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LETTER TO THE EDITOR

Diffusion on amorphous substrates

I Avramov

Institute of Physical Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

E-mail: avramov@ipchp.ipc.bas.bg

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Abstract. We consider diffusion on substrates with frozen disorder. While in the ordered state the moving particle always meets the same energy barrier, in the amorphous state there is a fairly broad distribution of the height of the barriers. The effective activation energy E_{eff} that controls the diffusion process is not equal to the average activation energy barrier. In fact, E_{eff} is the highest barrier that the moving particle must overcome. In this way E_{eff} can be determined by solving a particular percolation problem. The threshold concentration depends on the length of the percolating cluster. Consequently, E_{eff} is also size dependent. So it is shown that the diffusion coefficient depends on the distance of diffusion. The determination of the effective activation energy from the slope of the Arrhenius plot of the diffusion coefficient is misleading. The mean diffusion distance λ decreases strongly with temperature.

Introduction

The aim of the present contribution is to investigate the temperature dependence of some parameters important for surface diffusion on amorphous substrates. It is also demonstrated that, because of the disorder, the diffusion coefficient becomes distance dependent: $D = D(L)$. We investigate the diffusion coefficient D and the mean diffusion distance λ . The latter depends on the average desorption time τ_{des} (see [1, 2]) as

$$\lambda = \sqrt{D\tau_{des}} \quad (1)$$

where the diffusion coefficient D depends on the intermolecular distance d and is inversely proportional to the average jump time τ :

$$D = \frac{d^2}{2\tau}. \quad (2)$$

The two above-mentioned characteristic times depend, as usual, on the activation energies of desorption and of surface diffusion respectively:

$$\tau_{des} = \tau_0 \exp\left(\frac{E_{des}}{kT}\right) \quad \tau = \tau_0 \exp\left(\frac{E_{eff}}{kT}\right). \quad (3)$$

The temperature dependence of λ is easily obtained from equations (1)–(3) in the form

$$\lambda = \frac{d}{\sqrt{2}} \exp\left[\frac{E_{des} - E_{eff}}{2kT}\right]. \quad (4)$$

Since $E_{des} > E_{eff}(T)$ it follows that λ decreases with temperature. Note that, because of the disorder, the effective activation energy for surface diffusion $E_{eff} = E_{eff}(T)$ is temperature dependent, so no straight line is expected in an Arrhenius plot ($\ln \lambda$ versus $1/T$). The reasons for the temperature dependence of $E_{eff}(T)$ are discussed below.

The model

Any particle that moves much faster than the main building units of the system meets a state [3] of 'static disorder'. There are channels of motion along which the barriers appear according to a given distribution function $f(E)$ determined by the structure of the substrate. The successive jumps are strongly correlated and the motion from the origin to a distant area is a typical percolation theory problem.

Earlier [3, 4], it was proposed that one could define the activation energy that determines the rate of this process as the upper limit E_c of the integral

$$\int_0^{E_p} f(E) dE = p_c^\infty \quad (5)$$

where the threshold concentration p_c^∞ depends on the number n of escape channels and on the space dimension Δ . There have been (see for instance [5]) a number of estimations of p_c^∞ . Here we use the formula

$$p_c^\infty = \frac{\Delta}{(\Delta - 1)n}. \quad (6)$$

The probability distribution function $f(E)$ representing the probability that a channel has barrier of height between E and $E + dE$ is normalized according to

$$\int_0^\infty f(E) dE = 1. \quad (7)$$

The surface diffusion is a two-dimensional case, $\Delta = 2$, so $p_c = 2/n$.

It can be shown (for details, see the appendix) that the upper limit E_p is

$$E_p = E_{max} - a\sigma \quad (8)$$

where σ is the dispersity of the probability distribution function $f(E)$ and the dimensionless parameter a is between 0.4 and 1.

Strictly speaking, the mean jump time τ is

$$\tau(E_{eff}) = \int_0^{E_p} f(E)\tau(E) dE. \quad (9)$$

It can be shown that the approximation $E_{eff} \approx E_p$ is sufficiently accurate for the purposes of the present investigation.

It is known (see [5]) that the threshold $p_c(L)$ depends on the length L of the percolating cluster. Here we adopt the approximation

$$p_c(L) = p_c^\infty \left[1 - \left(\frac{d}{L} \right)^\nu \right] \quad (10)$$

that follows straightforwardly from the discussion on this problem given in [5]. The power ν depends on the dimensionality Δ of the space, $\nu \simeq 0.74$ for $\Delta = 2$. It is seen that the percolation threshold for diffusion to a distance of $10d$ is only about 80% of p_c^∞ . The effective activation energy $E_{eff}(L)$ for diffusion to a distance L can be determined by analogy with equation (10) as

$$E_{eff}(L) = E_{max} - a\sigma + \sigma \ln \left[1 - \left(\frac{d}{L} \right)^\nu \right]. \quad (11)$$

