right)^{\mu}. \tag{21}$$

The results of comparing the spectrum $\varphi(k)$ calculated according to (9) with the model distributions (18)–(20) are shown in Fig. 3. The distributions (18) and (19) differ from zero for arbitrarily large relaxation rates, while their asymptotic forms as $k \to \infty$ coincide [$\varphi(k) \propto k^{-(1+\alpha)}$]; as (4) shows, this leads to an unphysical divergence of all the moments of the spectra (18) and (19), starting with the first. In addition, the real physical system can possess only a bounded spectrum of relaxation rates (i.e., there exists an upper bound k_0). The presence of a power-law "tail" in the Kohlrausch distribution (18) is associated with the considerable decrease in the maximum of the spectrum compared with that calculated using (9) (Fig. 2, curves *1* and *2*). The sharp cutoff in the spectrum (19) in the region of small rates (Fig. 3, curve *3*) leads to a considerable disagreement with the spectra (9) and (18). Obviously, the model TLS spectrum (20) cannot lead to fractional-exponential relaxation (Fig. 3, curve *4*). Thus, our comparison of the relaxation spectra shown in Fig. 3 demonstrates the advantage of an approach based on representations involving hierarchically constrained structural relaxation.

An interesting feature of this model of SR is the possibility of obtaining sharply asymmetric spectra $\varphi(k)$ that are displaced toward the point $k = k_{\min}$ for systems that, according to the classification given above, correspond to the case of weak nonequilibrium character ($\ln\lambda > 1$). These quasiequilibrium spectra arise for large increases in the cooperativeness parameter μ, or, which is equivalent, for decreases in the fractional exponent α (Fig. 4). An analysis similar to that carried out in Ref. 1 shows that this quasinonequilibrium character for large μ (Fig. 4, curve *5*) leads to a structural relaxation $q(t)$ (curve *4*) which possesses fractional-exponential behavior only after a sufficiently large time $t > t_0 = N/\mu\tilde{k}$ has passed ($\tilde{k} \ll k_0$ for $\mu > 1$),

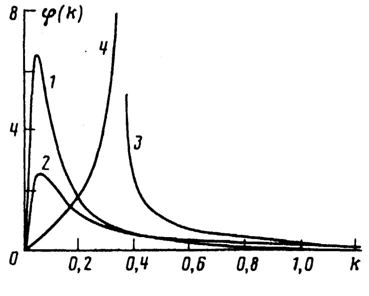

FIG. 3. Normalized spectra of relaxation rates calculated using various expressions: (*1*): Eq. (9), (*2*): Eq. (18), (*3*): Eq. (19), (*4*): Eq. (20). Here $\alpha = 0.5, \mu = 1, \ln\lambda = 0.16$.

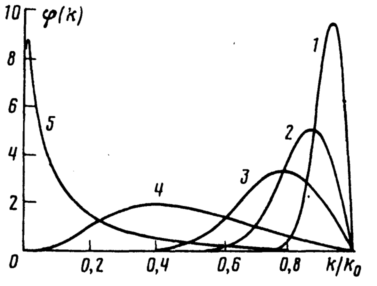

FIG. 4. Normalized calculated spectra $\varphi(k)$ [expressions (9) to (15)] for $\varepsilon = 0.01$ and $\ln\lambda = 10$: (*1*): $\mu = 0.3$, (*2*): 0.6, (*3*): 1.0, (*4*): 3.0, (*5*): 9.0.

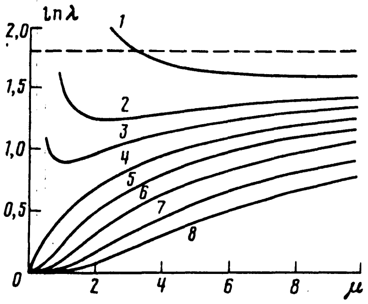

FIG. 5. Phase diagram for the model of cooperative relaxation: (*1*): $k_0\tau = 0.1$, (*2*): 0.3, (*3*): 0.5, (*4*): 1.0, (*5*): 2.0, (*6*): 5.0, (*7*): 20.0, (*8*): 100; $\exp C = 1.781$.

