Driven activation vs. thermal activation

P. Ilg\textsuperscript{1} and J.-L. Barrat\textsuperscript{2}

\textsuperscript{1} ETH Zürich, Polymer Physics, HCI H541 - CH-8093 Zürich, Switzerland
\textsuperscript{2} Université Lyon I, Laboratoire de Physique de la Matière Condensée et des Nanostructures; CNRS, UMR 5586
43 Bvd. du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

received 10 April 2007; accepted in final form 31 May 2007
published online 21 June 2007

PACS 64.70.Pf – Glass transitions
PACS 05.40.–a – Fluctuation phenomena, random processes, noise, and Brownian motion
PACS 05.70.Ln – Nonequilibrium and irreversible thermodynamics

Abstract – Activated dynamics in a glassy system undergoing steady shear deformation is studied by numerical simulations. Our results show that the external driving force has a strong influence on the barrier crossing rate, even though the reaction coordinate is only weakly coupled to the nonequilibrium system. This “driven activation” can be quantified by introducing an effective temperature, which is close to the one determined from the fluctuation-dissipation relation. This conclusion is supported by analytical results for a simplified model system.

Introduction. – Activated rate theory is ubiquitous in the description and understanding of dynamical processes in condensed matter, physical chemistry or materials science. The basic problem, known as the “barrier crossing” or “Kramers problem”, is that of a single degree of freedom, coupled to a heat bath, and moving in a double-well potential. The “barrier crossing rate” is defined as the average time taken by the system to switch from a potential well to the other, under the influence of thermal noise. In general, the single degree of freedom, often called “reaction coordinate”, is coupled to a complex, fluctuating environment. The “thermal noise” is a schematic description of the interaction with this environment.

This approach has been applied to a wealth of different problems. We can for example mention diffusion in solids, in which case the reaction coordinate is an atomic position, and the noise is associated with thermal vibrations. In isomerization reactions, the reaction coordinate is an internal coordinate of the molecule, coupled to a liquid solvent. In nucleation theory, the internal coordinate describes a collective fluctuation of an order parameter, and the “barrier” is interpreted as a free energy, rather than energy, barrier. Other examples involve the Eyring theory of plasticity in solids, in which the activated process is associated with a local strain change.

The analysis of the barrier-crossing problem is often associated with the names of Eyring, who proposed the so-called “transition state approximation” \cite{1}, and of Kramers, who made the first complete analysis of the problem in the limits of low and high friction \cite{2}. Since then, many refinements of the theory have been studied and are reviewed in ref. \cite{3}. In all cases, it turns out that an essential factor in the reaction rate, which to a large extent governs the variation with temperature $T$, is the Arrhenius contribution:

$$r(T) \sim \exp(-\Delta E/k_BT),$$

where $\Delta E$ is the energy barrier to overcome. The exponential variation of the Arrhenius factor (1) is, in fact, the hallmark of activated processes.

As discussed above, activated processes are often invoked in the description of the dynamical response of condensed matter systems. As such, they will typically take place under nonequilibrium conditions. The deviation from equilibrium can be weak, e.g. during the flow of a Newtonian liquid, in which case the applicability of eq. (1) is straightforward. In other cases, however, the same equation is applied to systems that are strongly out of equilibrium, in the sense that their response to an external driving force is strongly nonlinear, or that their phase space distribution is very different from the equilibrium, Gibbs-Boltzmann distribution.

A prototypical example of such a strongly nonequilibrium situation is the flow of a glassy system. Such a flow can be induced only by stresses larger than the yield stress (see, e.g., \cite{4} for the effect of strain and temperature in glassy solids). In the absence of flow, the relaxation is very slow, and the system is out of equilibrium.
and non-stationary [5,6]. The flow produces a nonequilibrium steady state [7–9], with a typical relaxation time that is fixed internally by the applied stress or the strain rate. This situation has attracted a considerable amount of theoretical and experimental interest, in two different contexts. The first one is the rheology of “soft glasses” (emulsions, pastes, colloidal glasses, foams). The second one is the plastic deformation of bulk metallic glasses. In both cases, approaches have been proposed that introduce a “noise temperature” [10] or “disorder temperature” [11,12]. In [10], this noise temperature replaces the actual temperature in eq. (1). In such models, the effective temperature is introduced in a somewhat empirical manner.

