

## Diffusion in a tilted periodic potential with entropic barriers

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

2009 J. Phys.: Condens. Matter 21 465102

(<http://iopscience.iop.org/0953-8984/21/46/465102>)

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

Download details:

IP Address: 129.252.86.83

The article was downloaded on 30/05/2010 at 06:04

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

# Diffusion in a tilted periodic potential with entropic barriers

Yang Liu and Bao-Quan Ai

Laboratory of Quantum Information Technology, ICMP and SPTE, South China Normal University, Guangzhou, People's Republic of China

E-mail: [aibq@hotmail.com](mailto:aibq@hotmail.com)

Received 11 June 2009, in final form 4 October 2009

Published 26 October 2009

Online at [stacks.iop.org/JPhysCM/21/465102](http://stacks.iop.org/JPhysCM/21/465102)

## Abstract

Diffusion of Brownian particles in a periodic channel is investigated in the presence of a tilted spatially periodic potential. Reduction of spatial dimensionality from two or three dimensions to an effective one-dimensional system entails the appearance of not only an entropic barrier but also an effective diffusion coefficient. It is found that diffusion exhibits striking features which are different from those observed in the previous cases. The interplay between the potential barriers and entropic barriers makes the phenomena richer. Remarkably, two temperature values exist at which the Peclet number takes its maximum.

## 1. Introduction

The phenomenon varying from the diffusion of ions and macromolecular solutes through the channels in biological membranes [1], transport in zeolites [2] and nanostructures of complex geometry [3], controlled drug release [4] to diffusion in man-made periodic porous materials [5] can be considered as constrained transport. Motion in these systems can be induced by imposing different concentrations at the ends of the channel, or by the presence of external driving forces supplying the particles with the energy necessary to proceed.

Diffusion of Brownian particles in tilted periodic potentials has been studied in a number of papers [6–11]. Reimann *et al* [6, 7] found that the diffusion may be greatly enhanced compared to free thermal diffusion, with an enhancement of up to 14 orders of magnitude. Dan and Jayannavar [8] found that nonhomogeneous dissipation can induce enhancement and suppression of diffusion as a function of temperature. Recently, Heinsalu *et al* [11] found the appearance of the second resonant peak of the diffusion coefficient versus the driving force in a dimer.

The above studies on diffusion have revolved around the energy barrier. However, in some cases, such as soft condensed matter and biological systems, the entropy barriers should be considered [12–24]. Brownian particles, when moving in a confined geometry, instead of diffusing freely in the host liquid phase, undergo a constrained motion, where their kinetic behavior could exhibit peculiar behavior. Recently, Reguera *et al* [19] used the mesoscopic nonequilibrium thermodynamics theory to derive the general kinetic equation

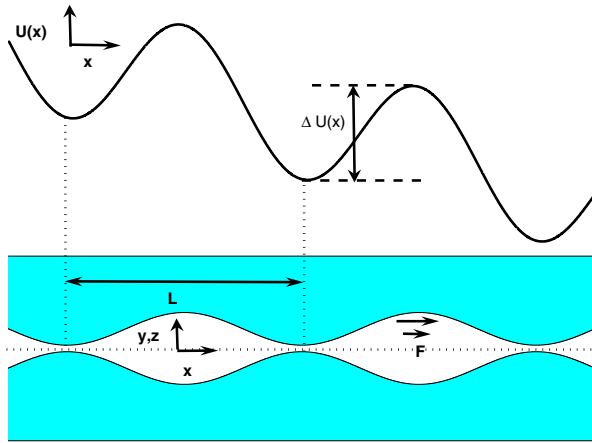
of the motor system and analyzed in detail the case of diffusion in a domain of irregular geometry in which the presence of the boundaries induces an entropy barrier when approaching the dynamics by a coarsening of the description. In their recent work [15] they studied the diffusion of Brownian particles moving in a symmetric channel with a biased external force and found that a regime existed where the effective diffusion coefficient in the presence of entropic barriers decreases with temperature which is different from that in the case of energy barriers.

