Hopping diffusion across interfaces

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We study the hopping diffusion on a linear chain with different hopping rates on the left or right of the origin. The relevance of our model with respect to experiments on interdiffusion between different solid materials is pointed out.

Molecular transport across a simple interface between two different solid materials, e.g., metallic or semiconductor films or between solid ionic conductors represents a considerable theoretical challenge if discreteness of the jumps is properly taken into account. In this short note we present the simplest model-preserving discreteness and a minimal description of jump rates in both lattices. It is composed of two different one-dimensional Ising lattices meeting at the origin and treated with Kawasaki kinetics (like the Glauber model[1]) with the spin-flip rate α in the "positive direction" lattice and β in the "negative direction" lattice. If σ_l is the Ising spin variable for lattice site $l\,(\sigma_l=\pm 1)$ then the occupation number of site l is $n_l=(1+\sigma_l)/2$. Thus the occupation number transport equation is equivalent to the Glauber kinetic equation for spins.

We write the transport equations of our model

$$\dot{n}_l=\begin{cases}\alpha(n_{l+1}-2n_l+n_{l-1}), & \text{for } l\geq 1, \quad (1)\\ \alpha(n_1-n_0)+\beta(n_{-1}-n_0), & \text{for } l=0, \quad (2)\\ \beta(n_{l+1}-2n_l+n_{l-1}), & \text{for } l\leq -1, \quad (3)\end{cases}$$

subject to the initial condition

$$n_l(t=0)=\begin{cases}1, & \text{for } l\leq 0,\\ 0, & \text{for } l>0.\end{cases} \quad (4)$$

Denoting the Laplace transform (LT) of $n_l(t)$ by $\bar{n}_l(s)=\int_0^\infty dt\, e^{-st}n_l(t)$, one has the difference equations

$$s\bar{n}_l=\begin{cases}\alpha(\bar{n}_{l+1}-2\bar{n}_l+\bar{n}_{l-1}), & \text{for } l\geq 1, \quad (5)\\ \alpha(\bar{n}_1-\bar{n}_0)+\beta(\bar{n}_{-1}-\bar{n}_0)+1, & \text{for } l=0, \quad (6)\\ \beta(\bar{n}_{l+1}-2\bar{n}_l+\bar{n}_{l-1})+1, & \text{for } l\leq -1. \quad (7)\end{cases}$$

This system is solved by the ansatz

$$\bar{n}_l=\begin{cases}\bar{n}_0 v^l, & \text{for } l\geq 0, \quad (8)\\ \left(\bar{n}_0-\frac{1}{s}\right)w^{|l|}+\frac{1}{s}, & \text{for } l\leq 0, \quad (9)\end{cases}$$

with v and w given by

$$v=4\alpha(\sqrt{s+4\alpha}+\sqrt{s}\,)^{-2}, \quad (10)$$

$$w=4\beta(\sqrt{s+4\beta}+\sqrt{s}\,)^{-2}. \quad (11)$$

Equation (6) allows us to determine $\bar{n}_0(s)$ as

$$\bar{n}_0(s)=\frac{1}{s}\frac{\sqrt{s+4\beta}+\sqrt{s}}{\sqrt{s+4\beta}+\sqrt{s+4\alpha}}. \quad (12)$$

In the special case of $\alpha=\beta$ the symmetry of the solution is expressed by the fact that

$$n_l(t)+n_{-l+1}(t)=1, \quad \text{for } l\geq 0.$$

The same result for the $\bar{n}_l(s)$ can be obtained if we start from a more general point of view. The solution $n_l(t)$ for $l\geq 0$ is given by the initial and boundary values $n_l(t=0)$ and $n_0(t)$ by the following expression which is a slight generalization of an equation due to Widder,[2]

$$n_l(t)=\sum_{k=0}^{\infty}[K_{|l-k|}(t)-K_{|l+k|}(t)]n_k(0)+\int_0^t dt'\,H_l(t-t')n_0(t'). \quad (13)$$

The functions H and K are

$$K_l(t)=e^{-2\alpha t}I_{|l|}(2\alpha t), \quad (14)$$

$$H_l(t)=\frac{|l|}{t}K_{|l|}(t). \quad (15)$$

(I_l is the modified Bessel function.)

The LT of H and K are[3]

$$\bar{H}_l(s)=v^{|l|}$$

and

$$\bar{K}_l(s)=[s(s+4\alpha)]^{-1/2}v^{|l|}. \quad (16)$$

If we use the initial condition (4) and apply Eq. (13) also for $l\leq 0$ (with β replacing α), then we can express the whole set of $\bar{n}_l(s)$ by $\bar{n}_0(s)$ only. Finally, $\bar{n}_0(s)$ is determined from particle number conservation. This leads to the same expressions (8), (9), and (12).