Another concept of effective temperature, rooted in statistical mechanics ideas, was introduced in [13,14], based on the “fluctuation-dissipation ratio”. At equilibrium, the fluctuation-dissipation theorem states that the ratio between integrated response and correlation functions (FDR) is equal to the temperature. Cugliandolo et al. [13] showed how this concept could be extended to out-of-equilibrium systems, by defining the effective temperature from the FDR, which now differs from the thermal bath temperature. It was proposed that a thermometer probing a nonequilibrium system on long time scales would actually be sensitive to this effective temperature, and this result was checked numerically on simple models [8,9,15]. Experimental evidence supporting this definition of an effective temperature has been found, e.g., in [16,17].

In this contribution, we explore the influence of an external driving force on the rate of a simple activated process. Our primary objective is here to check how the external drive, and the “noise” it generates, can influence the dynamics of an internal degree of freedom, which is not directly coupled to the driving force. A very standard way of quantifying the results is to use the Arrhenius representation, which provides an operational way of introducing an “activation temperature”, that can be compared to other calculations of effective temperatures in nonequilibrium systems.

**Model description.** — Our approach involves the simulation of the classical Kob-Andersen “binary Lennard-Jones” model undergoing shear flow, similar to the one used in ref. [8]. In order to probe activated dynamics, one appealing possibility would be to identify and study the activated events that actually give rise to the flow at low temperature, in the spirit of [10]. This approach, however, is difficult and could yield ambiguous results, as the flow is self-consistently coupled to these events. We therefore make use of the flexibility of numerical modeling to devise a very simple “activated degree of freedom” that has only a weak coupling to the existing flow in our system. This is achieved by replacing each particle of the minority species $r_B^j$ by a peanut-shaped “dumbbell” with coordinates $r_B^j \pm (u_j/2)e^z$, with fixed orientation along $e^z$, the direction perpendicular to the shear plane. Let $V^{\alpha\beta}(r) = \epsilon^{\alpha\beta}[(\sigma^{\alpha\beta}/r)^{12} - (\sigma^{\alpha\beta}/r)^6]$ denote the binary Lennard-Jones interaction potential. Each center of force in the dumbbell carries half of the particle interaction, i.e. $\epsilon^{BB} = 0.25$ and $\epsilon^{AB} = 0.75$ are chosen half the values used in the Kob-Andersen model. The separation between the two centers of force $u$ is small enough that the perturbation of the surrounding fluid can be neglected. The important feature of the model is the fact that the two centers of force are related through an internal “reaction coordinate” $u$, which evolves in a bistable intramolecular potential $V(u) = (V_0/u_0^2)(u^2 - u_0^2)^2$, where $u_0 = 0.1$ (in Lennard-Jones units) is the equilibrium dumbbell separation (see fig. 1b). Each dumbbell is therefore a simple “two-state” system which can undergo, under the influence of the interactions with the surrounding fluid, an “isomerization reaction”. This reaction corresponds to exchanging the positions of the two centers of force (see fig. 1).

This “isomerization” will be the focus of our study. Its rate can be studied as a function of the imposed barrier height, of the external temperature $T$ and on the driving force, which is here quantified by the shear rate $\dot{\gamma}$. We have chosen to work under conditions for $T$ and $\dot{\gamma}$ that have been well characterized previously [8] ($T = 0.3$ and $\dot{\gamma} = 10^{-3}$, in Lennard-Jones units) and to concentrate on the influence of barrier height $\Delta E = V_0$. At this temperature, the system would not undergo structural relaxation on the time scales that can be achieved using computer simulation. Under the influence of the external drive, a relaxation on a time scale $\tau_\alpha \approx 100$ is observed. This time scale is very well separated from microscopic, vibrational time scale, so that our system is a practical realization of the theoretical concepts described in ref. [13].