The presence of entropic barriers accompanied by energy barriers may induce a peculiar phenomenon in particle diffusion. How Brownian particles diffuse in entropic potentials accompanied by energy potentials becomes an interesting problem. In the present work, we extend the previous work on diffusion to the case of periodic entropic barriers accompanied by periodic longitudinal energy barriers. We focus on finding how the interplay between the energy barriers and entropic barriers affects the particle diffusion.

## 2. Models and methods

In this paper, we study the diffusion of Brownian particles in a periodic channel with a tilted periodic potential. The overdamped dynamics can be described by the following Langevin equations written in a dimensionless form [12–14, 22–24]:

$$\eta \frac{dx}{dt} = -\frac{\partial U(x)}{\partial x} + \sqrt{\eta k_B T} \xi_x(t), \quad (1)$$



**Figure 1.** Schematic diagram of a channel confining the motion of Brownian particles under a tilted periodic potential. The upper part is the tilted periodic potential  $U(x) = -Fx + \sin(2\pi x/L + \theta)$  with a barrier height of  $\Delta U(x)$ . The shape of the channel is described by its half-width  $\omega(x) = a \sin(\frac{2\pi x}{L}) + b$ .

(This figure is in colour only in the electronic version)

$$\eta \frac{dy}{dt} = \sqrt{\eta k_B T} \xi_y(t), \quad (2)$$

$$\eta \frac{dz}{dt} = \sqrt{\eta k_B T} \xi_z(t), \quad (3)$$

where  $t$  is the time,  $x, y, z$  are the three-dimensional coordinates,  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature and  $\eta$  is the viscous friction coefficient.  $\xi_{x,y,z}(t)$  is the Gaussian white noise with zero mean and correlation function:  $\langle \xi_i(t) \xi_j(t') \rangle = 2\delta_{i,j} \delta(t - t')$  for  $i, j = x, y, z$ .  $\langle \dots \rangle$  denotes an ensemble average over the distribution of noise.  $\delta(t)$  is the Dirac delta function. The shape of the channel is described by its half-width (figure 1):

$$\omega(x) = a \sin\left(\frac{2\pi x}{L}\right) + b, \quad (4)$$

where  $a$  is the parameter that controls the slope of the tube and  $b - a$  is the parameter that determines the half-width at the bottleneck.

$U(x)$  is the tilted periodic potential (figure 1):

$$U(x) = -Fx + U_0(x), \quad (5)$$

where  $F$  is a constant force and  $U_0(x)$  is a symmetric periodic potential with periodicity  $L$ :

$$U_0(x) = \sin\left(\frac{2\pi}{L}x + \theta\right), \quad (6)$$

where  $\theta$  is the phase difference. The channel is assumed to be delimited by rigid, smooth walls, which means that it is impossible for the particles inside the channel to move out of the channel through the channel wall.

The motion equation of Brownian particles moving along the axis of the 3D (or two-dimensional (2D)) channel can

be correctly described by the Fick–Jacobs equation which is derived from the 3D (or 2D) Smoluchowski equation after elimination of  $y$  and  $z$  coordinates by assuming equilibrium in the orthogonal directions [18, 20]. The reduction of the coordinates may involve not only the appearance of an entropic barrier but also the effective diffusion coefficient. When  $|\omega'(x)| < 1$ , the  $x$ -dependent diffusion coefficient is [19]

$$D(x) = \frac{D_0}{[1 + \omega'(x)^2]^\alpha}, \quad (7)$$

where  $D_0 = k_B T / \eta$  and  $\alpha = 1/3, 1/2$  for the 2D and 3D cases. The prime stands for the derivative with respect to the space variable  $x$ .

