

A many-body stochastic approach to rotational motions in liquids: complex decay times in highly viscous fluids [☆]

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A two-body Smoluchowski equation, including a solute molecule and a collective solvent mode, is developed for studying reorientational dynamics in complex fluids. Multiexponential decay correlation functions for first- and second-rank observables are computed. They exhibit bifurcation and other properties related to typical observations on glassy and supercooled liquids.

1. Introduction

Reorientational relaxation in complex liquids is still lacking a unified treatment that is capable of dealing with the relevant stochastic processes without excessive complications. A significant challenge is offered by the study of highly viscous, glassy and supercooled liquids. Rotational relaxation of flexible short chain and small rigid molecules in supercooled organic liquids have been studied in the past by researchers including Johari [1,2] and Williams [3,4]. Typical systems considered were CH₂Cl₂ and C₆H₅-Cl in cis-decaline. More recently, Nozaky and Mashimo [5] have described a series of results on the dielectric friction of polyvinylacetate over a large range of frequencies. Supercooled liquids with highly anisotropic interactions, mainly due to hydrogen bonding (alcohols and water) have been studied by Floriano and Angell [6]. Magnetic resonance techniques have been applied to the study of relaxation processes in glassy systems. This includes the deuterium NMR study by Dries et al. of the glass transition in toluene, polystyrene and supercooled orthophenyl [7]. It provided spin relaxation times (T_1 and T_2) and spin-alignment data that yield accurate in-

formation on slow molecular reorientations on the time scale 10^{-4} to 10^2 s.

A rough model for explaining far-infrared data measured for supercooled decaline was proposed a few years ago by Reid and Evans [8,9] as an application of the so-called "itinerant oscillator theory". In a recent series of papers, Kivelson and Miles [10] and Kivelson and Kivelson [11] have focused their attention on the rotational relaxation of small molecules reorienting in supercooled organic fluids, and they attempted a partial interpretation based on a "three-variable" model [12]. Although the experimental data have to be considered incomplete, experimental techniques sensitive to both first-rank tensor correlation functions (IR, dielectric relaxation, shear compliance relaxation) and to second-rank tensor correlation functions (NMR, ESR, Raman scattering) suggest the presence of two main relaxation processes, usually named α and β . Above a given "bifurcation temperature", T_B only the faster β process is observed: it has a low activation energy and the ratio between the first-rank correlation β time (τ_1^β) and the second-rank correlation β time (τ_2^β) is close to 3, indicating diffusive behavior,

$$\tau_1^\beta / \tau_2^\beta \approx 3. \quad (1)$$

Below T_B , the slower process α is characterized by a higher activation energy and a ratio between the first- and second-rank correlation times close to 1,

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$$\tau_1^\alpha / \tau_2^\alpha \approx 1, \quad (2)$$

which could suggest the presence of a strong collisional relaxation process. This is, of course, a simplified picture reflecting the uncertainty in the experimental data. In many cases both the α and the β processes are better described as non-exponential functions, or as convolutions of many exponential functions [13]. Moreover, high frequency librational processes are observed in dielectric relaxation experiments (Poley absorption or γ process) usually as broad signals that are nearly temperature independent.

A theoretical interpretation of these experimental features is hardly obtained in the usual context of single-body stochastic descriptions, based on a Brownian model for a reorienting rigid molecule in an isotropic solvent. The presence of two main relaxation processes is a clear indication of the necessity of adopting a many-body model, in which the phase space of stochastic coordinates is enlarged to include some description of the collective nature of the *solvent* interacting with the solute. In ref. [11] Kivelson and Kivelson attempt a study of two different models of an intrinsic two-body nature, in which the system includes a solute body interacting with a solvent body via a *first-rank* torsional potential (i.e. with a single well) that depends upon their relative orientation. (They also consider a one-body model in which an activated process is added to the free rotation of the solute body in the form of a static potential with different wells (their model (c).) In their first two-body model both the solute and the solvent bodies are engaged in Brownian (slow diffusion) motion (model (a)); in the second one the solvent body is described as an object jumping suddenly from one orientation to the other (model (b)).

