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Alexander M. Berezhkovskii ; Leonardo Dagdug

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Alexander M. Berezhkovskii[1] and Leonardo Dagdug[2,a)]

AFFILIATIONS

[1] Mathematical and Statistical Computing Laboratory, Office of Intramural Research, Center for Information Technology, National Institutes of Health, Bethesda, Maryland 20892, USA
[2] Physics Department, Universidad Autonoma Metropolitana-Iztapalapa, 09340 Mexico City, Mexico

[a)] **Author to whom correspondence should be addressed:** dll@xanum.uam.mx

ABSTRACT

Diffusive transport of particles in a biased periodic potential is characterized by the effective drift velocity and diffusivity, which are functions of the biasing force. We derive a simple exact expression for the effective diffusivity and use it to show that the force dependence of this quantity may be a nonmonotonic function with a maximum [as shown in the work of Reimann *et al.* Phys. Rev. Lett. **87**, 010602 (2001) for periodic sinusoidal potential] or with a minimum, or a monotonic function. The shape of the dependence is determined by the shape of the periodic potential.

Transport of Brownian particles in biased periodic potentials is considered in numerous publications because researchers face this phenomenon in various fields of science and engineering. A classical book by Risken[1] discusses in detail five applications of this phenomenon: pendulum, superionic conductor, Josephson tunneling junction, rotation of dipoles in a constant field, and phase-locked loops. One can learn about other applications, as well as new results in the field from recent papers[2–5] and references therein. This paper focuses on biased diffusion in a one-dimensional periodic potential $V(x)$ of period L, $V(x+L) = V(x)$. Unbiased diffusion in this potential can be described at long times (after many interwell transitions have been made) as effective free diffusion with the diffusivity given by the Lifson-Jackson (LJ) formula,[6]

$$D_{eff}^{LJ} = \frac{D_0 L^2}{\left(\int_{-L/2}^{L/2} e^{-\beta V(x)} dx\right)\left(\int_{-L/2}^{L/2} e^{\beta V(x)} dx\right)}, \tag{1}$$

where D_0 is the particle intrinsic diffusivity, $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant, and T is the absolute temperature. One can find an alternative derivation of this formula in Ref. 7.

In the presence of a biasing force F, the particle acquires an effective drift velocity, $v(F)$, which monotonically increases with the force. $v(F)$ is proportional to F at small and large F, where it is given by $v(F)|_{F\to 0} = \beta D_{eff}^{LJ} F$ (the Einstein relation) and $v(F)|_{F\to\infty} = \beta D_0 F$, since $V(x)$ can be neglected, as $F \to \infty$. In between the two limiting cases, the drift velocity is a nonlinear monotonic function of F. Different exact expressions for $v(F)$ connecting the two limits can be found in Refs. 8–10.

Another characteristic of biased diffusion in a periodic potential is the force-dependent effective diffusivity, $D_{eff}(F)$, which changes from D_{eff}^{LJ} at $F = 0$ to D_0, as $F \to \infty$. In Ref. 9, it is shown that for a periodic sinusoidal potential, $D_{eff}(F)$, in contrast to $v(F)$, is a nonmonotonic function of F. The diffusivity increases with F at low bias, reaches a maximum, and then decreases approaching D_0, as $F \to \infty$, from above. This was obtained using an exact expression for $D_{eff}(F)$ derived in Ref. 9,

$$D_{eff}(F) = \frac{D_0 L^2 \int_0^L I_+^2(x) I_-(x) dx}{\left(\int_0^L I_+(x) dx\right)^3}, \tag{2}$$

where $I_{\pm}(x) = \int_0^L \exp[\beta(\pm V(x) \mp V(x \mp y) - Fy)]dy$. The nonmonotonic force dependence of $D_{eff}(F)$ was found by performing the integrations in Eq. (2) numerically. As shown in Ref. 11, small deviations from a strictly periodic sinusoidal potential (weak disorder) may significantly increase the maximum value $D_{eff}(F)$, making the enhancement of the effective diffusivity over D_0 even more pronounced.