In the presence of longitudinal drive  $F$  and the external periodic potential, the dynamics of Brownian particles moving along the axis of the channel can be described by [14, 19, 21–24]

$$\begin{aligned} \frac{\partial P(x, t)}{\partial t} &= \frac{\partial}{\partial x} \left[ D(x) \frac{\partial P(x, t)}{\partial x} + \frac{D(x)}{k_B T} \frac{\partial A(x, t)}{\partial x} P(x, t) \right] \\ &= -\frac{\partial J(x, t)}{\partial x}, \end{aligned} \quad (8)$$

where we define a free energy  $A(x, t) := E - TS = U(x) - T k_B \ln h(x)$ ; here  $E = U(x)$  is the energy,  $S = k_B \ln h(x)$  the entropy,  $h(x)$  the dimensionless width  $2\omega(x)/L$  in the 2D case and the dimensionless transverse cross section  $\pi[\omega(x)/L]^2$  of the tube in the 3D case.  $J(x, t)$  is the probability current density.  $P(x, t)$  is the probability density for the particle at position  $x$  and time  $t$ . It satisfies the normalization condition  $\int_0^L P(x, t) dx = 1$  and the periodicity condition  $P(x, t) = P(x + L, t)$ .

The stationary average velocity  $\langle v \rangle$  can be defined by the relation

$$\langle v \rangle = \langle \dot{x} \rangle = \lim_{t \rightarrow \infty} \frac{\langle x(t) \rangle}{t}, \quad (9)$$

and the dispersion of the position can be characterized by the effective diffusion coefficient defined as

$$D_{\text{eff}} = \lim_{t \rightarrow \infty} \frac{\langle x^2(t) \rangle - \langle x(t) \rangle^2}{2t}, \quad (10)$$

where  $\langle \dots \rangle$  is the average over all realizations of the thermal noise and initial condition.

Based on equation (8), we can obtain the stationary average velocity  $\langle v \rangle$  and the effective diffusion coefficient  $D_{\text{eff}}$  by following the method in [6, 7, 25] (see [6, 7] and references therein):

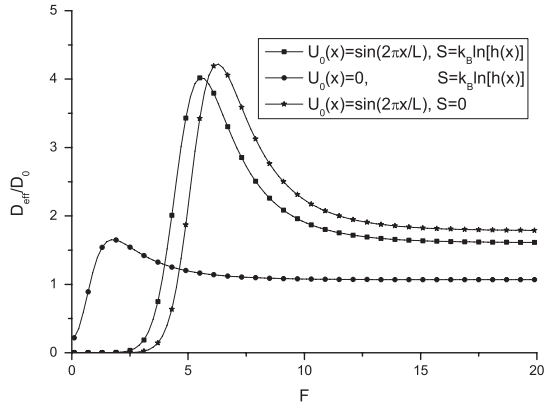
$$\langle v \rangle = LJ = \frac{L(1 - e^{-FL/k_B T})}{\int_0^L dx I(x)}, \quad (11)$$

$$D_{\text{eff}} = \frac{L^2 \int_0^L dx \int_{x-L}^x dz \frac{D(z)}{D(x)} \frac{e^{A(x)/k_B T}}{e^{A(z)/k_B T}} [I(z)]^2}{[\int_0^L dx I(x)]^3}, \quad (12)$$

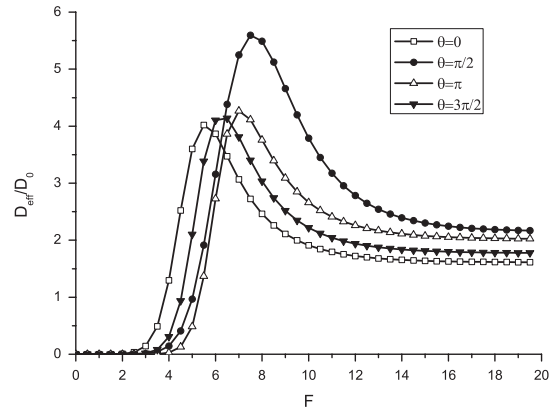
where

$$I(x) = \frac{e^{A(x)/k_B T}}{D(x)} \int_{x-L}^x dy e^{-A(y)/k_B T}. \quad (13)$$