The discussion is based on approximate calculations of correlation functions of first- and second-rank tensors for the reorientation of the solute. The fast β process is related to the reorientation of the solute within the potential well, while the slow α process is associated with the reorganization of the potential itself, due to the relaxation of the local structure. On the long time scale of the α process, the conditional probability for the system is given by the time-independent probability of having the solute in a certain orientation within the well, multiplied by

the conditional probability for the reorganization of the potential (i.e. of the solvent structure body). Then by choosing a Brownian diffusive or a strong collision description for the solvent structure relaxation one recovers model (a) or model (b). Kivelson and Kivelson argue that model (b) is more favorable for interpreting actual glass transition phenomena in liquids, since it would give results close to eq. (2), but model (c) may be of some interest in solids. Model (a) is ultimately interpreted as a "renormalization of the tagged particle, resulting in a larger rotating pseudoparticle", without significant departures in the ratio between the slow motion first- and second-rank correlation times, from the expected diffusion-like value of three.

In this Letter we wish to consider a more detailed analysis of many-body stochastic models applied to the study of glassy fluids, taking advantage of a general theoretical and computational methodology we have been developing for the study of rotational relaxation in complex liquids [14]. Our main purpose here is to show that whenever the constraint of a single relaxing body is removed, and a two- (or higher-) body description is allowed, qualitative new features (not just quantitative details) emerge; and that they seem to be in accord with some of the features observed in experiments.

In the following we shall consider a two-body Smoluchowski equation for spherical rotators, interacting only via a potential of first or second rank in the relative orientation of body 1 (the solute probe) and body 2 (the solvent cage or "slowly relaxing local structure"). Instead of employing highly approximate procedures for evaluating correlation functions of interest, we shall use a complete computational treatment, based on the matrix representation of the full time evolution operator. This is made conveniently possible by the use of a very efficient set of basis functions (which is generated by taking advantage of the spherical symmetry of the liquid) and then by applying a powerful iterative algorithm for diagonalizing the matrix (the Lanczos algorithm and/or the conjugate gradient algorithm). Although the calculations presented here are only a partial overview of our main results, they demonstrate the strong influence of the interacting potential as well as the wide range of behavior that can be obtained without having to invoke any strong collision relax-

ation, and this can be of considerable interest for the analysis of the glass transition problem.

2. The model

We shall denote by Ω_1 a set of Euler angles defining the orientation of the solute molecule (hereafter body 1). Since we suppose that, given the high viscosity of the system, inertial effects are negligible, the conjugate angular momentum is not included in the relevant set of degrees of freedom, i.e. a purely Smoluchowski description for the solute is employed. A second rotating top, described by an analogous set of coordinates and momenta Ω_2 is coupled to the probe. It might be thought of as a collective structure of solvent molecules reorienting at roughly the same range of rates at which the probe moves. The time evolution of the probability density for the system is assumed to be governed by an operator \hat{L} ,

$$\hat{L} = \hat{L}_1 + \hat{L}_2, \quad (3)$$

where \hat{L}_1 and \hat{L}_2 are the rotational Smoluchowski operators for the first and second top. An isotropic fluid, corresponding to spherical symmetry is assumed for simplicity; the explicit form of the rotational operator for the n th body ($n=1, 2$) is

$$\hat{L}_n = D_n J_n \exp(-V/k_B T) J_n \exp(V/k_B T). \quad (4)$$

Here J_n is the operator (defined according to Hwang and Freed [15]), proportional to the infinitesimal rotation operator and D_n is the diffusion coefficient for the n th body. The interaction potential V is expressed as a sum of pair potentials involving the two bodies,

$$\frac{V(\Omega_1, \Omega_2)}{k_B T} = -u_1 P_1(\Omega_2 - \Omega_1) - u_2 P_2(\Omega_2 - \Omega_1), \quad (5)$$

where P_n stands for the Legendre polynomial of degree n .