The question naturally arises whether the existence of a maximum in the force dependence of the effective diffusivity is a general universal property of biased diffusion in periodic potentials or it is a specific feature of biased diffusion in a sinusoidal potential. Here, we show that the function $D_{eff}(F)$ not necessarily has a maximum. It may have a minimum where the effective diffusivity is lower than $D_{eff}(0) = D_{eff}^{LJ}$ and then increases. It is also possible that $D_{eff}(F)$ is monotonic in F. In both cases, $D_{eff}(F)$ approaches D_0, as $F\to\infty$, from below and not from above. This is demonstrated using a new exact expression for $D_{eff}(F)$ derived in this paper,

$$D_{eff}(F) = \frac{D_0 L^2}{\left(\int_{-L/2}^{L/2} e^{-\beta U(x)}dx\right)\left(\int_{-L/2}^{L/2} e^{\beta U(x)}dx\right)}\left(\frac{\sinh(\beta FL/2)}{\beta FL/2}\right)^2, \tag{3}$$

where $U(x) = V(x) - Fx$. One can see that $D_{eff}(F)$ in Eq. (3) reduces to D_{eff}^{LJ} in Eq. (1), as $F \to 0$. Therefore, we will refer to the expression in Eq. (3) as a generalized Lifson-Jackson formula. This expression is much simpler than its counterpart in Eq. (2). The simplicity of Eq. (3) allows us to derive analytical expressions for $D_{eff}(F)$ for periodic cusp and square-well potentials. These expressions are used to show that the function $D_{eff}(F)$ has a minimum in the case of a periodic cusp potential and is a monotonic function of F in the case of a periodic square-well potential.

To derive the expression in Eq. (3), we generalize the approach used by Lifson and Jackson[6] to derive their formula [Eq. (1)]. Consider the mean round-trip (RT) time of a particle diffusing between two reflecting boundaries located at points a and b. This mean time, denoted by $\tau_{RT}(a, b)$, is the sum of the mean first-passage times between the two points, $\tau(a \to b)$ and $\tau(b \to a)$,

$$\tau_{RT}(a, b) = \tau(a \to b) + \tau(b \to a). \tag{4}$$

The two mean first-passage times are given by

$$\tau(a \to b) = \frac{1}{D_0}\int_a^b e^{\beta U(y)}dy \int_a^y e^{-\beta U(x)}dx \tag{5}$$

and

$$\tau(b \to a) = \frac{1}{D_0}\int_a^b e^{\beta U(y)}dy \int_y^b e^{-\beta U(x)}dx. \tag{6}$$

Summing up $\tau(a \to b)$ and $\tau(b \to a)$, we arrive at

$$\tau_{RT}(a, b) = \frac{1}{D_0}\left(\int_a^b e^{\beta U(x)}dx\right)\left(\int_a^b e^{-\beta U(x)}dx\right). \tag{7}$$

When points a and b are separated by the distance LN, $b = a + LN$, $N = 1, 2, \ldots$, the integrals entering Eq. (7) are

$$\int_a^b e^{\beta U(x)}dx = \int_a^{a+LN} e^{\beta U(x)}dx = \left(\int_a^{a+L} e^{\beta U(x)}dx\right)\frac{1 - e^{-\beta FLN}}{1 - e^{-\beta FL}} \tag{8}$$

and

$$\int_a^b e^{-\beta U(x)}dx = \int_a^{a+LN} e^{-\beta U(x)}dx = \left(\int_a^{a+L} e^{-\beta U(x)}dx\right)\frac{e^{\beta FLN} - 1}{e^{\beta FL} - 1}. \tag{9}$$

Substitution of the above expressions into Eq. (7) leads to

$$\tau_{RT}(a, a + LN) = \frac{1}{D_0}\left(\int_a^{a+L} e^{\beta U(x)}dx\right)\left(\int_a^{a+L} e^{-\beta U(x)}dx\right) \times \left(\frac{\sinh(\beta FLN/2)}{\sinh(\beta FL/2)}\right)^2. \tag{10}$$