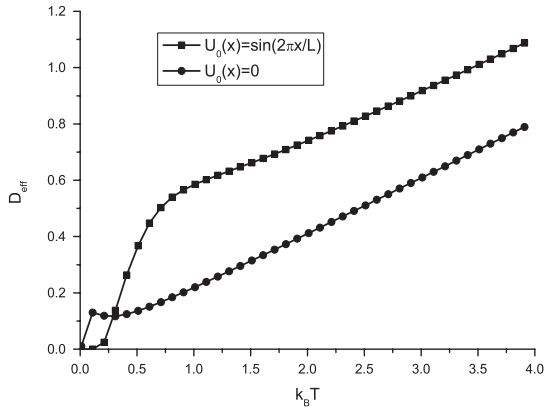
Another interesting quantity is the efficiency of the diffusive transport which depends on both the average velocity and diffusion coefficient. Therefore, here we introduce this



**Figure 2.** Dependence of the ratio  $D_{\text{eff}}/D_0$  on the external driving force  $F$  at  $D_0 = k_B T = 0.1$ ,  $a = 1/2\pi$ ,  $b = 1.02/2\pi$  and  $L = 2\pi$  for three cases: (a) potentials and entropic barriers, (b) only potentials and (c) only entropic barriers.



**Figure 4.** The ratio of  $D_{\text{eff}}$  and  $D_0$  versus external force  $F$  for different phase difference at  $D_0 = 0.1$ ,  $a = 1/2\pi$ ,  $b = 1.02/2\pi$  and  $L = 2\pi$ .



**Figure 3.** The effective diffusion coefficient versus  $D_0$  at  $F = 1.0$ ,  $a = 1/2\pi$ ,  $b = 1.02/2\pi$  and  $L = 2\pi$  for two cases: only entropic barriers and only energy barriers.

quantity—the Peclet number—to measure the efficiency of the diffusive transport and defined it as [9, 10, 26]

$$Pe = \frac{\langle v \rangle L}{D_{\text{eff}}}. \quad (14)$$

The Peclet number can either be enhanced by an increase of net current (i.e. the stationary mean velocity) and/or by a decrease of the effective diffusive diffusion, resulting in a maximal value.

### 3. Results and discussion

For simplicity, we take  $k_B = 1.0$ ,  $\eta = 1.0$  through this paper and the channel wall is assumed to have a sinusoidal profile.

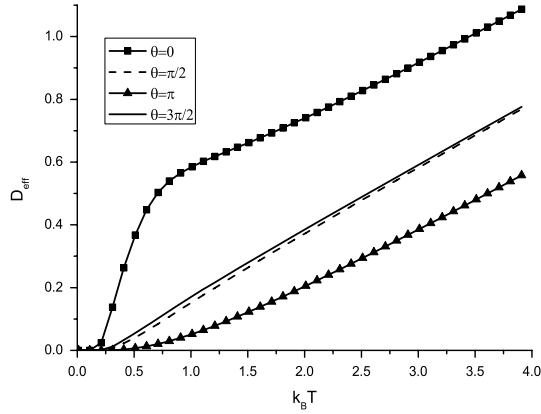
In figure 2 we plot the ratio  $D_{\text{eff}}/D_0$  as a function of external force  $F$  for three cases: (a) energy barriers with entropic barriers, (b) only potentials and (c) only entropic barriers. It can be seen from the figure that the effective diffusion coefficient exhibits a maximum as a function of  $F$  for three cases. When  $F \rightarrow \infty$  the free energy  $A(x)$  barriers vanish. Then the diffusion becomes free ( $D_{\text{eff}}/D_0 \rightarrow$

1). For the case with only entropic barriers, when  $F$  is small, the entropic barrier is slightly smaller compared to the temperature. So, it can immediately and dramatically increase with  $F$ . However, for the case with energy barriers, the effective diffusion coefficient will go to zero for small values of  $F$ .