The complete time evolution operator obeys all the requirements of detailed balance as described by Stillman and Freed [16]; the probability density tends to the equilibrium function defined by the Boltzmann distribution with respect to the total energy of the system given by the potential in eq. (5).

Computational treatment. One is interested in

evaluating correlation functions for the reorientational relaxation of the probe

$$G_{jm}^R(t) \equiv \langle Y_{jm}^*(t) | Y_{jm}(0) \rangle, \quad (6)$$

with $j=1,2$ as well as the associated spectral densities $J_{jm}^R(\omega)$ given by the Fourier-Laplace transforms of eq. (6). Due to the spherical symmetry (i.e. isotropic liquids) eq. (6) is the same for all values of m .

As noted above, we perform this task effectively by adopting a matrix representation for the operator \hat{L} using an efficient set of basis functions, which are obtained by the systematic application of standard angular momentum coupling techniques [14], in order to benefit from the full spherical symmetry. In the appropriate coupled representation we find that only two coupled degrees of freedom are relevant [14] (from the initial six). In general, not very large basis sets are required (up to order 10^3) for this task. Only 50–100 s of supercomputer CPU time were required for each spectral density calculation.

For each computed correlation function, the final outcome of the calculation is given by the collection of distinct time decay constants that contribute to the time evolution of the process. Each time decay constant τ_i is the inverse of an eigenvalue λ_i of the Fokker-Planck operator. Thus the spectral density can be expanded as a sum of Lorentzians, according to the general expansion [17–19]

$$J(\omega) = \text{Re} \sum_i \frac{c_i}{i\omega + \lambda_i} \quad (7)$$

and a weight c_i is associated with each eigenvalue λ_i . Usually, in all the many-body models we have studied a few dominant eigenvalues (or clusters of close eigenvalues are found to give an important contribution to the process. In the present case, when the potential is zero or very small, or when the second body (solvent structure) is much faster than the first one (solute), the system behaves as a single Brownian spherical rotator in an isotropic fluid. A unique decay constant is observed, proportional to $j(j+1)$, where j is the rank of the correlation function, and no bifurcation (i.e. the simultaneous presence of two different relaxation constants) is allowed. When the interaction potential is significant (large u_1 and/or u_2 , corresponding to low temperature), a second, slower relaxation process appears, provided that the

solvent body is slow enough (see section 3).

By increasing the potential, the relative weight of the second relaxation process is increased. Furthermore, the relative ratios of first- and second-rank correlation times are significantly changed. In section 3 we describe some numerical results illustrating the effect of changes in the energetic and diffusional parameters of the system.

3. Results and discussion

We have selected two cases that we believe are of major interest in dealing with the glass transition problem. A variety of additional cases will be described elsewhere [14]. Our present intention is to show the relevance and versatility of the model rather than to attempt to reproduce (or fit) the detailed behavior of the experiments.

The first case that we are going to consider is equivalent to Kivelson's model (a). A first-rank potential is turned on between body 1 and 2, so that only u_1 is different from 0. Thus the motion of both bodies is constrained to a "single well" potential in their relative orientation (i.e. a single minimum in the range $0 \leq \beta_{12} \leq \pi$, where β_{12} is the axial angle of the Euler set $\Omega_2 - \Omega_1$). In the following we will consider the solvent body as an object that is much slower than the solute. Due to the collective nature of the solvent body (a cage of solvent molecules surrounding the solute rotating probe), it is reasonable to suppose that its dimensions are much larger than the solute. We have chosen a value of 100 for the ratio D_1/D_2 . The diffusion coefficient for body 1, D_1 has been taken as 10^{10} s^{-1} , a reasonable value in many experimental situations (of course all our results scale linearly with D_1 so that the tables herein can be adjusted to any value of D_1 consistent with $D_1/D_2 = 100$).

As a second case, we have considered a second rank interaction potential between the two bodies, i.e. we have allowed only u_2 to be different from 0. The potential energy then has two equivalent wells (in the range $0 \leq \beta_{12} \leq \pi$); the bodies can librate within or jump between them [20]. Again body 2 is taken much larger and slower than body 1 ($D_1/D_2 = 100$).