Further quantities of interest are the penetration depths

$$\langle l^{\pm}(t)\rangle=\sum_{l=1}^{\infty} l n_{\pm l}(t)\ , \quad (17)$$

whose Laplace transforms are found to be

$$\langle \bar{l}^{+}(s)\rangle=\bar{n}_0(s)\frac{\alpha}{s}, \quad \langle \bar{l}^{-}(s)\rangle=\left(\bar{n}_0(s)-\frac{1}{s}\right)\frac{\beta}{s}. \quad (18)$$

In the continuum limit at times t and distances l approaching infinity in such a way that l^2/t is kept finite we find from (16) that K and H are given by the asymptotic representations (l is replaced by the continuous variable x):

$$\bar{H}(x,s)=e^{-|x|\sqrt{s/\alpha}}, \quad (19)$$

$$\bar{K}(x,s)=e^{-|x|\sqrt{s/\alpha}}/(2\sqrt{s\alpha}). \quad (20)$$

The LT of (13) now simplifies to the usual expression[2]

$$\bar{n}(x,s)=\int_0^\infty dx'\,[\bar{K}(x-x',s)-\bar{K}(x+x',s)]\,n(x',0)+\bar{H}(x,s)\,\bar{n}(0,s). \tag{21}$$

This is the solution of the diffusion equation with diffusion coefficient α for the positive x direction subject to the given functions $n(x,0)$ and $\bar{n}(0,s)$. Under the analogous initial condition to (4)

$$n(x,0)=\theta(-x) \tag{22}$$

(θ is the unit step function), we obtain by the same procedure as used before

$$\bar{n}(0,s)=\frac{1}{s}\frac{\sqrt{\beta}}{\sqrt{\alpha}+\sqrt{\beta}}, \tag{23}$$

which has to be compared with the limit of $\bar{n}_0(s)$ given in (12) for small $s \ll \alpha,\beta$ [note that by Eq. (23), $n(0,t)$ is independent of t].

The solution $n(x,t)$ can finally be written as[4]

$$n(x,t)=\begin{cases}\dfrac{\sqrt{\beta}}{\sqrt{\alpha}+\sqrt{\beta}}\,\mathrm{erfc}\left(\dfrac{x}{2\sqrt{\alpha t}}\right), & \text{for } x\geqslant 0\ ,\\[2ex] 1-\dfrac{\sqrt{\alpha}}{\sqrt{\alpha}+\sqrt{\beta}}\,\mathrm{erfc}\left(-\dfrac{x}{2\sqrt{\beta t}}\right), & \text{for } x\leqslant 0\ .\end{cases} \tag{24}$$

$n(x,t)$ is continuous at $x=0$ and fulfills the conservation of current condition

$$\alpha\frac{\partial}{\partial x}n(0^+,t)=\beta\frac{\partial}{\partial x}n(0^-,t)\ . \tag{25}$$

The asymmetry of $n(x,t)$ in the presence of different rates α and β leads to nonequal penetration depths for $x \geqq 0$ and $x \leqq 0$,

$$\langle x^+(t)\rangle=\frac{\sqrt{\beta}}{\sqrt{\alpha}+\sqrt{\beta}}\alpha t\ ,\quad \langle x^-(t)\rangle=\frac{\sqrt{\alpha}}{\sqrt{\alpha}+\sqrt{\beta}}\beta t\ . \tag{26}$$

Therefore, $\langle x^+(t)\rangle/\langle x^-(t)\rangle=\sqrt{\alpha/\beta}$, in contrast to the time-dependent ratio $\langle l^+(t)\rangle/\langle l^-(t)\rangle$ in the discrete case, see Eq. (18). A quantitative illustration of discreteness effects is given in Fig. 1. There we show the decay of $n_0(t)$,

$$n_0(t)=\frac{1}{\alpha-\beta}\{\alpha e^{-2\alpha t}[I_0(2\alpha t)+I_1(2\alpha t)]-\beta e^{-2\beta t}[I_0(2\beta t)+I_1(2\beta t)]\}\ , \tag{27}$$

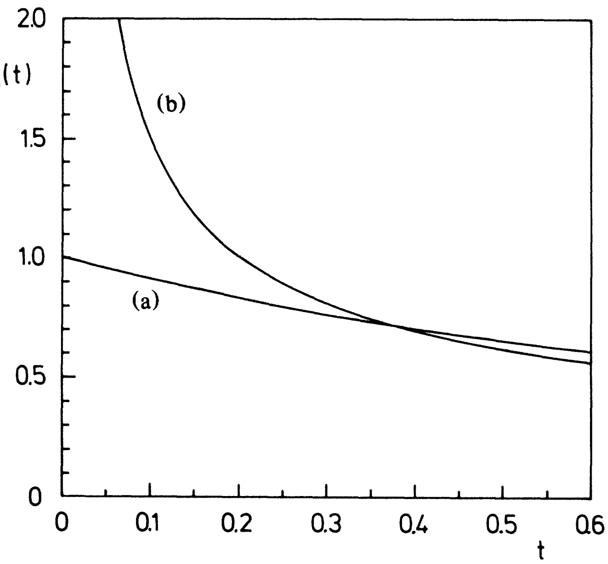

FIG. 1. Decay of $n_0(t)$ for the rates $\alpha=1$ and $\beta=0.1$. Curve (a) results from Eq. (27) and (b) is the continuum limit $n(0,t)$.

obtained from the simpler initial condition $n_l(0)=\delta_{l,0}$, and compare it with its behavior $n(0,t)=[\sqrt{\pi t}\,(\sqrt{\alpha}+\sqrt{\beta})]^{-1}$ in the continuum limit.

Experimental techniques, such as perturbed γ-γ angular correlation (PAC)[5] or Rutherford backscattering[6] have successfully been used in the past for probing interdiffusion processes at the interface between solid materials. A depth resolution of a few atomic distances should make it possible to obtain direct information about the occupation $n_l(t)$ of probe atoms near the interface. Our model suggests that useful microscopic information, for example, jump rates across the interface, could be deduced from such experiments. Clearly, for an actual comparison our model has to be extended by taking into account more realistic material parameters, for example, a potential energy difference and a difference in lattice structure between the two phases.

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