Figure 3 shows the effective diffusion coefficient as a function of temperature for two cases: only entropic barriers and only energy barriers. For the case with only energy barriers, the diffusion increases with temperature monotonically. At low temperature, the particles cannot pass the barriers and the diffusion coefficient goes to zero. The effective diffusion coefficient versus temperature for the case with entropic barriers is different from that with energy barriers. Temperature dictates not only the thermal noise intensity but also the height of the entropic barriers. The competition between these two factors will induce a peak and valley in the  $D_{\text{eff}}-T$  profile. Therefore, there exists a region of temperature in which the diffusion coefficient decreases as the temperature increases.

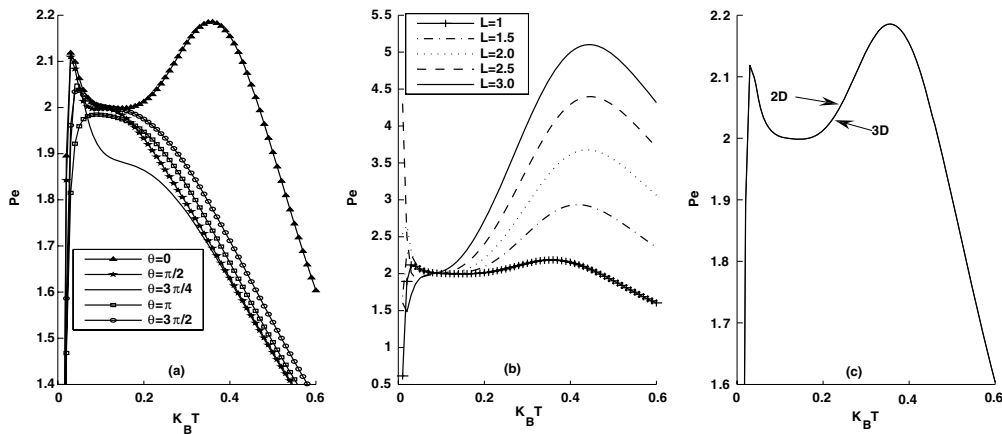
Figure 4 shows  $D_{\text{eff}}/D_0$  as a function of the constant force  $F$  for different phase differences at  $D_0 = 1.0$ . From the figure we can see that there exists a value of  $F$  at which  $D_{\text{eff}}/D_0$  takes its maximum value. The height and position of the peak is strongly influenced by the phase difference. Therefore, one can control the diffusion by changing the phase difference.

In figure 5, the dependence of  $D_{\text{eff}}$  on the temperature  $T$  is illustrated for different phase differences  $\theta = 0, \pi/2, \pi, 3\pi/2$  at  $F = 1.0$ . The effective diffusion coefficient increases monotonically with temperature as expected. When the temperature is very low compared to the height of the free energy barriers, Brownian particles are trapped in the wells. So, there is no diffusion until the temperature is high enough to make the Brownian particles escape from the wells. For  $\theta = 0$ , the curve increases dramatically with temperature, whereas, for  $\theta = \pi$ ,  $D_{\text{eff}}$  increases slowly with temperature compared to the case  $\theta = 0$ . Remarkably, even at low temperature  $D_{\text{eff}}$  increases linearly with temperature for  $\theta = \pi/2$  and  $3\pi/2$  which denotes the free diffusion. In the two cases the entropic barriers and energy barriers will cancel each other.



**Figure 5.** The effective diffusion coefficient versus temperature for different phase differences at  $F = 1.0$ ,  $a = 1/2\pi$ ,  $b = 1.02/2\pi$  and  $L = 2\pi$ .