It is seen that the diffusion coefficient is both temperature dependent (through σ) and distance dependent. The combination of equations (2), (3) and (11) yields

$$D(L) = D_\infty \left[1 - \left(\frac{d}{L} \right)^\nu \right]^{-\sigma/kT} \quad (12)$$

where $D_\infty = D(L \rightarrow \infty)$ stands for

$$D_\infty = \frac{d^2}{2\tau_0} \exp \left\{ -\frac{E_{max} - a\sigma}{kT} \right\}. \quad (13)$$

Temperature dependence of σ

There is a strong relationship between the entropy S and the dispersity σ of the system:

$$\sigma = \sigma_r \exp \left[\frac{2(S - S_g)}{ZR} \right]. \quad (14)$$

Here σ_g is the dispersity at the reference state with entropy S_g and Z is the whole number of escape channels in the bulk of the system (please note that it is larger than the number of channels along the surface of the substrate, $Z > n$). One can easily express the entropy dependence of E_{eff} by combining equations (14) and (13). It is useful to choose for the reference state the glass transition temperature T_g . The temperature dependence of the entropy is

$$S(T, P) - S_g = \int_{T_r}^T C_p \, d \ln \tilde{T} \approx C_p \ln \frac{T}{T_g}. \quad (15)$$

The dispersity σ is expressed through equations (14) and (15) as

$$\sigma = \sigma_g \left(\frac{T}{T_g} \right)^\beta \quad (16)$$

where β is proportional to the ratio of the heat capacity C_p and the gas constant R :

$$\beta = \frac{2C_p}{ZR} \approx 0.2 \frac{C_p}{R}. \quad (17)$$

With this notation the diffusion coefficient becomes

$$\ln D = \ln \left(\frac{d^2}{2\tau_0} \right) - \left[E_{max} \frac{T_g}{T} - \sigma_g \left\{ a - \ln \left[1 - \left(\frac{d}{L} \right)^\nu \right] \right\} \left(\frac{T}{T_g} \right)^{\beta-1} \right] (kT_g)^{-1}. \quad (18)$$

The final expression for the mean diffusion distance λ is

$$\lambda = \frac{d}{\sqrt{2}} \exp \left\langle \frac{E_{des}}{2kT_g} \left\langle \left[1 - \frac{E_{max}}{E_{des}} \right] - \left[\sigma_g \left\{ a - \ln \left[1 - \left(\frac{d}{L} \right)^\nu \right] \right\} \left(\frac{T}{T_g} \right)^\beta \right] (kT_g)^{-1} \right\rangle \frac{T_g}{T} \right\rangle. \quad (19)$$

Discussion

Figure 1 shows the dependence of the diffusion coefficient on distance (in units of d) for a typical dispersity value $\sigma/kT = 10$ (solid curve) and for $\sigma/kT = 1$ (dashed curve). In both cases $\nu = 74$. It is seen that diffusion proceeds much faster at short distances. This could be of importance for steps interacting on a substrate, for nucleation processes etc. Results giving an indication that motion over a short distance differs from the diffusive regime over long distances were reported earlier in [6, 7], although the reasoning there was different from the arguments presented here.

It is a common assumption that the activation energy for surface diffusion on amorphous substrates is not temperature dependent. This is why it is determined, usually, from the slope

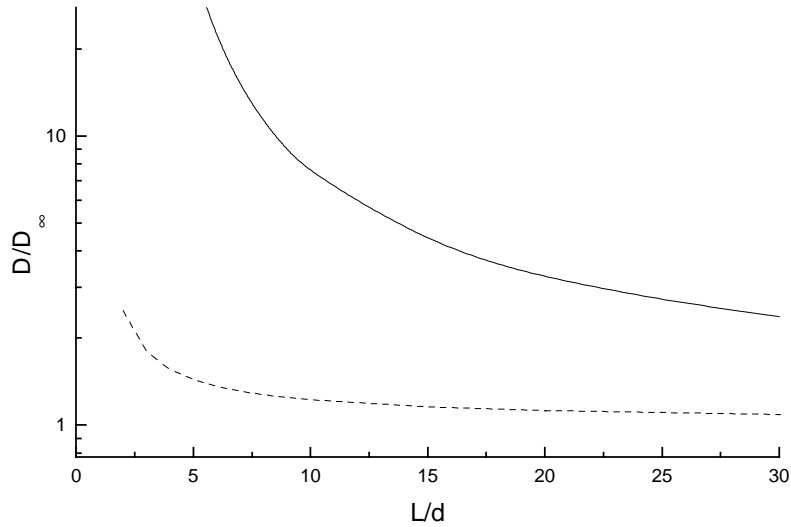


Figure 1. The dependence of the diffusion coefficient on distance. Solid curve: $\sigma/(kT) = 10$; dashed curve: $\sigma/(kT) = 1$.