Determination of reaction rates is a notoriously difficult challenge for numerical simulations, as the activated events typically take place on much larger time scales than
the short-time vibrations of the intramolecular bonds. A number of sophisticated methods [18] have been developed to bypass this intrinsic difficulty, either from biased simulations, or by making use directly of the rate formula 1. Unfortunately, such methods always assume that the system is close to thermal equilibrium, and are therefore inapplicable in our case. The forward flux method recently proposed in [19] is applicable to nonequilibrium systems. However, only a single reaction coordinate per system can be treated with this method, which is impractical for the present situation. As a result, we have to use “brute force” simulations to obtain reaction rates from the study of individual trajectories, which seriously limits the range of barrier heights that can be considered.

Methods. – The SLod equations of motion appropriate for a fluid undergoing simple shear were integrated with a leapfrog algorithm using a time step of \(\Delta t = 5 \times 10^{-4}\) in reduced Lennard-Jones units [8]. For the dumbbell particles, the leapfrog algorithm is applied to the center-of-mass and relative positions and momenta. Lees-Edwards periodic boundary conditions [8] are employed in order to minimize effects due to the finite system size. Constant temperature conditions are ensured by rescaling the velocity components in the \(z\)-direction (perpendicular to the shear plane) of all particles at each time step. We verified from some parameter values that the Gaussian isokinetic thermostat gives identical results within the numerical uncertainties.

The reaction rate \(r\) is determined from the number correlation function \(C(t)\) by

\[
C(t) = \langle \delta n(t) \delta n(0) \rangle \approx \exp[-rt/\langle n \rangle],
\]

where \(\delta n(t) = n(t) - \langle n \rangle\) and \(n(t)\) equals one if \(u(t) > u_B\) and zero otherwise [20]. The systems studied contain \(N = 2048\) particles, 410 of which are dumbbells. Equation (2) is evaluated from an ensemble average over 20–40 independent systems. The results are found to be independent of the exact location of the dividing surface \(u_B\) in the vicinity of the barrier maximum \(u_B = 0\). The fast initial decay of \(C(t)\) is well described by transition state theory. Escape rates are extracted from fits to eq. (2) for intermediate times \(5 \leq t \leq 10\). We verified that very similar results are found within a broad range \(1 \leq t \leq 30\), before the correlation function finally decays to zero, in full agreement with theoretical expectation [20]. For relatively low barrier heights \(V_0/T \lesssim 3\), \(C(t)\) decays more rapidly, so that we extracted rates for shorter times, \(0.5 \leq t \leq 1\).

In the following, we present results for the reaction rate as a function of \(V_0\) based on the study of the decay in the number-number correlation function [20]. We adopt common practice by giving all temperature and energy values in terms of the depth of the Lennard-Jones potential \(\epsilon\).

![Figure 2](image-url) 

**Fig. 2:** (Color online) Trajectories of the internal dumbbell coordinate for different barrier heights. The thermal bath temperature is \(T = 0.3\) in reduced Lennard-Jones units, and the shear rate is \(\dot{\gamma} = 10^{-3}\).

Results and conclusion. – Figure 2 illustrates the difficulty of the approach, by showing the trajectories of selected dumbbells for different values of the barrier at \(T = 0.3\). For \(V_0/kT = 1\), barrier crossings are so common that describing them trough classical rate theory is problematic. For \(V_0/kT = 10\), the crossings become very unlikely, so that the determination of the rate becomes difficult. This leaves us with typically two decades in terms of variation of the reaction rate.