The curves of Peclet number versus temperature for different phase differences are depicted in figure 6(a) at  $F = 1.0$ . The Peclet number is extremely sensitive to noise intensity and phase difference. For the case  $\theta = 0$ , the Peclet number versus temperature has two maxima. The appearance of the two peaks is due to the appearance of double-barrier behavior in the free energy. The first peak is very sharp and sensitive to the temperature. But the second one is more broad and slightly higher than the first one. The other curves possess a single peak. This phenomenon is largely caused by the shape of free energy which is influenced by temperature and phase difference. In figure 6(b), the influence of a change of  $L$  on the results for  $\theta = 0$  and  $F = 1.0$  is shown. The increase of  $L$  leads to an enhancement in the second peak and a suppression or an enhancement in the first peak. The reason for this phenomenon is that the long periodicity of the tube can make the tube more straight and facilitate a particle moving forward along the tube. The dependence of  $Pe$  on the temperature for 2D and 3D at  $\theta = 0$ ,  $F = 1.0$  is depicted in figure 6(c). The results of the 2D case are the same as that of the 3D case. So, the influence of dimension on the results can be neglected.



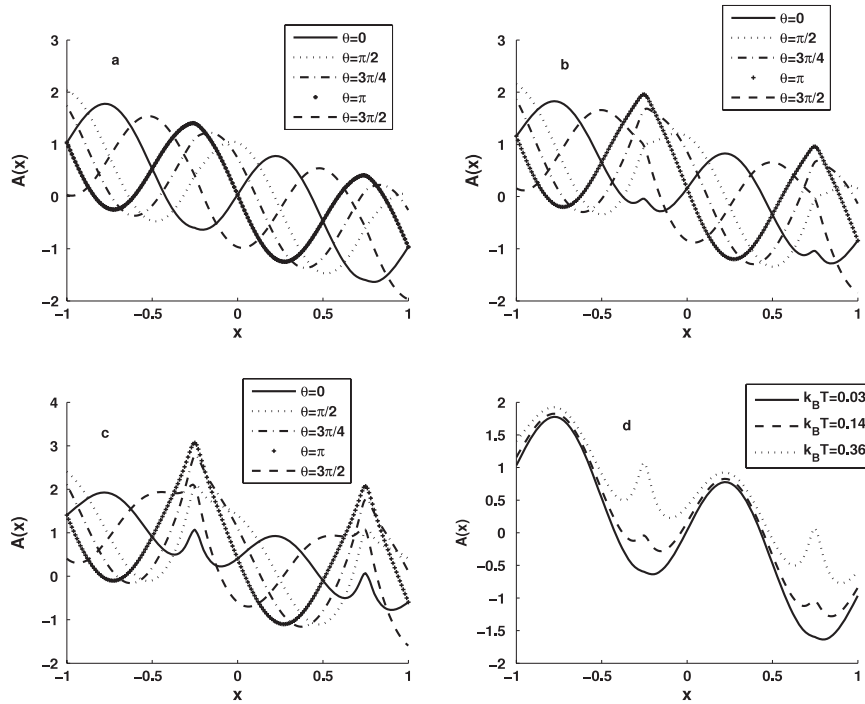
**Figure 6.** The Peclet number as a function of temperature at  $F = 1.0$ ,  $a = 1/2\pi$  and  $b = 1.02/2\pi$ . (a) For different phase differences; (b) for different spatial periodicity  $L$  at the phase difference  $\theta = 0$ ; (c) for 2D and 3D at phase difference  $\theta = 0$ .

In order to illustrate the change from double peaks to a single peak in the Peclet number versus temperature (see figure 6), the free energy potentials  $A(x)$  along the  $x$  coordinate are plotted in figure 7 for different phase differences at  $k_B T = 0.03$  (the first peak position),  $k_B T = 0.14$  (the minima position) and  $k_B T = 0.36$  (the second peak position). For the case  $\theta = 0$ , the free energy  $A(x)$  exhibits a double-barrier behavior at  $k_B T = 0.36$  and  $0.14$  (see figure 7(d)). However, for the other case, it exhibits single-barrier behavior rather than double-barrier behavior. So, we can conclude that the first peak in the Peclet number versus  $k_B T$  is induced by the main barriers. To obtain the second peak in the Peclet number, the additional potential barrier must be high enough ( $k_B T = 0.36$ ). However, when the additional barrier is not high enough and steep ( $k_B T = 0.14$ ), it may hinder the current and facilitate the effective coefficient, and then reduce the efficiency.