In both cases we have computed for each value of

the potential the "total" correlation times τ_1 , τ_2 and the "partial" correlation times τ_1^β , τ_2^β , τ_1^α and τ_2^α . The "total" correlation times τ_1 and τ_2 are defined as the spectral densities (for correlation function of rank 1 and 2) evaluated at zero frequency; the "partial" correlation times α and β have been evaluated from the analysis of the eigenvalue spectrum for each calculation, i.e. the dominant eigenvalues have been selected, and they have been assigned either to the slow process α or to the fast process β . Usually one finds just two dominant eigenvalues, one for each process; sometimes a cluster of close eigenvalues have been found for the β process, and a weighted average has been taken. Alternatively, one can simply force fit the correlation function to a sum of exponentials

$$G(t) = \sum_{i=1}^n c_i \exp(-t/\tau_i). \quad (8)$$

Then by taking $n=1$ another estimate of the total correlation time is obtained, while the choice $n=2$ would yield the best fit to two decay constants, i.e. the α and β processes; we have found that as long as the second body is kept much slower than the solute body ($D_2 \ll D_1$) the two procedures give practically the same results.

We show in table 1 results for the case of a first-rank potential. One can easily note that when the potential is increased, the slow process becomes more and more important in determining the time decay of both the first- and second-rank correlation functions. According to Kivelson and Kivelson, the first- and second-rank slow correlation times (τ_1^α and τ_2^α) are very close to the values expected for the free rotation of the second huge body; that is the solute does indeed behave as a gigantic particle. The ratio between τ_1^α and τ_2^α is always very close to three, the typical value of a free Brownian rotator. The corresponding ratio for the fast β process ranges from 3 to 1.5. Note that τ_2^β has a weak maximum for $u_1 \approx 2k_B T$. In fig. 1 we show the first-rank (fig. 1a) and second-rank (fig. 1b) correlation functions at increasing u_1 . The increasing importance of the α process is made evident by the very slow decay to zero for large potentials, in both cases.

A completely different situation is found when a second-rank potential interaction exists between the bodies. The results are presented in table 2. Again a slow process appears when the potential is non-zero,

Table 1
Total (τ_1, τ_2) and partial ($\tau_1^f, \tau_2^f, \tau_1^b, \tau_2^b$) correlation times ^{a)}

$u_i/k_B T$	$\langle P_2(\Omega_i) \rangle$ ^{b)}	$\tau_1 \times 10^{10} (\text{s}^{-1})$	$\tau_1^f \times 10^{10} (\text{s}^{-1})$	$\tau_1^b \times 10^{10} (\text{s}^{-1})$	$\tau_2 \times 10^{10} (\text{s}^{-1})$	$\tau_2^f \times 10^{10} (\text{s}^{-1})$	$\tau_2^b \times 10^{10} (\text{s}^{-1})$	τ_1^f/τ_2^f	τ_1^b/τ_2^b
0.0	0.000	0.500	0.500 (1.000)		0.167	0.167 (1.000)		3.000	
0.5	0.016	1.846	0.489 (0.959)	50.02 (0.027)	0.175	0.170 (0.998)	16.67 (0.001)	2.876	3.000
1.0	0.060	5.410	0.461 (0.810)	50.07 (0.095)	0.244	0.179 (0.992)	16.69 (0.005)	2.575	3.000
1.5	0.123	10.12	0.415 (0.800)	50.13 (0.194)	0.451	0.187 (0.979)	16.71 (0.016)	2.219	3.000
2.0	0.194	14.97	0.379 (0.674)	50.22 (0.292)	0.712	0.190 (0.935)	16.73 (0.039)	1.994	3.001
2.5	0.263	19.37	0.327 (0.602)	50.25 (0.380)	1.381	0.187 (0.925)	16.75 (0.072)	1.748	3.000
3.0	0.328	23.11	0.298 (0.496)	50.32 (0.456)	2.027	0.182 (0.861)	16.77 (0.001)	1.637	3.000
3.5	0.386	26.20	0.255 (0.469)	50.33 (0.518)	2.722	0.171 (0.843)	16.78 (0.153)	1.491	2.999
4.0	0.436	28.74	0.248 (0.393)	50.37 (0.560)	3.422	0.165 (0.773)	16.79 (0.196)	1.503	2.999

^{a)} These are calculated for $D_1 = 10^{10} \text{ s}^{-1}$ and $D_2 = 10^8 \text{ s}^{-1}$ for increasing first-rank potential coupling. For each partial correlation time the relative weight is given (in parentheses).

