Thermodynamics of a Brownian particle in a nonconfining potential

Oded Farago
Department of Biomedical Engineering, Ben-Gurion University of the Negev, Be'er Sheva 85105, Israel

(Received 17 December 2020; accepted 11 June 2021; published 6 July 2021)

We consider the overdamped Brownian dynamics of a particle starting inside a square potential well which, upon exiting the well, experiences a flat potential where it is free to diffuse. We calculate the particle's probability distribution function (PDF) at coordinate x and time t, $P(x,t)$, by solving the corresponding Smoluchowski equation. The solution is expressed by a multipole expansion, with each term decaying $t^{1/2}$ faster than the previous one. At asymptotically large times, the PDF *outside* the well converges to the Gaussian PDF of a free Brownian particle. The average energy, which is proportional to the probability of finding the particle *inside* the well, diminishes as $E \sim 1/t^{1/2}$. Interestingly, we find that the free energy of the particle, F, approaches the free energy of a freely diffusing particle, F_0, as $\delta F = F - F_0 \sim 1/t$, i.e., at a rate faster than E. We provide analytical and computational evidence that this scaling behavior of δF is a general feature of Brownian dynamics in nonconfining potential fields. Furthermore, we argue that δF represents a diminishing entropic component which is localized in the region of the potential, and which diffuses away with the spreading particle without being transferred to the heat bath.

DOI: 10.1103/PhysRevE.104.014105

I. INTRODUCTION

Single-particle Brownian motion constitutes one of the fundamental models in statistical mechanics. It is the simplest example of diffusion, which is one of the most important mechanisms of molecular and energy transport in nature [1]. It is also used as a means to introduce the elusive concept of coupling between a thermodynamic system and a heat bath, which forms the basis for Molecular Dynamics simulations [2]. When the particle is confined to a finite space by an external potential field $U(x)$, its probability distribution function (PDF) relaxes at large times to the Boltzmann's equilibrium distribution: $P(x, t \to \infty) = P_{\rm eq}(x) = \exp[-\beta U(x)]/Z$ [3]. Here, $\beta = 1/k_B T$, where k_B is Boltzmann's constant, T is the temperature which is assumed to be uniform in space, and $Z = \int_{-\infty}^{\infty} \exp[-\beta U(x)]dx$ is the normalizing partition function. Brownian dynamics in confined (closed) molecular systems are perceived as stochastic trajectories in the configurational phase space [4]. For a single Brownian particle it is expected, by virtue of the ergodicity hypothesis, that the time average of an observable over a sufficiently long stochastic trajectory coincides with the ensemble average over the equilibrium PDF, $P_{\rm eq}(x)$ [5].

A very different scenario arises when the particle diffuses in a spatially unbounded system. Consider, for instance, an overdamped Brownian particle moving in a potential field which has the form

$$U(x) = \begin{cases} U(x) & \text{for } |x| < x_0, \\ 0 & \text{for } |x| \geqslant x_0, \end{cases} \tag{1}$$

or, more generally, a potential field that decays faster than $1/x$. The PDF of the particle, $P(x,t)$, solves the Smoluchowski equation [6]

$$\frac{\partial P(x,t)}{\partial t} = D\frac{\partial}{\partial x}\left\{e^{-\beta U(x)}\frac{\partial}{\partial x}[e^{\beta U(x)}P(x,t)]\right\}, \tag{2}$$

where D is the diffusion coefficient of the medium. In a nonconfining potential field of the form of Eq. (1), the partition function Z is divergent. The PDF does not relax to the Boltzmann equilibrium distribution but rather continues to spread indefinitely. Is it still possible to define a statistical-mechanical framework for such a class of nonequilibrium processes? This question has been recently addressed by Aghion *et al.* who argued that the long-time asymptotic form of the PDF is given by [7,8]

$$P(x,t) \simeq \frac{e^{-\beta U(x)}}{\sqrt{4\pi Dt}}e^{-x^2/4Dt} = e^{-\beta U(x)}G(x,t), \tag{3}$$

where $G(x,t) = \exp(-x^2/4Dt)/\sqrt{4\pi Dt}$ is the "fundamental" Gaussian solution, i.e., the PDF of a particle diffusing in a flat potential (free diffusion), subject to the Dirac delta-function initial condition, $P(x, t=0) = \delta(x)$. Thus, for $x \ll \sqrt{Dt}$, we have $P(x,t) \simeq \exp[-\beta U(x)]/\sqrt{4\pi Dt}$, which has a similar form to the Boltzmann equilibrium PDF, but with a time-dependent partition coefficient

$$Z^* = \sqrt{4\pi Dt}. \tag{4}$$

Writing that $\lim_{t\to\infty} Z^* P(x,t) = \exp[-\beta U(x)]$, means that the Boltzmann factor is reached at sufficiently long times and plays the role of an infinite invariant density [7–15]. This paves the way to formulating a nonequilibrium statistical framework which is based on concepts from the infinite ergodic theory relating ensemble and time averages of non-normalizable densities.