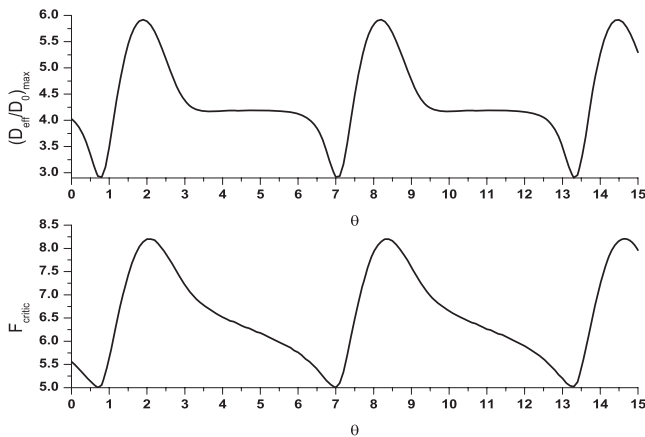
In figure 8 we plot the critical force corresponding to the maximal effective diffusion coefficient and the height of the peak as a function of  $\theta$  at  $D_0 = 0.1$ . The peak height and position are very sensitive to the phase difference. The critical force can be shifted from 5 to 8.2. The peak height can be shifted from 2.8 to 5.8. We can see that the phase difference corresponding to the maximal (minimal) effective diffusion coefficient is the same as the phase difference at which the critical force is maximum (minimum). Another feature is that a region of  $\theta$  exists where the critical force decreases, while the peak height remains steady.

#### 4. Conclusions

In this paper we have investigated the diffusion in a tilted periodic potential with entropic barriers. Its striking features radically differ from those occurring in the cases only with energy barriers or entropic barriers. The interplay between the energy barriers and entropic barriers makes the phenomena richer. In the presence of entropic potentials together with energy potentials, the effective diffusion coefficient as a function of the external force has maxima like those in the case with only entropic barriers or energy barriers. The



**Figure 7.** The free energy  $A(x)$  along the  $x$  coordinate for different phase differences  $\theta = 0, \pi/2, 3\pi/4, \pi$  and  $3\pi/2$  at  $a = 1/2\pi$ ,  $b = 1.02/2\pi$  and  $L = 2\pi$ : (a)  $k_B T = 0.03$ ; (b)  $k_B T = 0.14$ ; (c)  $k_B T = 0.36$ ; (d) the free energy  $A(x)$  along the  $x$  coordinate for different temperatures  $k_B T = 0.03$ ,  $k_B T = 0.14$  and  $k_B T = 0.36$  at the phase difference  $\theta = 0$ .



**Figure 8.** The maximum ratio  $D_{\text{eff}}/D_0$  and critical external force  $F_{\text{critic}}$  versus the phase difference  $\theta$  for  $D_0 = 0.1$ ,  $a = 1/2\pi$ ,  $b = 1.02/2\pi$  and  $L = 2\pi$ .

additional external potentials can largely enhance the effective diffusion coefficient compared to the case only with entropic barriers, though the effective diffusion coefficient is slightly lower than that in the case with only energy potentials (see figure 2). In the case with the energy and entropic potentials, the effective diffusion coefficient increases monotonically with temperature as expected. The effective diffusion coefficient and Peclet number are very sensitive to the shape of free energy and temperature. The peak value of the effective diffusion coefficient and its position (critical force) are sensitive to the phase difference  $\theta$  which influences the shape of  $A(x)$ . The  $D_{\text{eff}}$  may be higher than that in the case with only energy

potentials with a properly chosen  $\theta$ . Another important feature we found is that two temperature values exist at which the Peclet number takes its maximum. The change of phase difference makes the free energy  $A(x)$  deformation. Its shape can be shifted from double-peak behavior to single-peak behavior. Clearly, the model is too simple to provide a realistic description of real systems: however, the results we have presented may have applications in many processes, such as diffusion of ions and macromolecular solutes through the channels in biological membranes [1], transport in zeolites [2] and nanostructures of complex geometry [3], controlled drug release [4] and diffusion in man-made periodic porous materials [5].

