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The average jump rate and diffusion in disordered systems

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Abstract. The average jump rate for particles undergoing diffusion in disordered systems is calculated for arbitrary concentrations of particles. The disorder model considered is a combination of site-energy and barrier-energy disorder. Uniform and Gaussian distribution functions are used as examples. The average jump rate does not show Arrhenius behaviour in general, but can in particular cases. The tracer diffusion coefficient is deduced from the average jump rate in the low-concentration limit for the site-energy disorder model for which there are no spatial correlations in successive jumps. For models where spatial correlations do occur, expressions for the diffusion coefficient and the average jump rate can be used to obtain information about the correlations.

1. Introduction

The average jump rate of particles undergoing diffusion in an ordered system is a straightforward parameter. The usual physical model assumed is that a particle has a rate of attempted jumps, which is of Arrhenius form, to a nearest-neighbour site and that the attempted jump is successful if the target site is vacant. The average rate of jumps Γ away from a site is then

$$\Gamma = Z\Gamma_0(1-c)\mathrm{e}^{-\beta E} \tag{1}$$

where Γ_0 is a constant, E is the energy barrier, c is the probability of the target site being occupied by a particle, Z is the coordination number of the structure and $\beta = 1/(kT)$.

The average jump rate becomes more complicated to evaluate when the sites for the diffusing particles are not equivalent. An example is the jump rate of vacancies at very low concentrations in metals containing dilute impurities. The jump rate of a vacancy depends on its proximity to a solute atom and the evaluation of the average jump rate requires consideration of the different possible jump rates near an impurity weighted by the probability of occupation of the vacancy at each type of site. The average jump rate can then be evaluated for particular jump frequency models (Ishioka and Koiwa 1984).

Similar considerations apply to the average jump rate of particles diffusing in disordered systems; it is necessary to consider the possible jump rates in the system and weight these with the occupation probabilities. A common model for diffusion in disordered systems is that in which the site energies are described by some distribution function $N_s(E)$ and the jumps occur to neighbouring sites over barriers which have another distribution $N_b(E)$. These distributions will be assumed to be independent functions although correlations between site energies and barrier energies could certainly occur in practice.

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The average jump rate $\overline{\Gamma}$ in disordered systems is of interest for several reasons. It is related to the tracer diffusion coefficient D by

$$D = \frac{\overline{R^2}(t)}{2dt} = \frac{\overline{R^2}(t)}{2dN(t)}\frac{N(t)}{t} = \frac{1}{2d}\overline{R^2}\,\overline{\Gamma} \tag{2}$$

where d is the dimensionality of the system, $\overline{R^2}(t)$ is the mean square displacement after a long time t, $N(t)$ is the mean number of jumps in a time t, $\overline{R^2} = \overline{R^2}(t)/N(t)$ is the mean square displacement per jump and $\overline{\Gamma} = N(t)/t$ is the average jump rate. If successive jumps of a particle are not correlated, then $\overline{R^2}$ is the mean square distance $\overline{R_1^2}$ for a single jump. For diffusion models with no correlations, knowledge of the average jump rate then gives D. If there are correlations between successive jumps then $\overline{R^2} = f\overline{R_1^2}$ where f is the correlation factor. Alternatively, a correlation factor f_1 could be defined by $\overline{R^2} = f_1 a^2$ where a is the mean jump distance. If the diffusion coefficient is known in such cases, an expression for $\overline{\Gamma}$ can provide information on the correlation factors. How $\overline{\Gamma}$ depends on temperature, particle concentration c and the distribution functions is relevant in both cases to understanding the microscopic details of diffusion.

It has been shown by Limoge and Bocquet (1990) and Mussawisade *et al* ((1997), to be referred to as MWK) that a suitable combination of site-energy and barrier-energy disorder can cause near-Arrhenius behaviour of the temperature dependence of the diffusion constant D. It is of interest to analyse the dependence of the average jump rate on temperature and particle concentration in order to determine the relative roles of $\overline{\Gamma}$ and correlation effects in producing this result.

The average jump rate is also of importance in Monte Carlo simulations of diffusion in disordered systems. Knowledge of $\overline{\Gamma}$ would only require the calculation of the time-independent quantity $\overline{R^2}$ in a simulation to obtain D from equation (2). Verification of a computed $\overline{\Gamma}$ from a simulation against a rigorous calculated value could also be a useful check on the simulation.