when the basic processes of exponential relaxation have practically ended [$q(t) \ll 1$]. In this case, the Kohlrausch relaxation time τ (21) satisfies the condition $k_0\tau < 1$, i.e., the characteristic rate τ^{-1} lies outside the spectrum $\varphi(k)$. However, this paradox is only apparent: the condition $q \ll 1$ for $t > t_0$ can be satisfied only by the fractional exponent $\exp[-(t/\tau)^\alpha]$ ($\alpha \leqslant 0.1$) with very small τ, i.e., in the present case of a weakly nonequilibrium system the quantity τ is a fictitious relaxation time whose origin is determined by the fact that for $0 < t < t_0$ the relaxation is exponential with a rate close to k_0.

It must be emphasized that this situation is completely analogous to that studied in Ref. 4, where the model structural relaxation function $q(t)$ used possessed three regimes of temporal behavior [in this case the crossover time t_0 is identically equal to the quantity $\tau_{\min}$ in Ref. 4, Eq. (6a)]. However, there is a significant difference between the approach used in Ref. 4 to describe glassy relaxation based on modeling of $q(t)$ and the approach of this paper [modeling the spectrum $\varphi(k)$]: our analysis of the continuous analogue of relation (4), taking (15) into account, leads to the presence of a preexponential factor in the Kohlrausch regime of behavior for $q(t)$ [compare with Ref. 4, Eq. (6b)]:

$$q(t) \approx (1+\mu)^{-1}(t/t_0)^\alpha \exp[-(t/\tau)^\alpha], \quad t > t_0. \tag{22}$$

As a consequence of this, the behavior of $\varphi(k)$ at the lower boundary of the spectrum near the accumulation point $k = k_{\min}$ is smoother than in Ref. 4, that is, $\varphi(k = k_{\min}) = 0$. In particular, there is no delta-function singularity $\varphi(k) \propto \delta(k - k_{\min})$. However, in the case $\ln\lambda \ll \mu(\mu/\varepsilon)^{-1/\varepsilon}$ the width of the spectrum Δ is very small: $\Delta/k_{\min} \ll 1$, which corresponds to the replacement of Eq. (15b) by $k_{\min}$ for $n \gg n_1$.

It is convenient to classify the spectral singularities of structurally nonequilibrium systems (Figs. 2 and 3) based on the phase diagram of a model of isothermal cooperative relaxation. The latter is obtained if we consider the parameter $k_0\tau$ to be arbitrary and express $\ln\lambda$ as a function of μ from Eq. (21):

$$\ln\lambda = \exp C (k_0\tau)^{-1/\mu}\mu(1+\mu)^{-(1+1/\mu)}. \tag{23}$$

In this case, to each spectrum $\varphi(k)$ there corresponds a point on the plane $(\ln\lambda, \mu)$ (Fig. 5). Fixed values of $k_0\tau = \text{const}$ correspond to isolines on the phase diagram of the model (Fig. 5). The level curve $k_0\tau = 1$ is a separatrix, i.e., it separates regions of the phase space with weak ($k_0\tau < 1$) and strong ($k_0\tau > 1$) structural nonequilibrium character. For $\mu \gg 1$ the separatrix goes to its limiting value $\ln\lambda = \exp C$, i.e., the region lying above the line $\ln\lambda = \exp C$ always corresponds to weakly-nonequilibrium systems. The relaxation-time approximation (Sec. 2) corresponds to the limit $\ln\lambda \gg 1$; in this case, τ^{-1} significantly exceeds the upper boundary of the spectrum k_0 ($k_0 \ll 1$), and the regime of Kohlrausch relaxation is unrealized in practice.

From the data of Fig. 5 it is clear that the criterion $\ln\lambda < 1$ for the regime of strongly nonequilibrium systems is not always precise. In particular, for $\mu \ll 1$ cooperative effects do not play a significant role, and even for small values of $\ln\lambda$ the many-particle system turns out to be only weakly out of equilibrium. According to (23), the separatrix in the region of small μ behaves as $\ln\lambda \approx \mu \exp C$; therefore, the criterion for strong equilibrium character in this case is the inequality $\ln\lambda \ll \mu \exp C \ll 1$.