SL of the Arrhenius plot of the diffusion coefficient:

$$\text{SL} \equiv \frac{\partial \lg D}{\partial(1/T)} = -\frac{E_{max}}{2.3k} \left\langle 1 - \frac{\sigma_g}{E_{max}} (1 - \beta) \left[\left\{ a - \ln \left[1 - \left(\frac{d}{L} \right)^\nu \right] \right\} \left(\frac{T}{T_g} \right)^\beta \right] (kT_g)^{-1} \right\rangle. \quad (20)$$

It is seen that a straight line is expected only for $\beta = 1$. Moreover, even in this case the slope SL will be E_{max} , not the effective activation energy E_{eff} . This is why the activation energy is, usually, overestimated and an incorrect value of the pre-exponential constant is assumed in order to obtain an appropriate value of the diffusion coefficient. Figure 2 represents, in Arrhenius coordinates, the temperature dependence of diffusion coefficient D (in arbitrary units) for $\beta = 1$, $\beta = 2$ and $\beta = 4$. Although the curvature is not easy to discern experimentally, the value of β plays an important role. At high temperatures there is an increase of the slope with β . If not accounted for, this could cause an additional overestimation of the effective activation energy.

There is an important difference between the diffusion and self-diffusion processes. In the case of self-diffusion all particles move with comparable rates. So, if a tracer meets energy barriers that are too high, it does not need to overcome any of them. After a given time the configuration is changed because the surrounding particles have moved. In this case it seems more reasonable to average over the jump frequencies. So, the high frequencies (low energy barriers) dominate. On the other hand, in the case of diffusion through a frozen system the particle inevitably needs to overcome some barriers in order to percolate. The correct way to proceed is to average over the jump times.

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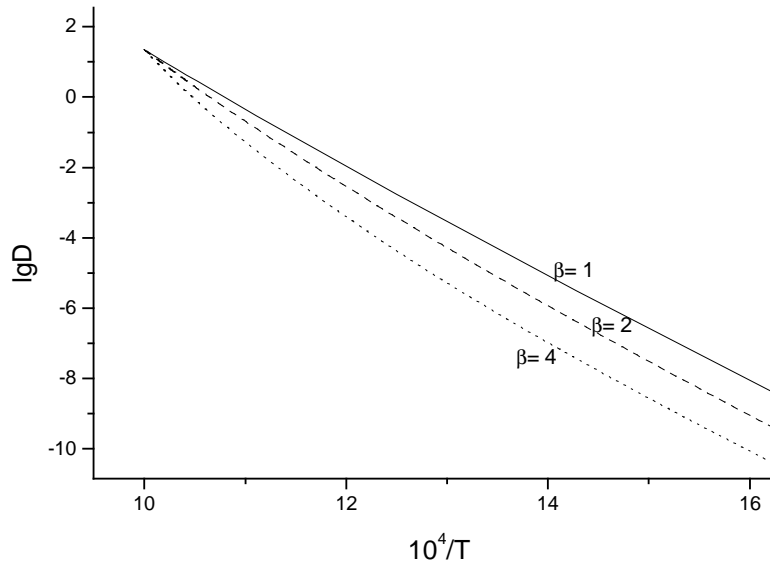


Figure 2. The temperature dependence of the diffusion coefficient D . The parameter β is given for each curve. The curves are drawn for $E_{max}/k = 30\,000$ and $\sigma_g/k = 10\,000$.

Appendix

Under the assumption that $f(E)$ is described as Poissonian distribution

$$f(E) = \exp\left(\frac{E - E_{max}}{\sigma}\right) \left\{ \sigma \left[1 - \exp\left(-\frac{E_{max}}{\sigma}\right) \right] \right\}^{-1}$$

equation (1) becomes

$$\left[\exp\left(\frac{E_c - E_{max}}{\sigma}\right) - \exp\left(-\frac{E_{max}}{\sigma}\right) \right] / \left[1 - \exp\left(-\frac{E_{max}}{\sigma}\right) \right] = p_c^\infty \quad (\text{A.1})$$

where σ is the dispersity of the system. Equation (A.1) can be simplified considerably; for $E_{max}/\sigma \gg 1$ it becomes

$$\exp\left(\frac{E_c - E_{max}}{\sigma}\right) \approx p_c^\infty. \quad (\text{A.2})$$

This means that the effective activation energy E_{eff} that controls the process of surface diffusion is determined as

$$E_{eff}^\infty = E_{max} + \sigma \ln p_c^\infty = E_{max} - a\sigma \quad (\text{A.3})$$

where $a = -\ln p_c^\infty = \ln(n/2)$.

Most frequently, the number of escape channels along an amorphous surface is between 5 and 6, so $a \approx 1$. A similar result is easily obtained for Gaussian distributions, only in this case $a \approx 0.4$.

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