The corresponding reaction rates, determined from the correlation function of the dumbbell internal coordinate, are shown in fig. 3. At \(T = 0.8\), \(\dot{\gamma} = 10^{-3}\), the rates obey the equilibrium Arrhenius law (1), showing that under these conditions the drive is only a weak perturbation to the system. We now concentrate on the rates obtained at \(T = 0.3\) and \(\dot{\gamma} = 10^{-3}\). The reaction rates are clearly influenced by the external driving imposed to the system. To show this, we use the rates obtained at a rather high temperature, \(r_{eq}(T = 0.8)\), to extrapolate to \(T = 0.3\). The equilibrium extrapolation \(r_{ext}\) is achieved using the Arrhenius formula, i.e. \(r_{ext}(T = 0.3) = r_{eq}(T = 0.8) \times \exp(-V_0/0.8 - V_0/0.3)\). Clearly, the extrapolated rates are significantly lower than those actually observed under shear, except at low barrier heights (high rates) were the two estimates almost coincide. The difference between the extrapolated rates and the measured ones is an indicator of the inadequacy of the standard Arrhenius formula, using the thermal bath temperature, in the driven system.

In spite of the limited range of accessible rates, it is clear from fig. 3 that the rates in a glassy system under shear do not obey Arrhenius behavior of the form \(\exp(-V_0/T)\) over the whole range of barrier heights under study. While this law is relatively well obeyed at low barriers and large crossing rates, it would significantly underestimate the
rate for high barriers. Instead, at high barrier rates, the crossing rate is considerably increased. If an attempt is made to fit the results to an “effective Arrhenius factor”, a value of $T_{\text{eff}} \approx 0.6$ is obtained.

Under the same conditions, a completely different determination of the effective temperature [8], based on the fluctuation-dissipation approach mentioned above, yields $T^* \approx 0.65$. This is in good agreement with the present fit to an Arrhenius law. The determination of $T_{\text{eff}}$ based on reaction rates is of limited accuracy, such that we cannot exclude that $T_{\text{eff}}$ and $T^*$ actually differ slightly or that $T_{\text{eff}}$ is slightly dependent on barrier height. A more precise determination of $T_{\text{eff}}$ would require larger barrier heights, which is computationally quite demanding. Note, that $V_0 = 3$ corresponds for $T = 0.3$ already to the rather high barrier height of $V_0/kT = 10$.

In fig. 3, we also display the results obtained for the rates at a slightly higher value of the shear, $\dot{\gamma} = 10^{-2}$. The separation of time scales between relaxation time and microscopic times is less marked than for the low shear rates ($\tau_\alpha \approx 10$ in this case). It appears that the increase in shear induces a change in the prefactor for the rates, rather than in the barrier height dependence. This is consistent with the relatively weak influence of shear rate on effective temperature reported earlier [8].

It is interesting to discuss the time scale at which the crossover between the two Arrhenius laws, characterized either by the bath temperature or an effective temperature, takes place. A natural guess would be to associate this crossover with a value of the rate that corresponds to the inverse of the $\alpha$ relaxation time. The general idea is, that fluctuations taking place on longer time scales will be associated with a higher temperature [8,13]. In fig. 3 we see that this guess overestimates the crossover rate by a factor of 5 in the case of $\dot{\gamma} = 10^{-3}$. It is not clear at this point, whether this difference is significant or reflects merely some arbitrariness in the definition of relaxation times.

We expect the activation temperature to be isotropic. Indeed, the conformation change of a dumbbell is associated with a compression along the dumbbell axis. Such fluctuating compression waves result only very indirectly from the shear flow, and it seems unlikely that their strength is strongly correlated with the direction of shear. In fact, since the shear rate is very low, all quantities looked at so far are isotropic to a very good approximation.

The simulation results presented above suggest that the activated dynamics is governed by an elevated temperature $T_{\text{eff}} \approx 0.6 > T$. This temperature is consistent with the effective temperature $T^* = 0.65$ found in extensive simulation studies on the fluctuation-dissipation relation in this system [8]. In order to investigate the relation between $T_{\text{eff}}$ and $T^*$ and to rationalize our simulation results, we study the following toy model proposed in [21].