5. ASYMMETRY OF THE $\varphi(k)$ SPECTRA AND ITS CONNECTION WITH THE STRUCTURAL NONEQUILIBRIUM PARAMETER

Using the relations (9) and (15) derived above for $\varphi(k)$, let us investigate the moments, and also the position of the maximum and width of the spectrum of rates for isothermal SR in glasses. The general expression for the moments of the spectral density has the form ($l = 0,1,2,...$):

$$\langle k^l \rangle = \int_0^\infty dk k^l \varphi(k)$$

$$= N k_0^l \int_0^\infty dn \exp[-n \ln\lambda - \mu l \xi(s,n)] = N k_0^l (I_1 + I_2 + I_3). \tag{24}$$

Here it is convenient to break up the integral into integrals I_1, I_2, and I_3 with limits $[0,1]$, $[1,n_1]$, and $[n_1,\infty]$ respectively. For $\ln\lambda \gg 1$ the primary contribution to the moments is given by the region of integration $n \ll 1$; therefore, the integrals I_2 and I_3 can be neglected, while the integral I_1 has the form

$$I_1=\int_0^1 dn\exp(-n\ln\lambda-\mu lb_1n^{0,5})$$

$$=N^{-1}\{1-\exp(-v)-\pi^{1/2}u\exp(u^2)$$

$$\times[\operatorname{erf}(u+(\ln\lambda)^{0,5})-\operatorname{erf}(u)]\},\qquad(25)$$

where $v=\ln\lambda+\mu lb_1$, $u=1/2\,(\ln\lambda)^{-1/2}\mu lb_1$, and $\operatorname{erf}(x)$ is the error function.

In the limit where

$$\lambda\ln\lambda\gg\lambda\gg\ln\lambda\gg(\ln\lambda)^{1/2}\gg1,\quad u\ll1,\qquad(26)$$

holds, we retain only the principal terms in (25), e.g., terms of order $\exp(-v)\propto\lambda^{-1}$ are neglected, and obtain

$$\langle k^l\rangle\approx k_0{}^l(1-\pi^{1/2}u+2u^2),\qquad(27)$$

i.e., in a system with weak structural nonequilibrium character all the moments are close to k_0^l, which is a consequence of the narrowness of the distribution w_n in this case (Fig. 2a and Sec. 4). In particular, the expression for the dispersion of the distribution of rates takes the form

$$\sigma^2=\langle k^2\rangle-\langle k\rangle^2,\quad\sigma\approx\left(1-\frac{\pi}{4}\right)^{1/2}\frac{k_0\mu b_1}{(\ln\lambda)^{1/2}}.\qquad(28)$$

In the opposite case of a system with strong structural nonequilibrium character ($\ln\lambda\ll1$), the principal contribution to the moments (24) comes from the integrals I_1 and I_2. In fact, the integral I_3 in this case is estimated to be

$$I_3=\exp[-\mu l(C+1/\varepsilon)]\int_{n_1}^{\infty}dn\exp(-n\ln\lambda)$$

$$=\exp[-\mu l(C+1/\varepsilon)]\lambda^{-n_1}(\ln\lambda)^{-1},\qquad(29)$$

which is a small quantity ($Nk_0^lI_3\approx k_{\min}\lambda^{-n_1}$) when the normalization N in (24) is taken into account. We assume here that the inequality $n_1^{-1}\ll\ln\lambda\ll1$ is fulfilled. Then Eqs. (15) and (24) lead to the following expressions for the integrals I_1, I_2:

$$I_1\approx\frac{2}{(\mu lb_1)^2}[1-(1+\mu lb_1)\exp(-\mu lb_1)],\qquad(30)$$

$$I_2\approx\exp(-\mu lC)\sum_{m=v}^{\infty}\frac{1}{m!}(-\mu lC)^mE_{m+\mu l}(\ln\lambda),\qquad(31)$$

where $E_n(x)$ is the exponential integral. For the first moments of the spectral density $\varphi(k)$ when $\mu=1$ we have

$$\langle k\rangle\approx Nk_0\biggl\{\frac{2}{b_1{}^2}[1-(1+b_1)\exp(-b_1)]$$

$$+\exp(-C)[-2C-\ln\ln\lambda$$

$$-\ln C+E_1(C)]\biggr\}\approx\tilde{k}\ln\lambda(-\ln\ln\lambda)\ll k_0,\qquad(32)$$

$$\langle k^2\rangle\approx Nk_0{}^2\biggl\{\frac{2}{(2b_1)^2}[1-(1+2b_1)\exp(-2b_1)]$$

$$+\exp(-2C)\left(1-\frac{1}{e}\right)\biggr\}\propto k_0{}^2\ln\lambda\ll k_0{}^2.\qquad(33)$$