^{b)} Order parameter (equilibrium average of the second Legendre polynomial in Ω_i , assuming the second body is fixed).

Table 2
Total (τ_1, τ_2) and partial ($\tau_1^f, \tau_2^f, \tau_1^b, \tau_2^b$) correlation times ^{a)}

$u_2/k_B T$	$\langle P_2(\Omega_1) \rangle$ ^{b)}	$\tau_1 \times 10^{10} (\text{s}^{-1})$	$\tau_1^f \times 10^{10} (\text{s}^{-1})$	$\tau_1^b \times 10^{10} (\text{s}^{-1})$	$\tau_2 \times 10^{10} (\text{s}^{-1})$	$\tau_2^f \times 10^{10} (\text{s}^{-1})$	$\tau_2^b \times 10^{10} (\text{s}^{-1})$	τ_1^f/τ_2^f	τ_1^b/τ_2^b
0.0	0.000	0.500	0.500 (1.000)		0.167	0.167 (1.000)		3.000	
0.5	0.106	0.529	0.422 (0.563)	0.669 (0.435)	0.355	0.166 (0.892)	16.69 (0.011)	2.542	0.040
1.0	0.220	0.642	0.355 (0.490)	0.939 (0.494)	0.981	0.163 (0.827)	16.69 (0.049)	2.177	0.056
1.5	0.334	0.890	0.297 (0.422)	1.357 (0.557)	2.039	0.159 (0.811)	16.70 (0.113)	1.867	0.081
2.0	0.439	1.353	0.247 (0.337)	2.020 (0.627)	3.399	0.148 (0.760)	16.75 (0.190)	1.668	0.120
2.5	0.530	2.162	0.193 (0.305)	3.059 (0.682)	4.879	0.136 (0.653)	16.76 (0.279)	1.419	0.183
3.0	0.605	3.522	0.173 (0.250)	4.752 (0.731)	6.302	0.124 (0.559)	16.77 (0.396)	1.395	0.283
3.5	0.664	5.738	0.134 (0.238)	7.401 (0.771)	7.571	0.110 (0.467)	16.79 (0.443)	1.218	0.440
4.0	0.711	9.167	0.124 (0.173)	11.40 (0.800)	8.645	0.102 (0.375)	16.80 (0.511)	1.215	0.678

^{a)} These are calculated for $D_1 = 10^{10} \text{ s}^{-1}$ and $D_2 = 10^8 \text{ s}^{-1}$ for increasing second-rank potential coupling. For each partial correlation time the relative weight is given (in parentheses).

^{b)} Order parameter (equilibrium average of the second Legendre polynomial in Ω_1 , assuming the second body is fixed).