The average jump rate is a relevant parameter in some Monte Carlo calculations of rates of nuclear spin–lattice relaxation due to diffusion in disordered systems (Hua *et al* 1997). These Monte Carlo simulations calculated the required magnetic dipolar correlation functions in terms of the average jump rate. The form of $\overline{\Gamma}$ is then needed to obtain the relaxation rates as functions of temperature. An approximate analysis of $\overline{\Gamma}$ for a uniform distribution of site energies was undertaken by Hua *et al* (1997). Another approach to calculating nuclear spin-relaxation rates in disordered systems has recently been developed (Cameron and Sholl 1999) which is based on the technique described here for evaluating $\overline{\Gamma}$.

There has been considerable effort devoted to analysing diffusion in disordered systems for a model of diffusion on ordered lattices with the disorder imposed on the jump rates (see, for example, Kehr and Wichmann (1996), MWK, Kirchheim (1997)). The analysis developed here for the average jump rate and diffusion does not require the assumption of geometric ordering.

The general expression for the average rate of jumps $\overline{\Gamma}$ due to diffusion in disordered systems is derived in section 2. It is assumed that the particles diffuse amongst a set of sites which have a specified site-energy distribution and also have an independent barrier-energy distribution for jumps between sites. It is also assumed that only a single particle may occupy a site and that the energy distributions are independent of temperature and the concentration of the diffusing species. The theory could be extended to more general conditions if appropriate models for correlations between the distribution functions, or the effects of interactions between the particles were assumed. The form of $\overline{\Gamma}$ for a uniform distribution and a Gaussian distribution

are considered as examples in section 3. A complete analytic solution is possible for the uniform distribution. Applications to the theory of tracer diffusion are discussed in section 4.

2. Average jump rate

The probability of occupation of a site in a disordered system depends on the normalized site-energy distribution $N_s(E)$. When multiple occupancy of a site is excluded, the probability of occupation of a site with energy E is given by the Fermi–Dirac function

$$p(E) = \frac{1}{\mathrm{e}^{(E-\mu)\beta} + 1} \tag{3}$$

where μ is the chemical potential. The chemical potential is related to the average concentration of diffusing particles by

$$c = \int_{-\infty}^{\infty} p(E) N_s(E)\, \mathrm{d}E. \tag{4}$$

The average jump rate $\overline{\Gamma}$ is then

$$\overline{\Gamma} = \frac{1}{c} \int_{-\infty}^{\infty} p(E) N_s(E)\, \mathrm{d}E \int_{-\infty}^{\infty} N_b(E_1) Z(1-c) \Gamma(E, E_1)\, \mathrm{d}E_1 \tag{5}$$

where $\Gamma(E, E_1)$ is the rate of jumps from a site with energy E to one of Z nearest neighbours across a barrier with energy E_1 and $N_b(E_1)$ is the normalized distribution of barrier energies. The factor $(1-c)$ accounts for the blocking of this attempted jump if the target site is occupied. It will be assumed that $\Gamma(E, E_1)$ is of the Arrhenius form:

$$\Gamma(E, E_1) = \Gamma_0 \mathrm{e}^{-(E_1 - E)\beta} \tag{6}$$

and that Γ_0 is a constant. Since it is assumed that the site-energy distribution $N_s(E)$ and the barrier-energy distribution $N_b(E_1)$ are independent functions, the value of the number Z of nearest neighbours may be taken as the mean coordination number.

The expression (5) for the average jump rate could be generalized to include more general models in which there are correlations between the energy E of a site, the number of neighbours Z, the value of Γ_0 and the barrier-energy distribution $N_b(E_1)$. Such models would require assumptions regarding the nature of the correlations and the appropriate weightings of the functions in the integrals.

It is useful to express $\overline{\Gamma}$ in terms of the jump rate $\overline{\gamma}$ corresponding to the rate for the average site energy $\overline{E}$ and average barrier energy $\overline{E_1}$, defined by

$$\overline{\gamma} = Z(1-c)\Gamma_0 \mathrm{e}^{-(\overline{E_1} - \overline{E})\beta}. \tag{7}$$

The frequency $\overline{\gamma}$ is thus the mean jump rate for δ-function distributions and is of Arrhenius form. The ratio $\overline{\Gamma}/\overline{\gamma}$ shows the deviation of $\overline{\Gamma}$ from Arrhenius behaviour. Changing the variables E and E_1 to

$$\epsilon = (E - \overline{E})/(\overline{E_1} - \overline{E}) \qquad \text{and} \qquad \epsilon_1 = (E_1 - \overline{E_1})/(\overline{E_1} - \overline{E})$$

and defining

$$\beta_1 = (\overline{E_1} - \overline{E})\beta \qquad \text{and} \qquad \mu_1 = (\mu - \overline{E})/(\overline{E_1} - \overline{E})$$

equation (5) can be written as

$$\overline{\Gamma}/\overline{\gamma} = F_s(\beta_1, c) F_b(\beta_1) \tag{8}$$

$$F_s(\beta_1, c) = \frac{1}{c} \int_{-\infty}^{\infty} p(\epsilon) N_s(\epsilon) \mathrm{e}^{\epsilon\beta_1}\, \mathrm{d}\epsilon \tag{9}$$

$$F_b(\beta_1) = \int_{-\infty}^{\infty} N_b(\epsilon_1) \mathrm{e}^{-\epsilon_1\beta_1}\, \mathrm{d}\epsilon_1. \tag{10}$$