For the case $\mu\neq1$, the behavior of the moments (32) and (33) is changed in the following way: the double-logarithm asymptotic form in (32) and the second term in the curly brackets of (33) are replaced by the constant $(\mu l-1)^{-1}$, $l=1,2$. In this case, it is significant that in all the cases given here the dispersion of the distribution $\varphi(k)$ is

$$\sigma^2=\langle k^2\rangle-\langle k\rangle^2\approx\langle k^2\rangle\propto\ln\lambda,\qquad(34)$$

i.e., it is proportional to the structural nonequilibrium parameter. All of this is in agreement with numerical calculations of the relaxation rate spectra (Figs. 2 and 3, Sec. 4).

The expressions for the maximum and width of the spectrum $\varphi(k)$ in the limiting cases of systems with weak and strong structural nonequilibrium character can be obtained using the representations (9) and (15). Under the condition $\ln\lambda\gg\max(1,\mu^2)$, the maximum of the function $\varphi(k)$ (where k_m is the position of the maximum) lies in a region of relaxation rates close to the upper boundary of the spectrum k_0 ($k_m\approx k_0$), i.e., in the regions of small n we have for these quantities

$$k_m\approx k_0[1-\mu b_1(2\ln\lambda)^{-1/2}],\qquad(35)$$

$$\varphi(k_m)\approx(2/e)^{1/2}(k_0\mu b_1)^{-1}(\ln\lambda)^{1/2}.\qquad(36)$$

The width of the spectrum Δ at half-maximum is determined by the roots of the equation $\varphi(k)=(1/2)\varphi(k_m)$, which is conveniently written in the form

$$\exp[(x-r)^2]=hx,\ x=(n\ln\lambda)^{1/2},$$
$$r=\mu b_1(2\ln\lambda)^{-1/2}\ll1,\ h\approx(8e)^{1/2}\approx4{,}66.\qquad(37)$$

The expansion (37) in the small parameter $x\approx\tilde{x}-2r\tilde{x}$, where $\tilde{x}$ is either of the solutions to the equation $hx=\exp(x^2)$ ($x_1\approx1.37$, $x_2\approx0.225$), gives

$$\Delta\approx k_0\mu b_1(\ln\lambda)^{-1/2}(x_1-x_2).\qquad(38)$$

By comparing the relations (27) for the first moment ($l=1$) of the spectrum $\varphi(k)$ [for $\ln\lambda\gg\max(1,\mu^2)$ we can neglect the third term in brackets in (27) because $u\ll1$] with the coordinates of the maximum (35), we obtain the weak inequality $\langle k\rangle\leqslant k_{\min}$ [more precisely, $(k_{\min}-\langle k\rangle)/k_0\approx0.2\mu b_1(\ln\lambda)^{-1/2})$], i.e., the asymmetry of the narrow distribution of SR rates for weak nonequilibrium systems (Fig. 2a) is insignificant even in the presence of the "tail" extending toward small k.

In order to compare the width of the spectrum (38) with the dispersion (28), it is necessary to take into account the following: (a) according to (37), we have $x_1-x_2\approx1.15$; (b) the role of the width of the spectrum is played not by the dispersion itself but by the quantity

$$\Delta_\sigma=(8\ln2)^{1/2}\sigma=1{,}09k_0\mu b_1(\ln\lambda)^{-1/2}.\qquad(28')$$

Thus, we obtain $(\Delta-\Delta_\sigma)/k_0\approx0.06\,\mu b_1\,(\ln\lambda)^{-1/2}\ll1$, i.e., with good accuracy both quantities are the same, which is completely natural in the case of a system with weak structural nonequilibrium character. In this case, the resulting spectrum (Fig. 2a) is symmetric, and can be well approximated by a Gaussian distribution.