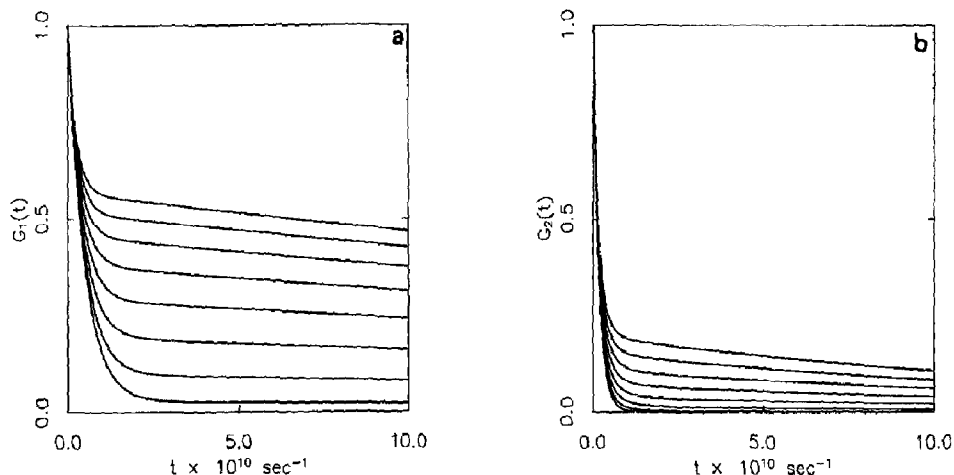


Fig. 1. Correlation functions for a first-rank potential; curves correspond to entries in table 1 (ranging consecutively from $u_1 = 0.5k_B T$ for the bottom curve to $u_1 = 4k_B T$ for the top curve). (a) First-rank correlation functions $G_1(t)$ (cf. eq. (6)), (b) second-rank correlation functions $G_2(t)$ (cf. eq. (6)).

and its relative weight (which is large even at low potentials) is increased when the potential is increased. In fig. 2 we have plotted $G_1(t)$ and $G_2(t)$ for increasing u_2 . One can easily notice, however, that whereas τ_2^a is very close to the expected value for a free Brownian rotator (i.e. it is proportional to $6D_2$), τ_1^a is completely altered, and it is much smaller than

one could expect from an analogy with the previous case. The somewhat surprising result is that the ratio τ_1^a/τ_2^a is *less than 1* in all the calculations. The ratio τ_1^b/τ_2^b is less affected, although it is significantly close to 1 for higher potentials.

An interpretation of the unusual behavior of the first-rank correlation function may be attempted by

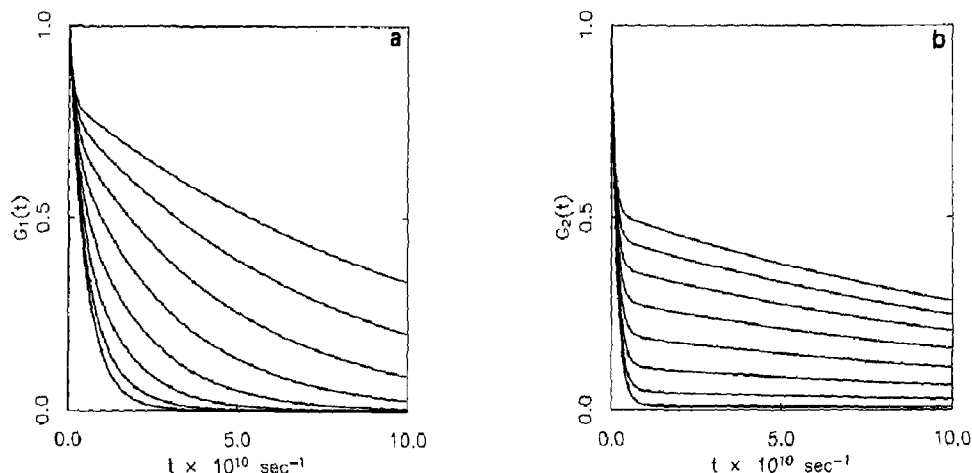


Fig. 2. Correlation functions for a second-rank potential; curves correspond to entries in table 2 (ranging consecutively from $u_2 = 0.5k_B T$ for the bottom curve to $u_2 = 4k_B T$ for the top curve). (a) First-rank correlation functions $G_1(t)$ (cf. eq. (6)), (b) second-rank correlation functions $G_2(t)$ (cf. eq. (6)).