## Acknowledgments

The work was supported by the National Natural Science Foundation of China under grant no. 30600122 and the Guangdong Provincial Natural Science Foundation under grant no. 06025073.

## References

- [1] Hille B 2001 *Ion Channels in Excitable Membranes* (Sunderland, MA: Sinauer Associates)
- [2] Kärger J and Ruthven D M 1992 *Diffusion in Zeolites and other Microporous Solids* (New York: Wiley)
- [3] Sheppard N F, Mears D J and Straks S W 1996 *J. Control. Release* **42** 15
- [4] Santini J T, Cima M J and Langer R 1999 *Nature* **397** 335  
Siegel R A 2000 *J. Control. Release* **69** 109
- [5] Matthias S and Müller F 2003 *Nature* **424** 53

- [6] Reimann P, Van den Broeck C, Linke H, Hänggi P, Rubi J M and Pérez-Madrid A 2001 *Phys. Rev. Lett.* **87** 010602
- [7] Reimann P, Van den Broeck C, Linke H, Hänggi P, Rubi J M and Pérez-Madrid A 2002 *Phys. Rev. E* **65** 031104
- [8] Dan D and Jayannavar A M 2002 *Phys. Rev. E* **66** 041106
- [9] Heinsalu E, Tammelo R and Örd T 2004 *Phys. Rev. E* **69** 021111
- [10] Heinsalu E, Örd T and Tammelo R 2004 *Phys. Rev. E* **70** 041104
- [11] Heinsalu E, Patriarca M and Marchesoni F 2008 *Phys. Rev. E* **77** 021129
- [12] Reguera D, Schmid G, Burada P S, Rubi J M, Reimann P and Hänggi P 2006 *Phys. Rev. Lett.* **96** 130603
- [13] Burada P S, Schmid G, Talkner P, Hänggi P, Reguera D and Rubi J M 2008 *BioSystem* **93** 16
- [14] Burada P S, Schmid G, Reguera D, Rubi J M and Hänggi P 2007 *Phys. Rev. E* **75** 051111
- [15] Schüring A, Auerbach S M, Fritzsche S and Haberlandt R 2002 *J. Chem. Phys.* **116** 10890
- [16] Dubbeldam D, Beerdsen E, Vlugt T J H and Smit B 2005 *J. Chem. Phys.* **122** 224712
- [17] Bhide S Y and Yashonath S 2003 *J. Am. Chem. Soc.* **125** 7425
- [18] Zwanzig R 1992 *J. Phys. Chem.* **96** 3926
- [19] Reguera D and Rubi J M 2001 *Phys. Rev. E* **64** 061106
- [20] Kalinay P and Percus J K 2005 *Phys. Rev. E* **72** 061203  
Kalinay P and Percus J K 2005 *J. Chem. Phys.* **122** 204701  
Kalinay P and Percus J K 2006 *Phys. Rev. E* **74** 041203
- [21] Berezhkovskii A M, Pustovoi M A and Bezrukov S M 2007 *J. Chem. Phys.* **126** 134706
- [22] Ai B Q and Liu L G 2006 *Phys. Rev. E* **74** 051114  
Ai B Q 2009 *Phys. Rev. E* **80** 011113
- [23] Ai B Q and Liu L G 2007 *J. Chem. Phys.* **126** 024706
- [24] Ai B Q and Liu L G 2008 *J. Chem. Phys.* **128** 024706
- [25] Hänggi P, Talkner P and Borkovec M 1990 *Rev. Mod. Phys.* **62** 251
- [26] Lindner B, Kostur M and Schimansky-Geier L 2001 *Fluct. Noise Lett.* **1** R25