Analogous calculations for the opposite case $\ln\lambda \ll 1$, $\mu \gg 1$, which corresponds to a strongly nonequilibrium system in the region of glass formation (Fig. 2b) lead to the following relations:

$$k_m \approx \tilde{k}\left(\frac{\ln\lambda}{1+\mu}\right)^{\mu} \ll k_0, \tag{39}$$

$$\varphi(k_m) \approx (\tilde{k}\mu)^{-1}\exp[-(1+\mu)]\frac{(1+\mu)^{1+\mu}}{(\ln\lambda)^{\mu}}. \tag{40}$$

Obviously, the rate k_m is small compared to k_0, i.e., the maximum of $\varphi(k)$ corresponds to the region of large n (Fig. 2b). In place of (37) the defining equation in this case is the following:

$$\exp x = \hbar x, \quad x = n\frac{\ln\lambda}{(1+\mu)}, \quad \hbar = 2^{1/(1+\mu)}e,$$
$$x_{1,2} \approx 1+\gamma \pm (\gamma^2+\gamma)^{1/2}, \quad \gamma = \frac{\ln 2}{1+\mu}. \tag{41}$$

As a result, for the width of the spectrum Δ we obtain

$$\Delta \approx \tilde{k}\frac{2\mu}{(1+\mu)^{\mu}}(\gamma^2+\gamma)^{1/2}(\ln\lambda)^{\mu}. \tag{42}$$

Taking the ratio of the first moment (32) and the coordinate maximum (39) for the case $\mu \approx 1$,

$$\langle k\rangle / k_m \propto -\ln\ln\lambda > 1, \tag{43}$$

we see that the asymmetry of the distribution $\varphi(k)$ becomes very significant: although we have $\langle k\rangle$, $k_m \ll k_0$ in a strongly nonequilibrium system, one is several times larger than the other. Analogous calculations for the case $\mu > 1$ lead to the relation $\langle k\rangle / k_{\min} \propto (\ln\lambda)^{1-\mu}$. These conclusions regarding the role of asymmetry are also confirmed by comparing Eqs. (34) and (42): for $\mu \approx 1$ and $\ln\lambda \ll 1$, the dispersion σ turns out to be considerably larger than the width of the spectrum Δ ($\sigma \gg \Delta$), which is possible only for a strongly asymmetric probability distribution (Figs. 2b and 2c).

The calculated functions (38) and (42) allow us to obtain an interpolation of the width Δ of the spectrum of rates for SR as a function of the structural nonequilibrium parameter $\ln\lambda$ over the entire range of variation of the latter (Fig. 6). As the departure from equilibrium increases ($\ln\lambda$ decreases), the quantity Δ initially increases monotonically, which corresponds to a shift in the maximum k_m of the spectrum from the upper boundary k_0 (Fig. 2c), and then for the case of a large departure from equilibrium ($\ln\lambda < 1$) it gradually falls to zero. In this case the spectral density $\varphi(k)$ gets closer and closer to the lower boundary of the spectrum $k \approx k_{\min}$.

Depending on the nonequilibrium parameter $\ln\lambda$, for a system far from equilibrium the position of the maximum (39) and the width of the spectrum (42) are proportional to one another (with a coefficient of proportionality depending only on μ). Analogous proportionality relations obtain for the case of weak nonequilibrium systems between the quantities $k_0 - k_m$ [see (35)] and Δ from (38). It is these relations that allow us to treat $\ln\lambda$ as the measure of the structural nonequilibrium character.

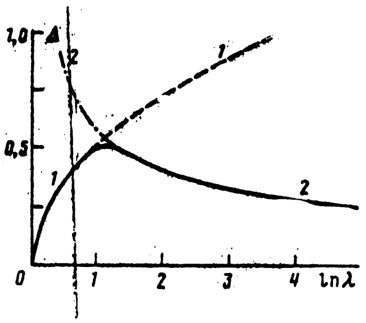

FIG. 6. Width of the spectrum of structural relaxation rates Δ as a function of the parameter $\ln\lambda$ calculated according to various expressions: (*1*): Eq. (42), (*2*): Eq. (38) ($\mu = 0.5$).

