

## Description of the dynamics in complex energy landscapes via metabasins: a simple model study

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2003 J. Phys.: Condens. Matter 15 S1237

(<http://iopscience.iop.org/0953-8984/15/11/341>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.119

The article was downloaded on 19/05/2010 at 08:25

Please note that [terms and conditions apply](#).

# Description of the dynamics in complex energy landscapes via metabasins: a simple model study

A Saksengwitt<sup>1</sup>, B Doliwa<sup>2</sup> and A Heuer<sup>1</sup>

<sup>1</sup> Institute of Physical Chemistry, Schlossplatz 4/7, D-48149 Münster and Sonderforschungsbereich 458, Germany

<sup>2</sup> Max Planck Institute for Polymer Research, 55128 Mainz, Germany

Received 6 December 2002

Published 10 March 2003

Online at [stacks.iop.org/JPhysCM/15/S1237](http://stacks.iop.org/JPhysCM/15/S1237)

## Abstract

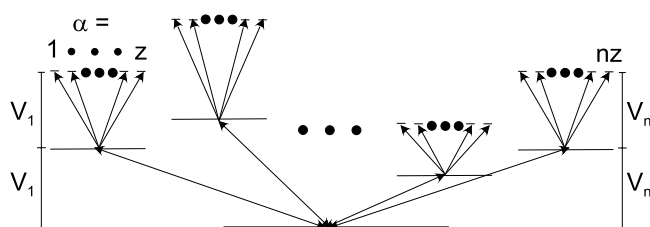
We study the dynamics in a simple hierarchical energy landscape. We compare a straightforward analytical approximation with the results of Monte Carlo simulations. The model is devised to mimic some aspects of the dynamics in supercooled liquids. We show that the concept of metabasins, as recently discussed in the framework of the potential energy landscape of glasses, emerges quite naturally.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The thermodynamic properties of glasses can be expressed in terms of the properties of the potential energy landscape (PEL), defined in the configuration space of the system [1, 2]. In particular, the properties of the local minima (inherent structures) are here of primary importance [3–5]. Recently, the first progress has been reported on also relating the dynamics to the PEL. For this purpose it was essential to define so-called metabasins (MBs) which contain a small number of adjacent inherent structures. It could be shown that the dynamics of binary Lennard-Jones mixture (BMLJ) can be interpreted as a random-walk-like dynamics between MBs and that the temperature-dependent diffusion constant is inversely proportional to the average residence time  $\langle\tau(T)\rangle$  in the MBs. It turned out that  $\langle\tau(T)\rangle$  is dominated by the contributions from long-lived MBs, corresponding to very stable structures in real space. Thus, knowledge of the individual residence times of the MBs, weighted with their occurrence probability à la Boltzmann, allows one to predict the diffusion constant [6].

For a given MB  $i$ , the average residence time  $\langle\tau_i(T)\rangle$  has been determined in two different ways. First, we performed repeated molecular dynamics simulations, always starting from the same MB and checking after which time this MB has been left. Interestingly, for the different MBs analysed in this way, we found an Arrhenius behaviour  $\langle\tau_i(T)\rangle = \tau_{0,i} \exp(\beta E_i)$ , where  $\beta = 1/k_B T$ . Second, we analysed the saddles around the MB via an explicit saddle-finding algorithm. Via some mapping (see below for more details), one could predict the activation



**Figure 1.** A sketch of the hierarchical model analysed in this work. There is one ground state,  $n$  first excited levels, and  $nz$  second excited levels.

energies  $E_i$  on the basis of these saddles. Thus we concluded that local analysis of saddles together with knowledge of the population of the MBs allows one to predict the macroscopic transport [7].

The complexity of the PEL, reflected, e.g., by the multitude of escape channels from one minimum and the multi-minimum nature of the escape processes render this mapping highly non-trivial and only approximate. Thus it may seem surprising that this mapping worked so well. In this short paper we would like to clarify the approximations by analysing a simple model which is devised to represent the complex PEL. Via simulations of this model we will see that the mapping does indeed work. Furthermore, this analysis is designed to give a further clarification of the MB concept.

## 2. The model

We analyse the escape from one ground state which has  $n$  escape channels. The energy levels as well as the possible transitions are indicated in figure 1. As soon as one of the *second* excited levels has been reached, we assume that the system has escaped from the ground state. All second excited levels have  $z$  degenerate states ( $z = 2000$  in this work). The value of  $z$  takes it into account that a PEL minimum is generally surrounded by many other minima (which, for reasons of simplicity, have been chosen as degenerate in this model). Each escape channel is characterized by an energy  $V_j$  ( $1 \leq j \leq n$ ) which separates the first excited state from the ground state and the second excited states from the first excited state.