The relationship between μ_1 and c is

$$c = \int_{-\infty}^{\infty} \frac{N_s(\epsilon)}{e^{(\epsilon-\mu_1)\beta_1}+1}\,d\epsilon. \tag{11}$$

A useful form for $F_s(\beta_1, c)$ is

$$F_s(\beta_1, c) = \frac{1-c}{c}e^{\mu_1\beta_1} \tag{12}$$

which can be verified by writing $(1-c)$ in the numerator as the normalization integral for $N_s(\epsilon)$ minus equation (11). For $N_s(\epsilon)$ an even function, it can be shown from equation (11) that if μ_1 is the chemical potential for a concentration c, then $-\mu_1$ is the chemical potential for the concentration $1-c$. It then follows from equation (12) that $F_s(\beta_1, 1-c) = F_s^{-1}(\beta_1, c)$ and $F_s(\beta_1, 1/2) = 1$. This result of Arrhenius behaviour for the site-energy model with $c = 0.5$ was found numerically for the special case of a uniform distribution by Hua *et al* (1997).

The functions $F_s(\beta_1, c)$ and $F_b(\beta_1)$ give the deviation of $\overline{\Gamma}$ from Arrhenius behaviour for the site-energy and barrier-energy disorder, respectively. The effects are decoupled and multiplicative, with the barrier-energy effects independent of c.

In the low-concentration limit $c \ll 1$, the chemical potential μ_1 becomes a large negative quantity, so equation (11) becomes

$$ce^{-\mu_1\beta_1} = \int_{-\infty}^{\infty} N_s(\epsilon)e^{-\epsilon\beta_1}\,d\epsilon. \tag{13}$$

The Fermi–Dirac function then becomes the Boltzmann distribution

$$p(\epsilon) = ce^{-\epsilon\beta_1}\Big/\left(\int_{-\infty}^{\infty} N_s(\epsilon)e^{-\epsilon\beta_1}\,d\epsilon\right) \tag{14}$$

and $F_s(\beta_1, c)$ becomes $F_s^{-1}(\beta_1)$ where

$$F_s(\beta_1) = \int_{-\infty}^{\infty} N_s(\epsilon)e^{-\epsilon\beta_1}\,d\epsilon. \tag{15}$$

The average jump rate in the low-concentration limit is therefore

$$\overline{\Gamma} = \frac{F_b(\beta_1)}{F_s(\beta_1)}\overline{\gamma}. \tag{16}$$

The deviations from Arrhenius behaviour due to the site-energy and barrier-energy disorders therefore tend to cancel in this limit and exact Arrhenius behaviour would occur if the distribution functions for the disorders were the same.

3. Examples

The form of $\overline{\Gamma}/\overline{\gamma}$ can be evaluated, analytically or numerically, for any specified distribution functions from equations (8)–(12). Two distributions are considered: a uniform distribution and a Gaussian distribution. The uniform distribution is

$$N(E) = \begin{cases} 1/(2\delta) & \text{for } \overline{E}-\delta < E < \overline{E}+\delta \\ 0 & \text{otherwise} \end{cases}$$

and the Gaussian distribution is

$$N(E) = (2\pi\sigma^2)^{-1/2}\exp[-(E-\overline{E})^2/(2\sigma^2)].$$

A complete analytic solution is possible for the uniform distribution. Integrating equation (11) gives the chemical potential μ_1 in the form

$$e^{-\mu_1\beta_1} = \frac{1}{x}\frac{x^2-x^{2c}}{x^{2c}-1} \tag{17}$$

where $x = \exp(\delta_1\beta_1)$ and $\delta_1 = \delta/(\overline{E_1} - \overline{E})$. The function $F_s(\beta_1, c)$ is then given by equation (12). The function $F_b(\beta_1)$ from equation (10) is $\sinh(\delta_1\beta_1)/(\delta_1\beta_1)$. For the Gaussian distribution, $F_b(\beta_1) = \mathrm{e}^{(\beta_1\sigma_1)^2/2}$ where $\sigma_1 = \sigma/(\overline{E_1} - \overline{E})$. It is necessary to evaluate $F_s(\beta_1, c)$ numerically in this case by computing μ_1 from equation (11) and then using equation (12).