In the absence of the periodic potential, $V(x) = 0$, this mean round-trip time, denoted by $\tau_{RT}^{(0)}(a, a + LN)$, is

$$\tau_{RT}^{(0)}(a, a + LN) = \frac{4}{D_0(\beta F)^2}\sinh^2(\beta FLN/2). \tag{11}$$

The mean round-trip time $\tau_{RT}(a, a + LN)$ in the presence of the periodic potential $V(x)$ can be considered as that at $V(x) = 0$, on condition that the diffusivity D_0 is replaced by the force-dependent effective diffusivity $D_{eff}(F)$. Then, Eq. (11) leads to

$$\tau_{RT}(a, a + LN) = \frac{4}{D_{eff}(F)(\beta F)^2}\sinh^2(\beta FLN/2). \tag{12}$$

Comparison of the two expressions for the mean round-trip time [Eqs. (10) and (12)], in which without loss of generality it is taken that $a = -L/2$, leads to the expression for $D_{eff}(F)$ given in Eq. (3). It is worth noting that although our derivation of $D_{eff}(F)$ does not consider the time dependence of the variance of the particle displacement, it, nevertheless, provides an exact expression for the effective force-dependent diffusivity.

As mentioned earlier, $D_{eff}(F)$ in Eq. (3) reduces to D_{eff}^{LJ}, as $F \to 0$, and to D_0, as $F \to \infty$. The rest of this paper focuses on the transient behavior of $D_{eff}(F)$ between the two limits for periodic sinusoidal, cusp, and square-well potentials. As we will see, depending on the shape of the potential, there are three qualitatively different types of the transient behavior: nonmonotonic with a maximum (sinusoidal potential), nonmonotonic with a minimum (periodic cusp potential), and monotonic (periodic square-well potential).

Sinusoidal potential. Figure 1 illustrates the nonmonotonic force dependence of $D_{eff}(F)$ with a maximum for a periodic sinusoidal potential, $V(x) = V_0 \sin(2\pi x/L)$. The four curves, drawn using Eq. (3), show the ratio $D_{eff}(F)/D_0$ as functions of the dimensionless biasing force, βFL, for four values of the dimensionless amplitude of the sinusoidal potential $\beta V_0 = 2.5$, 5, 7.5, and 10. Symbols are the values of the ratio obtained using Eq. (2). One can see perfect agreement between $D_{eff}(F)$ predicted by the two expressions.

Periodic cusp potential. Next we consider the force dependence of the effective diffusivity in the case of a periodic cusp potential, $V(x) = K|x|$, $-L/2 < x < L/2$, $V(x + L) = V(x)$. In this case, one can obtain an analytical expression for $D_{eff}(F)$. By performing the

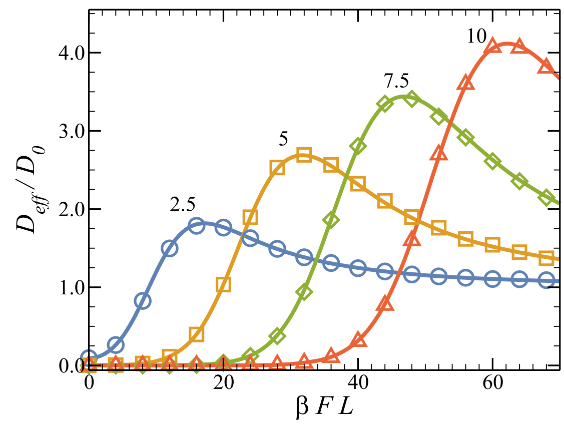

FIG. 1. Force dependences of the ratio $D_{eff}(F)/D_0$ with a maximum for a periodic sinusoidal potential, $V(x) = V_0 \sin(2\pi x/L)$. The numbers near the curves are the values of βV_0, the amplitude V_0 scaled by the thermal energy $k_B T = \beta^{-1}$. The curves are drawn by numerically calculating the integrals in Eq. (3), while the symbols are the values of the ratio obtained numerically using Eq. (2).