We first analyse the case  $n = 1$  and determine the escape rate  $\gamma_\alpha$  via the state  $\alpha$  (for  $n = 1 : 1 \leq \alpha \leq z$ ). It is possible to find a simple analytic expression for the rate. In the limit  $V/k_B T \gg 1$  the rate for entering the first level is  $\gamma_{01} = \Gamma_0 \exp(-\beta V)$  with some rate constant  $\Gamma_0$ . Starting from this level, the system has two options. Either it jumps up to the second level, or it jumps back to the ground state. The latter process is non-activated and has the rate  $\gamma_{10} = \Gamma_0$ . The average residence time  $1/\gamma_1$  on the first excited level is thus very short as compared to the residence time in the ground state, since  $\gamma_{01}/\gamma_{10} = \exp(-\beta V) \ll 1$  and  $1/\gamma_1 < 1/\gamma_{10}$  and thus  $1/\gamma_{01} \gg 1/\gamma_1$ . With some probability  $p_{1\alpha}$  the system jumps to the second excited state  $\alpha$  when leaving the first excited level. Thus the total rate to escape via the second excited state  $\alpha$  is given by the rate for reaching the first excited state times the probability of going up further to state  $\alpha$ , i.e.

$$\gamma_\alpha = \gamma_{01} p_{1\alpha} = \Gamma_0 \exp(-\beta 2V) / [1 + z \exp(-\beta V)]. \quad (1)$$

This approximation breaks down at high temperatures where the relation  $1/\gamma_{01} \gg 1/\gamma_1$  no longer holds.

Straightforward algebra yields for the apparent activation energy

$$E_{\text{app}}^{\alpha} \equiv -\frac{d}{d\beta} \ln \gamma_{\alpha} = V + V p_{\text{ret}}, \quad (2)$$

where

$$p_{\text{ret}} = 1 - z p_{1\alpha} = 1/[1 + z \exp(-\beta V)] \quad (3)$$

is the probability of returning to the ground state. Note that  $p_{\text{ret}}$  is strongly temperature dependent. In the limit of low temperatures one has  $p_{\text{ret}} \approx 1$  whereas for high temperatures one approaches  $1/(1+z) \approx 0$ . Thus the apparent activation energy changes from  $2V$  at low temperatures to  $V$  at high temperatures. The crossover temperature,  $T_c$ , between the two limiting scenarios is characterized by  $p_{\text{ret}} = 0.5$ , i.e.  $k_B T_c = V/\ln z$ . Thus, the relation  $V/(k_B T) \gg 1$  in the relevant temperature regime  $T \approx T_c$  is equivalent to  $\ln z \gg 1$ .

The physical interpretation of this crossover is very simple. At low temperatures the system basically has to jump up twice with an activated process giving rise to an apparent activation energy of  $2V$ . At higher temperatures the probability of reaching one of the second excited levels starting from the first excited level becomes higher than 0.5 as long as  $z > 1$ . The reason is that, due to the multitude of second excited levels, the entropy governs the further evolution of the system.

The relations for the apparent activation energy can be easily generalized to the case where several first excited levels exist, i.e.  $n > 1$  in our notation. Since all escape channels are uncoupled, one expects at low temperatures

$$\gamma = \sum_{\alpha=1}^{zn} \gamma_{\alpha} \quad (4)$$

where the sum is over the  $zn$  different escape channels. Now the apparent activation energy  $E_{\text{app}}$  can be written as

$$E_{\text{app}} = -\frac{d}{d\beta} \ln \sum_{\alpha} \gamma_{\alpha} = \sum_{\alpha} \frac{\gamma_{\alpha}}{\gamma} E_{\text{app}}^{\alpha}. \quad (5)$$

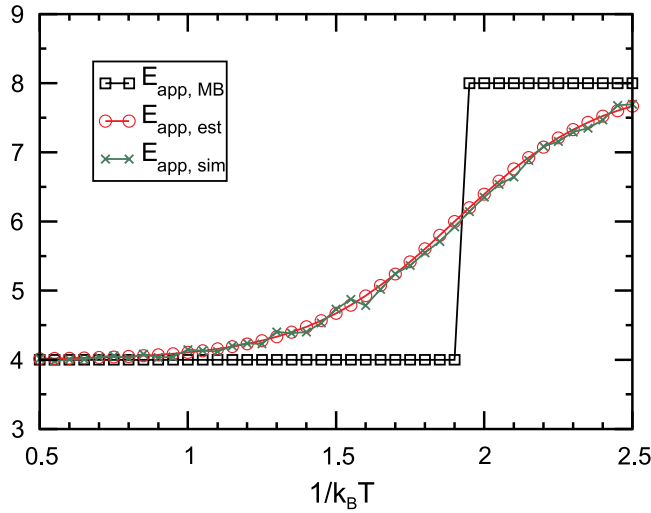
The factor  $\gamma_{\alpha}/\gamma$  can be interpreted as the probability that exit  $\alpha$  is taken.