Thus, from the point of view of statistics, the density distribution $\varphi(k)$ of SR rates in a strongly nonequilibrium (glassy) system is not self-averaging, i.e., its first and second moments differ considerably from the most probable value and width of the spectrum, respectively. Consequently, for a complete description of the relaxation spectra of such systems it is necessary to know either all the moments or an interpolation formula for $\varphi(k)$ over the entire range of variation of k.

6. THE CONNECTION BETWEEN THE SHAPE OF THE RELAXATION RATE SPECTRUM AND THE STRUCTURAL TEMPERATURE OF GLASS FORMATION FOR THE SYSTEM

In conclusion, let us discuss the question of the mutual relation of the statistical and thermodynamic characteristics of structural nonequilibrium behavior in glass-forming liquids. The shape of the $\varphi(k)$ spectrum we discussed above for the rates of isothermal SR is determined by the thermal "prehistory" of the sample, which we can describe within the framework of the thermodynamic two-temperature theory of glass formation (see, e.g., Refs. 2,8,9) by introducing a representation for the structural temperature θ, i.e., the effective temperature of a reservoir of glass structural degrees of freedom. In this case, the inequality $\theta > T$, where T is the temperature of the lattice heat bath, characterizes the degree of heating of the atomic network of the glass-forming system. This approach is analogous to the phenomenological concept of a fictitious temperature T_f (Ref. 10), which, however, can be defined only with respect to a certain specific property of the glass, such as density, compressibility, or coefficient of thermal expansion.

The following is a possible definition of the structural temperature Θ in terms of the shape of the spectrum $\varphi(k)$. Let us assume that the probability distribution w_n for the relaxing regions of the glass based on the hierarchy levels with index n is power-law-like and depends on the degree of nonequilibrium character $\Theta - T$ in the following way [compare with Eq. (3)]:

$$w_n \propto [\text{const}\cdot(\Theta - T)/\Theta]^n. \tag{44}$$

Relation (44) can contain an unknown numerical factor (const). For an equilibrium system ($\Theta - T$), within the framework of the discrete model for SR we have $w_n = \delta_{n0}$, and the relaxation function $q(t)$ (4) is exponential (Sec. 2).

In the general case, the width of the corresponding spectrum of relaxation rates $\varphi(k)$ has two limiting regimes of behavior (Sec. 5 and Fig. 6). For the case of weak nonequilibrium behavior ($\Theta \geqslant T$), based on (38) and (44) we obtain

$$\Delta \propto (\ln \lambda)^{-1/2} \propto \{\ln[\Theta/(\Theta-T)]\}^{1/2}, \qquad (45)$$

i.e., a square-root dependence is found for the nonequilibrium width of the spectrum. For systems far from equilibrium, where the primary contribution to the density $\varphi(k)$ is given by subsystems with large values of n, according to (42) we have for the width of the spectrum

$$\Delta \propto (\ln \lambda)^{\mu} \propto \{\ln[\Theta/(\Theta-T)]\}^{\mu}. \qquad (46)$$

Based on the data given in Fig. 6, we can conclude that in both cases (45) and (46) the thermodynamic parameter for the structural nonequilibrium character $\Theta - T$ can turn out to be quite large. Thus, within the framework of this model of cooperative SR it is easy to make use of the characteristic region of values of the heating parameter $0 \leqslant (\Theta - T)/\Theta \leqslant 0.1$ to 0.2, values that are attained for the rates ordinarily used in cooling a melt in the region of glass formation in order to obtain insulating and semiconducting glasses.[3] It is noteworthy that the characteristic time (21) in the fractional exponential of isothermal SR in a model with hierarchically constrained dynamics also depends on the thermodynamic heating parameter of the atomic network:

$$\tau \propto (\ln \lambda)^{-\mu} \propto \{\ln[\Theta/(\Theta-T)]\}^{-\mu}. \qquad (47)$$

In particular, it follows from this that in the case of an equilibrium system ($T = \Theta$) there is no Kohlrausch relaxation regime ($\tau = 0$), which agrees with the data in Sec. 4.