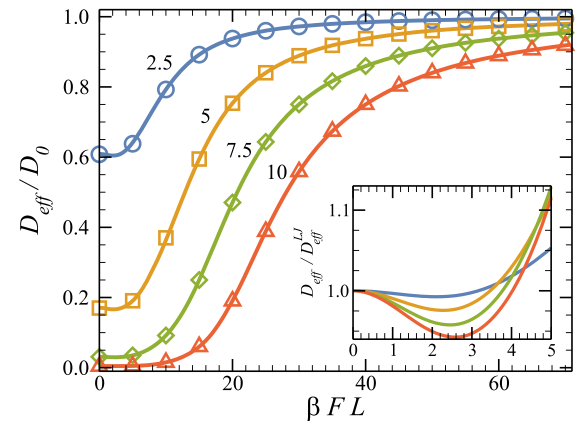

FIG. 2. Force dependences of the ratio $D_{eff}(F)/D_0$ with a minimum for a periodic cusp potential, $V(x) = K|x|$, $-L/2 < x < L/2$, $V(x + L) = V(x)$. The numbers near the curves are the values of βV_b, the barrier heights, $V_b = KL/2$, separating neighboring wells of the potential, scaled by the thermal energy $k_B T = \beta^{-1}$. The inset shows the ratios $D_{eff}(F)/D_{eff}^{LJ}$ illustrating the relative depths of the minima in the force dependence of the effective diffusivity. The curves are drawn by Eq. (3) in which Eq. (13) is used for the product of the integrals, while the symbols are the values of the ratio obtained numerically using Eq. (2).

integration, one can find that the product of the integrals entering Eq. (3) is

$$\frac{1}{L^2}\left(\int_{-L/2}^{L/2} e^{-\beta U(x)}dx\right)\left(\int_{-L/2}^{L/2} e^{\beta U(x)}dx\right) = \frac{W_1(\beta V_b, \beta FL/2) - W_2(\beta V_b, \beta FL/2)}{\left[(\beta V_b)^2 - (\beta FL/2)^2\right]^2}, \tag{13}$$

where $V_b = KL/2$ is the height of the barriers separating neighboring wells of the periodic cusp potential, and functions $W_1(v, z)$ and $W_2(v, z)$, $v = \beta V_b$ and $z = \beta FL/2$, are given by

$$W_1(v,z) = (v \sinh v - z \sinh z)^2 \tag{14a}$$

and

$$W_2(v,z) = v^2(\cosh v - \cosh z)^2. \tag{14b}$$

Substituting the result in Eq. (13) into Eq. (3), one arrives at an analytical expression for the effective diffusivity as a function of the biasing force. This force dependence of the effective diffusivity is illustrated in Fig. 2 for $\beta V_b = 2.5$, 5, 7.5, and 10. One can see that $D_{eff}(F)$ is a nonmonotonic function of F, which first decreases with the biasing force, reaches a minimum, and then increases approaching its asymptotic value D_0, as $F \to \infty$, from below. Symbols, representing the values of the ratio obtained using Eq. (2), are in perfect agreement with the dependences predicted by Eq. (3). The initial decrease in $D_{eff}(F)$ from $D_{eff}(0) = D_{eff}^{LJ} = D_0(\beta V_b/2)^2/\sinh^2(\beta V_b/2)$ is given by

$$D_{eff}(F)\big|_{F\to 0} = D_{eff}^{LJ}\left[1 - \frac{(\beta FL)^2}{24}\left(1 + \frac{12}{(\beta V_b)^2} - \frac{6}{\beta V_b}\coth(\beta V_b/2)\right)\right]. \tag{15}$$

The ratios $D_{eff}(F)/D_{eff}^{LJ}$ shown in the inset of Fig. 2 illustrate the relative depths of the minima.