recalling the qualitative difference existing for dynamic processes that take place in first rank, "one-well" potentials (such as our first case) and processes that take place in the presence of multistable potentials, i.e. potential surfaces with two or more wells separated by a barrier (such as our second case). Whenever local minima are present, the system can jump from one of them to another (while librating within a well between jumps). We may consider for simplicity the case of a single planar Brownian rotor reorienting in a two-minimum potential like $U/k_B T = \Delta \sin^2 \phi$, with Δ the potential barrier between the two equivalent minima. Stochastic motion for this and other planar multimimum systems has been studied by Moro and Nordio [20]. For this simple system, the jumping process is associated with a unique eigenvalue which depends exponentially on the potential parameter Δ according to an Arrhenius law (i.e. it is proportional to $\exp(-\Delta/k_B T)$). The corresponding eigenfunction Φ of the Smoluchowski operator is representative of the slow process of transition between the two equivalent potential wells, and it is antisymmetric with respect to the origin; i.e. it belongs to the B_1 irreducible representation of the C_{2v} group. Any correlation function with odd symmetry (e.g. $\sin \phi$) will be dominated by the low jump eigenvalue; correlation functions of even symmetry are not affected by the jumping process, and they can only monitor the librational motions within the wells.

Similar considerations can of course be applied to three-dimensional systems. Only *odd*-rank correlation functions are expected to be sensitive to the jumping process. So we may associate the slow first-rank correlation time τ_1^a with the jump motion of the solute body, at least for large ($u_2 > k_B T$) potential coupling, while the second-rank correlation time τ_2^a is related to the "free" rotation of the solute with a renormalized diffusion coefficient close to D_2 , such as is the case for the first-rank interaction potential. An indirect way to confirm this interpretation can be obtained by observing that τ_1^a does increase exponentially with the potential parameter u_2 , according to the expected Arrhenius law for an activated process.

In fig. 3 we have plotted $\log(1/\tau_1^a)$ (circles) and $\log(1/\tau_1^b)$ (triangles) versus T_0/T , where T_0 is a reference temperature corresponding to $u_2/k_B T_0 = 0.5$, $D_1 = D_1^0 = 10^{10} \text{ s}^{-1}$, $D_2 = D_2^0 = 10^8 \text{ s}^{-1}$. A common

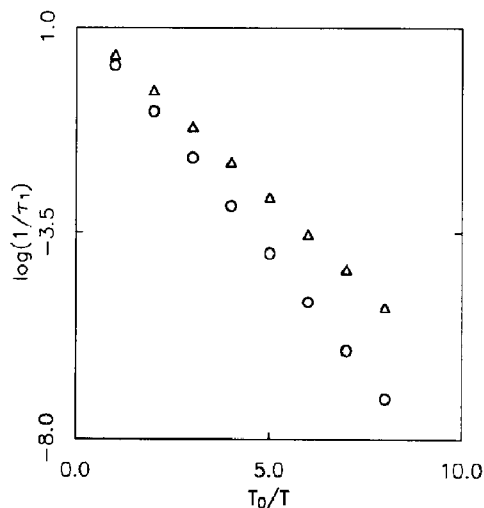


Fig. 3. $\log(1/\tau_1^a)$ (circles) and $\log(1/\tau_1^b)$ (triangles) as functions of the inverse of temperature (see text).

intrinsic activation energy E^* has been taken for D_1 and D_2 ,

$$D_{1,2} = D_{1,2}^0 \exp \left[-\frac{E^*}{k_B} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \quad (9)$$

and we have set $E^* = 2k_B T_0$. One can see that the α correlation time has an Arrhenius dependence on the temperature, but the activation energy is rescaled roughly as $E^* + u_2$.

The bifurcation effect has been rationalized in the above discussion largely as an energetic effect, i.e. as the result of a tight interaction between the small solute molecule and the massive solvent structure. However, one should consider the possibility that, at low temperatures, the dimensions of the solvent body are increased, due to the "aggregation" of new solvent molecules to the cage structure. This would ultimately be reflected in an activation energy E_2^* for D_2 significantly higher than the activation energy E_1^* for D_1 , which would lead to an increased ratio D_1/D_2 , and thus to an enhanced bifurcation effect. Finally, we note that in the limit $D_2 \rightarrow 0$ one would encounter behavior of the type expected for a glass transition.

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