Some examples of the effects of disorder on the average jump rate are shown in figure 1. The figure displays plots of $\ln[\mathrm{e}^{-\beta_1} F_s(\beta_1, c)]$ versus β_1 to show the types of deviation from Arrhenius behaviour. Results are shown for the uniform distribution with $\delta_1 = 0.3$ and $c = 0.7, 0.9$ and 0.99, and for the Gaussian distribution with $\sigma_1 = 0.15$ and $c \ll 1$, $c = 0.1$ and 0.3. For both distributions, exact Arrhenius behaviour results for site-energy disorder with $c = 0.5$, and the results for $1 - c$ can be deduced from $F_s(\beta_1, 1 - c) = F_s^{-1}(\beta_1, c)$. It can be seen that the effect of the site-energy disorder is to enhance the jump rate above the Arrhenius form (upward curvature) for $c > 1/2$ and to diminish it (downward curvature) for $c < 1/2$. The effect of barrier-energy disorder can also be deduced from the figure because the low-concentration limit of the site-energy disorder gives the inverse of the barrier-energy disorder function $F_b(\beta_1)$ for the same distribution function. For example, the enhancement of the average jump rate above the Arrhenius form for barrier-energy disorder for the Gaussian distribution in the figure is the same as the reduction below the Arrhenius form for the curve for $c \ll 1$ for the site-energy disorder. It should be noted that the approach of the curves in the figure to the limit of $c \ll 1$ is very slow for the Gaussian distribution, as can be seen from the difference between the curves for $c = 0.1$ and the limit $c \ll 1$.

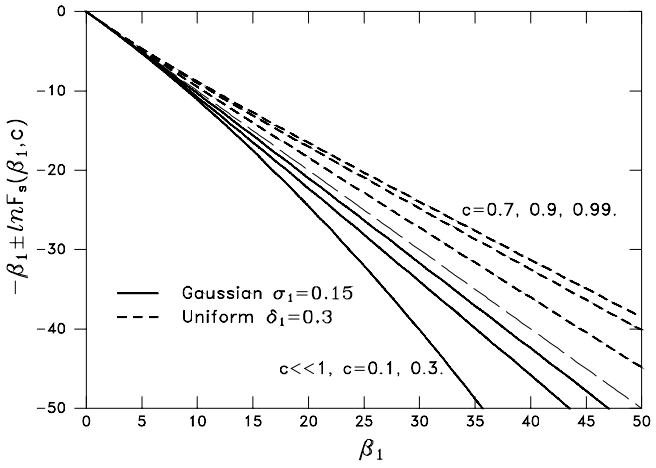

Figure 1. Plots of $\ln[\mathrm{e}^{-\beta_1} F_s(\beta_1, c)]$ versus β_1 for the uniform distribution with $\delta_1 = 0.3$ and $c = 0.7, 0.9$ and 0.99, and for the Gaussian distribution with $\sigma_1 = 0.15$ and $c \ll 1$, $c = 0.1$ and 0.3. The values of c shown in the figure label the groups of curves from left to right.

The combined effect of barrier-energy and site-energy disorder on the average jump rate is therefore the following. At low concentrations c the upward curvature due to the barrier-energy disorder tends to be cancelled by the downward curvature due to the site-energy disorder. The upward curvature due to the barrier-energy disorder is independent of c while the downward curvature due to the site-energy disorder decreases and becomes zero at $c = 0.5$. The resulting effect at $c = 0.5$ is therefore just the upward curvature due to the barrier-energy disorder. For concentrations $c > 0.5$, the two types of disorder add, to give enhanced upward curvature. The above conclusions are valid in all dimensions.

4. Diffusion

The tracer diffusion coefficient D involves the average jump rate $\overline{\Gamma}$ and the mean square displacement per jump $\overline{R^2}$ according to equation (2). The above expressions for $\overline{\Gamma}$ can therefore give D if $\overline{R^2}$ can be obtained. A model where this is possible is the low-concentration limit of site-energy disorder only. In this case there are no spatial correlations between successive jumps and so the correlation factor $f = 1$. The diffusion coefficient is then

$$D_{site} = \frac{1}{2d}\overline{R_1^2}\overline{\gamma}\Big/\left(\int_{-\infty}^{\infty} N_s(\epsilon)\mathrm{e}^{-\epsilon\beta_1}\,\mathrm{d}\epsilon\right) \tag{18}$$

from equations (2), (8) and (15). The value of $\overline{R_1^2}$ could be evaluated straightforwardly for any model of spatial disorder, taking into account the probabilities of occupation of sites and the weightings of possible jump distances. This expression for D agrees with that obtained by MWK for the case of diffusion on a lattice with disordered transition rates. The present derivation extends this exact result to diffusion on a system with structural disorder as well as disordered transition rates. The above result (18) for D_{site} is valid in all dimensions in the low-concentration limit for site-energy disorder. If the structure of the system does not depend on temperature, the temperature dependence of D is given by the temperature dependence of $\overline{\Gamma}$.