Periodic square-well potential. Finally, we consider the case of a periodic square-well potential $V(x)$, $V(x) = 0$, for $L/4 < |x| < L/2$, and $V(x) = V_b$, for $0 \le |x| < L/4$, $V(x + L) = V(x)$, where V_b is the height of the barriers separating neighboring wells of the potential. As we will see, in this case, $D_{eff}(F)$ is a monotonic function of the biasing force. Taking the integrals entering Eq. (3), it can be shown that $D_{eff}(F)$ is given by

$$D_{eff}(F) = \frac{4D_0\cosh^2(z)}{(2\cosh z - 1)(2\cosh z + 2\cosh(\beta V_b) - 1) + 1}, \quad z = \frac{1}{4}\beta FL. \tag{16}$$

The monotonic force dependence of $D_{eff}(F)$ given by Eq. (16) is illustrated in Fig. 3 for $\beta V_b = 2.5$, 5, 7.5, and 10. Using asymptotic behavior of $D_{eff}(F)$ in Eq. (16), as $F \to 0$ and $F \to \infty$, one can check that this function approaches its limiting values $D_{eff}(0) = D_{eff}^{LJ} = D_0/\cosh^2(\beta V_b/2)$ and $D_{eff}(\infty) = D_0$ from above and from below, respectively. In between, $D_{eff}(F)$ monotonically increases with F. As before, symbols representing the values of the ratio obtained using Eq. (2) agree perfectly with the dependences predicted by Eq. (16).

Finally, we note that one can generalize the expression for $D_{eff}(F)$ given in Eq. (3) to the case of position-dependent intrinsic diffusivity, where $D_0(x)$ is a periodic function of period L, $D_0(x + L) = D_0(x)$. The way that has been used to derive $D_{eff}(F)$ in Eq. (3) here leads to

$$D_{eff}(F) = \frac{L^2}{\left(\int_{-L/2}^{L/2} e^{-\beta U(x)}dx\right)\left(\int_{-L/2}^{L/2} e^{\beta U(x)}dx/D_0(x)\right)} \times \left(\frac{\sinh(\beta FL/2)}{\beta FL/2}\right)^2. \tag{17}$$

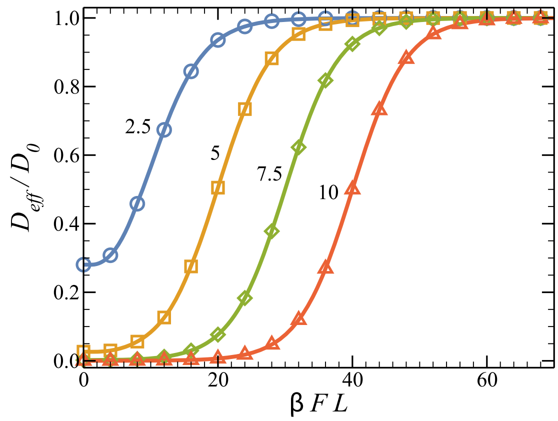

FIG. 3. Monotonic force dependences of the ratio $D_{eff}(F)/D_0$ for a periodic square-well potential, $V(x) = 0$, for $L/4 < |x| < L/2$, and $V(x) = V_b$, for $0 \le |x| < L/4$, $V(x + L) = V(x)$. The numbers near the curves are βV_b, the values of the barrier heights V_b separating neighboring wells of the potential, scaled by the thermal energy $k_B T = \beta^{-1}$. The curves are drawn using Eq. (16), while the symbols are the values of the ratio obtained numerically using Eq. (2).

To summarize, this work focuses on the force dependence of the effective diffusivity, $D_{eff}(F)$, of a particle diffusing in a biased periodic potential. For the first time, we have demonstrated that this dependence does not necessarily have a maximum, as shown in Fig. 1. It turns out that $D_{eff}(F)$ may have a minimum or be a monotonic function of the force, as shown in Figs. 2 and 3, respectively. The shape of the dependence is determined by the shape of the periodic potential. These results were obtained using an exact expression for $D_{eff}(F)$, the generalized Lifson-Jackson formula [Eq. (3)], derived in this work. This expression is much simpler than its counterpart in Eq. (2) that gives $D_{eff}(F)$ as a quadruple integral. As shown in Figs. 1–3, both expressions give the same values of $D_{eff}(F)$. The simplicity of Eq. (3) allowed us to derive explicit analytical expressions for $D_{eff}(F)$ for the periodic cusp and square-well potentials, Eq. (3) with the product of integrals in Eqs. (13) and (16), respectively, which are used to illustrate the two new types of the force dependences of the effective diffusivity shown in Figs. 2 and 3.

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