Intuitively, for  $T < T_c$  the ground state as well as the first excited level can be regarded as one effective state with many forward and backward jumps between the two levels. The escape from the bottom of the system to the first state beyond these two states, i.e. the second excited state, determines the apparent activation energy. In contrast, for  $T > T_c$  reaching the first excited state is the only relevant step for the escape, so leaving the ground state is determined by the height of the first excited state.

In our recent work analogous ideas gave rise to the notion of MBs. For a given escape path we determined, for each minimum, whether or not the probability  $p_{\text{back}}$  of jumping back to the origin is higher than 50%. For our present model one can identify  $p_{\text{back}}$  with  $p_{\text{ret}}$ . For more complex models, involving, e.g., more than two levels, one generally expects  $p_{\text{back}} \leq p_{\text{ret}}$  since a single back-jump is not sufficient for reaching the ground state again. In the limit of low temperatures, however, the two values will approach each other.

### 3. Simulations

For  $n = 1$ , i.e. for a single exit, we determined the apparent activation energy in three different ways. First, we performed straightforward Monte Carlo simulations and determined the average time when the system, starting in the ground state, reaches the second excited level.



**Figure 2.** The different apparent activation energies for  $n = 1$ ,  $z = 2000$ , and  $V = 4$ .

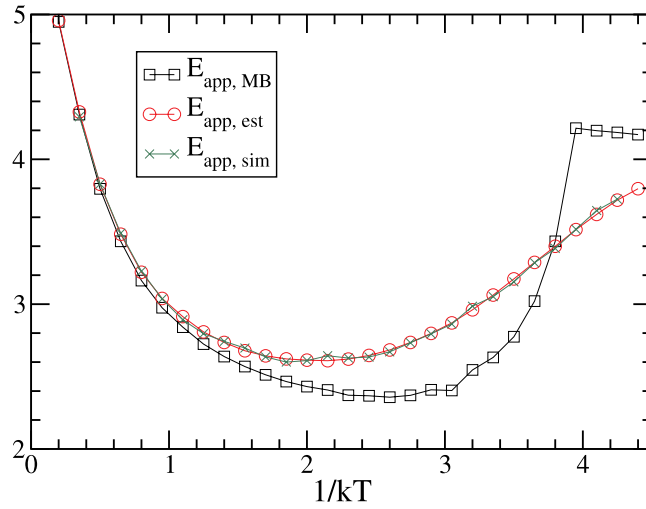
From this we determined  $E_{\text{app}}^{\text{sim}}$ . Second, we used equation (2) to estimate  $E_{\text{app}}^{\text{est}}$  and, third, we used the MB approximation by replacing  $p_{\text{ret}}$  by either 0 or 1 for  $p_{\text{ret}} > 0.5$  and  $p_{\text{ret}} < 0.5$ , respectively. The resulting apparent activation energy is denoted as  $E_{\text{app}}^{\text{MB}}$ . The temperature dependences of all three values are shown in figure 2. One can see a very good agreement of  $E_{\text{app}}^{\text{sim}}$  and  $E_{\text{app}}^{\text{est}}$ . Choosing significantly smaller values of  $z$ , minor deviations become visible between the two functions since the relation  $\ln z \ll 1$  is no longer fulfilled (not shown). On the MB level, the gradual increase of  $E_{\text{app}}^{\text{est}}$  with decreasing temperature is replaced by a sudden jump in  $E_{\text{app}}^{\text{MB}}$ .

One may expect the resulting differences between  $E_{\text{app}}^{\text{est}}$  and  $E_{\text{app}}^{\text{MB}}$  to be largely averaged out if  $n > 1$ . We chose  $n = 100$ , with different  $V$ s which are equally distributed between 1 and 10. The factors  $\gamma_{\alpha}/\gamma$  can be identified with the probability that the escape via state  $\alpha$  is taken.  $\gamma_{\alpha}/\gamma$  can thus be directly determined from the simulations. The results are shown in figure 3. Again we have an excellent agreement between  $E_{\text{app}}^{\text{est}}$  and  $E_{\text{app}}^{\text{sim}}$ . As expected also, the apparent activation energy  $E_{\text{app}}^{\text{MB}}$  is a good estimate of the true apparent activation energy  $E_{\text{app}}^{\text{sim}}$ , at least for  $1/kT < 2.5$ . For even lower temperatures the system is mainly escaping via paths with  $V$  close to the lower limit of 2. Then no effective averaging is present and the deviations, known from figure 2, are recovered.