Another exact result known is the expression for D in the low-concentration limit for one-dimensional diffusion on lattices with disordered transition rates (MWK), or on periodic structures with many inequivalent sites per unit cell (Braun and Sholl 1998). For a combination of independent site-energy and barrier-energy disorder, the result is, in the present notation,

$$D_{comb} = \frac{a^2\overline{\gamma}}{2}\Big/\left(\int_{-\infty}^{\infty} N_s(\epsilon)\mathrm{e}^{-\epsilon\beta_1}\,\mathrm{d}\epsilon\int_{-\infty}^{\infty} N_b(\epsilon_1)\mathrm{e}^{\epsilon_1\beta_1}\,\mathrm{d}\epsilon_1\right) \tag{19}$$

where a is the mean distance between sites. The occurrence of the mean separation squared in this expression, rather than the mean square jump distance as in (18), is a consequence of the periodicity of the lattice in the above models. It follows that an Arrhenius plot exhibits downward curvature for these models (MWK, Braun and Sholl 1998). The expression for the average jump rate enables the mean square jump distance $\overline{R^2}$ to be deduced from equation (2) and it is

$$(\overline{R^2}/a^2)^{-1} = \int_{-\infty}^{\infty} N_b(\epsilon_1)\mathrm{e}^{-\epsilon_1\beta_1}\,\mathrm{d}\epsilon_1\int_{-\infty}^{\infty} N_b(\epsilon_1)\mathrm{e}^{\epsilon_1\beta_1}\,\mathrm{d}\epsilon_1. \tag{20}$$

which shows the effect of the spatial correlations of the jumps as a result of the barrier-energy distribution. For a Gaussian distribution, $\overline{R^2}/a^2 = \mathrm{e}^{-\beta_1^2\sigma_1^2}$. A similar procedure is possible for any case where an exact, or approximate, result for D is available. The result for D combined with equation (2) and the expression for $\overline{\Gamma}$ enables $\overline{R^2}$ and the consequent correlation factor to be deduced.

An expression for D_{site} for the site-energy model valid for arbitrary concentration c can be obtained from equations (2) and (8), and may be expressed as

$$D = D_0\frac{(1-c)^2}{c}\mathrm{e}^{(\mu-\overline{E})\beta} \tag{21}$$

where the factor D_0 is

$$D_0 = \frac{\overline{R^2}}{2d}Z\Gamma_0\mathrm{e}^{-(\overline{E_1}-\overline{E})\beta}. \tag{22}$$

This expression for D has been obtained previously by Kirchheim (1997) using a different method. It was argued by Kirchheim that equation (21) is also a reasonable approximation

irrespective of the form of the barrier-energy distribution. The present derivation shows that if a barrier-energy distribution is also present, then the term $F_b(\beta_1)$ from equation (8) should also be included as a multiplicative factor in the expression for D. The effect of the approximation proposed by Kirchheim is therefore to neglect this concentration-independent term.

5. Conclusions

The expression for the average jump rate $\overline{\Gamma}$ has been derived for particles undergoing diffusion in disordered systems with site-energy and barrier-energy disorder. The results are valid in all dimensions and for all particle concentrations, and are not restricted to diffusion on lattices. Analytic results have been obtained for some simple cases. The theory developed here for independent site-energy and barrier-energy disorders could easily be extended to include correlations between the disorder distributions, the jump rate prefactor Γ_0 and the number of neighbours of a site. Such correlations are likely to occur in practice.

The tracer diffusion coefficient can be deduced from $\overline{\Gamma}$ if there are no spatial correlations between successive jumps, as in the case of a low concentration of diffusing particles for a model of random site energies. In cases where spatial correlations between successive jumps do occur, the expression for $\overline{\Gamma}$ can provide information about the spatial correlations.

The results derived for $\overline{\Gamma}$ should be of use in Monte Carlo simulations of diffusion and related phenomena. They can provide a useful check on the Monte Carlo simulations or can simplify the simulations by removing the necessity for inclusion of the time dependence in a simulation.

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