Another possible way to define the structural temperature θ differs from the one presented above only by replacing the difference $\Theta - T$ by the difference in inverse values $1/\Theta - 1/T$, which in principle does not change the character of the functions obtained above. In both cases, departures of the system from structural equilibrium can be interpreted as transitions to higher levels of the hierarchy. Therefore, the higher the degree of excitation, the more the structural temperature will differ from the temperature of the heat bath. Then the isothermal relaxation of the atomic structure obeys the equation

$$\Theta(t) - T \propto q(t), \qquad (48)$$

which is its form coincides with the solution to the equation of Tula and Narayanaswamy for $T = \text{const}$ (Refs. 8–10).

7. CONCLUSION

We have discussed structural relaxation in disordered condensed systems with strong interactions, i.e., glasses and glass-forming liquids. Starting from the postulate of a reservoir of structural degrees of freedom with hierarchical structure, we have proposed a model that allows us to describe systems with both weak and strong structural nonequilibrium character within the framework of single approach, to investigate their asymptotic behavior at large times, and to study the transition to a regime of nonequilibrium relaxation. Our model satisfies all the criteria for glass relaxation with hierarchically constrained dynamics,[1] and is characterized by a continuous distribution of relaxation rates $\varphi(k)$ that is bounded from above (k_0) and from below ($k_{\min}$). Based on our analysis of this model, we have shown that relaxing systems can be classified both in terms of their statistical properties (the degree of structural nonequilibrium character $\ln \lambda$) and dynamic properties (the cooperativeness parameter μ). We have investigated the behavior of the $\varphi(k)$ spectrum in detail and have obtained analytic expressions for its moments as well as the position of its maximum and width; our data from numerical calculations of $\varphi(k)$ for various values of the parameters $\ln \lambda$ and μ agree very well with the analytic results. Within the framework of the approach developed here, we have found a quantitative criterion for the departure from structural equilibrium of glass-forming systems based on the phase plane of the model in the variables ($\ln \lambda$, μ), according to the values of the product $k_0 \tau$: regions where $k_0 \tau > 1$ are found to be far from equilibrium, while those with $k_0 \tau < 1$ are found to have weak nonequilibrium character.

We have shown that the non-self-averaging behavior of the system is a consequence of asymmetry in the spectrum of relaxation rates, a consequence of which is that the first moment and dispersion of the distribution density $\varphi(k)$ differ significantly from the most probable value of the relaxation rate and the width of the spectrum, respectively.

It must be emphasized that this model of cooperative SR does not presuppose the disruption of ergodicity in the glass-forming state (in this connection compare with Refs. 11 and 12); the glass relaxation for asymptotically long times corresponds to ergodic behavior, for which there is no residual nonequilibrium character. It is important, however, that the limiting attainable time for experimental observation is not always asymptotically large from the point of view of SR. Within the framework of this model, this is associated with the fact that as a function of the parameters $\ln \lambda$ and μ the spectral density $\varphi(k)$ can turn out to be a very wide distribution of relaxation rates, which extends over many decades. If in this case the inverse maximum observation time t_m^{-1} falls within the region of the maximum of the spectrum $\varphi(k)$, then such a system for all attainable times ($0 < t < t_m$) behaves as a nonergodic system with considerable residual (frozen-in) structural nonequilibrium character. As shown above, this nonergodic behavior must differ from the quasinonergodic behavior characteristic of weakly nonequilibrium systems for large values of the cooperativeness parameter μ. In such systems, a regime of nonexponential relaxation arises only after exponentially long times, and the use of the fractional-exponential approximation for all time intervals leads to unphysical values of the Kohlrausch relaxation time τ when the shift in the relaxation regime (see Ref. 4) is taken into account.

In view of these comments, and the relations we have identified between the statistical and thermodynamic parameters of the structural nonequilibrium character, we can conclude that our model of cooperative SR can provide a theoretical scheme within the two-temperature description of the processes of glass formation that is realistic enough to interpret and quantitatively analyze experimental data on the glassy relaxation of real systems in the glass-forming temperature region.

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