#### 4. Discussion

The analysis of our simple model system has revealed that the apparent activation energy can be predicted by a straightforward analysis of barriers and that the concept of MBs appears quite naturally. As discussed in [7] the estimates of  $E_{\text{app}}$  can be easily generalized to more complex situations, involving more than two excitation levels. In particular, the complex energy landscapes of supercooled liquids can be characterized in this way. Here it is essential that each PEL minimum has many neighbours so that a tree-like structure as shown in figure 1 emerges.

Our previous BMLJ analysis can now be expressed in the terminology introduced above. First, we have performed repeated simulations from the individual centres of the MBs and



**Figure 3.** The different apparent activation energies for  $n = 100$ ,  $z = 2000$ , and  $V$  randomly distributed between 2 and 10.

determined the escape rate. From this we directly obtain  $E_{app}^{sim}$ . Second, by analysing the individual escape paths we have determined the minimum for which for the first time  $p_{back} < 0.5$  and which is thus the first minimum beyond the MB (see above). The resulting MB construction, together with explicit search routines for saddles, yields the individual escape energies  $E_{app}^{\alpha}$ . Third, by averaging over the individual escape paths we have obtained  $E_{app}^{MB}$ . Actually, for the estimate of  $E_{app}^{MB}$  via equation (5) the factors  $\gamma_{\alpha}/\gamma$  do not appear in practice. The reason is that the individual paths taken by the system upon repeated simulations are already weighted by this probability. Thus one only has to average over all values of  $E_{app}^{\alpha}$  encountered during the repeated simulations. This is essential, since the individual  $\gamma_{\alpha}$  include unknown prefactors.

One may ask why for the description of the escape dynamics the approximation of  $p_{ret}$  by either 0 or 1 is useful and whether the resulting minor inaccuracies could be avoided in our former BMLJ analysis. In principle this is possible, but it would require the analysis of the escape channel until  $p_{back} \approx 0$  and require in particular the determination of all saddles between the escape minima. Furthermore, the precise determination of  $p_{back}$  and thus  $p_{ret}$  is numerically very time-consuming. Therefore we have chosen the MB approximation in our BMLJ simulations.

Finally, we would like to discuss the temperature dependence of the apparent activation energies in figure 3. Since possible activation energies range between 2 and 20, it may come as a surprise that  $E_{app}^{sim}$  only varies between 2.7 and 5 in this broad temperature range. As mentioned before, in the case of the BMLJ system we could not even detect any variation of  $E_{app}^{sim}$  with temperature. These observations can be rationalized by invoking the MB concept. Upon decreasing temperature, more and more high barriers are suppressed. This effect would decrease the apparent activation energy. At the same time, however, the number of states in some MBs increases such that the activation energies stemming from the corresponding escape channels increase. Whereas in the BMLJ system the two effects seem to cancel each other, in the present model they happen in slightly different temperature regimes such that  $E_{app}^{sim}$  displays a minimum. This minimum, however, is very broad (a factor 3 between  $1/k_B T = 1$  and 3 where  $E_{app}^{sim}$  is basically constant). The same temperature range could be explored in the BMLJ

system so that *a priori* it is not evident whether the BMLJ PEL behaves very differently as compared to this simple model PEL. At present, we are trying to develop a refined PEL which reflects the properties of the BMLJ as closely as possible.

### Acknowledgments

The support by the NRW Graduate School of Chemistry, the SFB 458, and the SFB 262 is gratefully acknowledged.

### References

- [1] Goldstein M 1969 *J. Chem. Phys.* **51** 3728
- [2] Stillinger F H 1995 *Science* **267** 1935
- [3] Büchner S and Heuer A 1999 *Phys. Rev. E* **60** 6507
- [4] Sciortino F, Kob W and Tartaglia P 2000 *J. Phys.: Condens. Matter* **12** 6525
- [5] Mossa S, La Nave E, Tartaglia P and Sciortino F 2002 *Preprint* cond-mat/0209181
- [6] Doliwa B and Heuer A 2002 *Preprint* cond-mat/0205283
- [7] Doliwa B and Heuer A 2002 *Preprint* cond-mat/0209139