Consider a particle of mass $m$ at position $x$ moving in an external potential $V(x)$ under the influence of two thermal baths. One bath, associated with the fast degrees of freedom, is kept at temperature $T_{\text{fast}}$ and exerts an instantaneous friction force of strength $\Gamma_0$. The second bath, which mimics the slow degrees of freedom is held at temperature $T_{\text{slow}}$ and is described by the retarded friction coefficient (memory kernel) $\Gamma(t)$. The equations of motion read $\dot{x} = v$,

\[
\dot{v} = -V'(x) - \int_0^t ds \Gamma(t-s)v(s) - \Gamma_0 v(t) + \xi(t) + \eta(t).
\]

The fast bath is modeled as Gaussian white noise with $\langle \eta(t) \rangle = 0$, $\langle \eta(t)\eta(s) \rangle = 2\Gamma_0\delta(t-s)$, whereas the random force due to the slow bath is described by $\langle \xi(t) \rangle = 0$, $\langle \xi(t)\xi(s) \rangle = 2T_{\text{slow}}\Gamma(t-s)$. We use an exponentially decaying memory kernel $\Gamma(t) = \alpha^{-1}e^{-t/\alpha}$ for which the non-Markovian dynamics (3) can equivalently be rewritten as Markovian dynamics in an extended set of variables [22].

Exact solutions of the model (3) for harmonic potentials $V$ are presented in [21]. For barrier-crossing problems with double-well potentials $V$, no analytical solutions to (3) are known. We therefore extend the widely used transition state approximation to the present model after adiabatic elimination of the fast degrees of freedom. The resulting expression for the rate $\tau_{\text{TST}}$ is rather lengthy and will be presented elsewhere together with the (straightforward) procedure. For the double-well potential $V(x)$ considered above, the dependence of the rate $\tau_{\text{TST}}$ on the barrier height $V_0$ is again dominated by the Arrhenius factor, however with an effective temperature $T_{\text{eff,TST}} = T_{\text{fast}}w/[w + 4(T_{\text{fast}} - T_{\text{slow}})]$, where $w = T_{\text{slow}} + \alpha V''T_{\text{fast}}$ and $V'' = 8V_0/w_0^3$. Thus, if the slow and fast baths are both kept at the same temperature, $T_{\text{slow}} = T_{\text{fast}} = T$, one recovers the usual Kramers result with $T_{\text{eff,TST}} = T$. If,

Fig. 3: (Color online) Reaction rate as a function of barrier height, for fixed temperature and shear rate. Full squares: results for $T = 0.8$ (red) at equilibrium. $T = 0.3$ (black and blue), and different shear rates (full diamonds and circles correspond to $\dot{\gamma} = 10^{-2}$ and $\dot{\gamma} = 10^{-3}$, respectively). Open circles represent $r_{\text{ext}}$, an extrapolation of the high-temperature results to $T = 0.3$ as explained in the text.
however, $T_{\text{slow}} > T_{\text{fast}}$, the escape rate is enhanced due to $T_{\text{eff}},\text{STST} > T_{\text{last}}$. Due to the interplay between fast and slow dynamics in the barrier crossing, the effective temperature is in general intermediate between the temperature of the slow and the fast bath. These predictions are in agreement with the simulation results presented above. Furthermore, estimating the coefficient $\alpha \approx 0.01$ from the inverse high-frequency shear modulus for the Lennard-Jones system [22], the predicted effective temperature is $T_{\text{eff}},\text{STST} \approx 0.45$. In view of the simplicity of the model and the uncertainty in $\alpha$, the order of magnitude agreement with the observed $T_{\text{eff}}$ is reasonable.

In conclusion, we have shown that activated processes out of equilibrium are influenced by an external driving, even if the corresponding degree of freedom is weakly coupled to the drive. Qualitatively, this increase is the essential result from our simulations. From a more quantitative point of view, the analysis of the Arrhenius plot allows one to define operationally an effective activation temperature. (We note that the limited range of data available in principle allows also for other interpretations.) The link of this activation temperature to other definitions of effective temperature, and the time scale for the crossover from “thermal activation” to “driven activation” will have to be explored further. However, the results are consistent with a general picture involving a degree of freedom coupled to two different heat baths, one associated with short-time vibrations and one associated with shear-induced fluctuations, taking place on longer time scales and described by a higher temperature [21].

This “driven activation” (as opposed to “thermal” activation) could have interesting consequences for characterizing the effective temperature of nonequilibrium systems, by providing a “thermometer” based on activated processes. It can also be of importance within the theory of plasticity of amorphous materials, by providing a self-consistent description of the “noise” that induces local plastic events, within a classical statistical mechanics description involving a noise temperature [11,23]. An effective temperature was introduced phenomenologically in an Arrhenius activation law describing driven vortex lattices with quenched disorder [24]. Later on, it was found that this effective temperature approximately coincides with the one obtained by fluctuation-dissipation relations [25]. Inserting an effective temperature in Eyring’s rate theory of plasticity, T. Haxton and A. J. Liu were recently able to account for the flow curves of simple glassy systems at low temperatures [26].

REFERENCES

[1] Eyring H., J. Chem. Phys., 3 (1935) 107.
[2] Kramers H. A., Physica, 7 (1940) 284.
[3] Hänggi P., Talkner P. and Borkovec M., Rev. Mod. Phys., 62 (1990) 251.
[4] Rottler J. and Robins M. O., Phys. Rev. E, 68 (2003) 011507.
[5] Berthier L. et al., Science, 310 (2005) 1797.
[6] Flörchinger P. K. et al., Science, 296 (2002) 104.
[7] Berthier L., Barrat J.-L. and Kurchan J., Phys. Rev. E, 61 (2000) 5464.
[8] Berthier L. and Barrat J.-L., J. Chem. Phys., 116 (2002) 6228.
[9] Berthier L. and Barrat J.-L., Phys. Rev. Lett., 89 (2002) 095702.
[10] Sollisch P., Lequeux F., Hébraud P. and Cates M. E., Phys. Rev. Lett., 78 (1997) 2020.
[11] Langer J. S., Phys. Rev. E, 70 (2004) 041502.
[12] Langer J. S. and Lemaitre A., Phys. Rev. Lett., 94 (2005) 175701.
[13] Cugliandolo L., Kurchan J. and Peliti L., Phys. Rev. E, 55 (1997) 3898.
[14] Kurchan J., Nature, 433 (2005) 222.
[15] Ono I. K. et al., Phys. Rev. Lett., 89 (2002) 095703.
[16] Wang P., Song C. and Makse H. A., Nat. Phys., 2 (2006) 526.
[17] Herrison D. and Ocio M., Phys. Rev. Lett., 88 (2002) 257202.
[18] See, e.g., Dellago C., Bolhuis P. G. and Geissler P. L., Adv. Chem. Phys., 123 (2002) 1.
[19] Allen R. J., Warren P. B. and ten Wolde P. R., Phys. Rev. Lett., 94 (2005) 018104.
[20] Chandler D., J. Chem. Phys., 68 (1978) 2959.
[21] Ilg P. and Barrat J.-L., J. Phys.: Conf. Ser., 40 (2006) 76.
[22] Barrat J.-L., Chem. Phys. Lett., 165 (1990) 551.
[23] Lemaitre A. and Caroli C., cond-mat/0609689.
[24] Kolton A. B., Dominguez D. and Grønbech-Jensen N., Phys. Rev. Lett., 83 (1999) 3061.
[25] Kolton A. B. et al., Phys. Rev. Lett., 89 (2002) 227001.
[26] Haxton T. and Liu A. J., cond-mat/0706.235.