From Eq. (3) it follows that for $|x| \geqslant x_0$ [outside the nonconfining potential (1)] at large times, $P(x,t) \simeq G(x,t)$ [16]. That the PDF, $P(x,t)$, converges to the form of the fundamental Gaussian PDF, $G(x,t)$, means that, in a sense, the latter plays here a role reminiscent of the equilibrium Boltzmann distribution in a closed system (see Ref. [17]). It is, therefore, interesting to check how different thermodynamic quantities approach the values of their counterparts in the free diffusion $[U(x)=0]$ case. The energy and entropy of a freely diffusing particle are given by

$$E_0 = 0, \tag{5}$$

$$S_0 = -k_B \int_{-\infty}^{\infty} G(x,t)\ln[G(x,t)]dx = k_B\left[\ln(Z^*) + \frac{1}{2}\right]. \tag{6}$$

From Eqs. (1) and (3) it is easy to see that for $U(x) \neq 0$, the excess energy of the particle, $\delta E = E - E_0 \simeq \int_{-\infty}^{\infty} U(x)\exp[-\beta U(x)]dx/Z^*$, converges to zero with time as $\sim 1/t^{1/2}$. Similarly, one can check that the excess entropy, $\delta S = S - S_0 = -k_B\int_{-\infty}^{\infty} P(x,t)\ln[P(x,t)]dx - S_0$, also scales $\sim 1/t^{1/2}$.

With that said, it is important to understand that the PDF (3) is *not* a solution of Eq. (2), but rather the asymptotic form of the solution at large times. Equation (3) is, in fact, the first (leading) in a series of terms, each of which decays at large times $t^{1/2}$ faster than the previous one. In Ref. [8], the first correction term to Eq. (3) was calculated using an eigenfunction expansion. Here, we focus on a specific example of a square potential well, $U(x) = -U$ in Eq. (1). For this example, we calculate the first two correction terms to Eq. (3), which are sufficient for characterizing the asymptotic thermodynamic behavior of the system. This is done by using the method of images, taking advantage of the fact that for the derivation of the first two correction terms in the solution series expansion (in powers of $1/t^{1/2}$), only two images are needed. We find that while the excess energy and entropy with respect to free diffusion diminishes $\sim 1/t^{1/2}$ (see above), the excess Helmholtz free energy decays faster: $\delta F = \delta E - T\delta S \sim 1/t$. The square-well example is studied in Sec. II. In Sec. III we generalize the discussion to an arbitrary nonconfining potential field and find that $\delta F/k_BT = A^2/2Dt$, where A is a constant with dimensionality of length that can be related the second virial coefficient of the potential. This result constitutes a thermodynamic relation for the overdamped evolution of Brownian particles in nonconfining potentials. It is discussed in Sec. IV, where we argue that δF represents a diminishing component of the entropy which is localized in the region of the potential, and which is lost when the particle diffuses away from the potential well.

II. THE CASE OF A SQUARE POTENTIAL WELL

A. The spatial distribution

For a square potential well $U(x) = -U$, the solutions both inside ($|x| < x_0$), $P_<(x,t)$, and outside ($|x| > x_0$), $P_>(x,t)$, the well satisfy the the free diffusion equation $\partial_t P = D\partial_{xx}P$. They must be matched by two boundary conditions (BCs) at x_0. The first one is, obviously, the continuity of the flux

$$\partial_x P_<(x_0,t) = \partial_x P_>(x_0,t). \tag{7}$$

The second BC, which is known as the "imperfect contact" condition [18], reads

$$e^{-\beta U}P_<(x_0,t) = P_>(x_0,t). \tag{8}$$

This condition is widely used in many theoretical studies of mass and heat diffusion problems across sharp interfaces [19–21] (see a brief explanation and derivation in Ref. [22]). The coefficient

$$\sigma = e^{-\beta U} \tag{9}$$

is called the partition coefficient of the interface.

The problem of diffusion from a square well can be solved using the method of images. An "image" particle of size q located at $x = a$ generates a Gaussian distribution

$$P_{\rm image}(x,t) = qG(x-a,t) = q\frac{e^{-(x-a)^2/4Dt}}{\sqrt{4\pi Dt}} = q\frac{e^{-x^2/4Dt}}{\sqrt{4\pi Dt}}\left[1 + \frac{xa}{2Dt} + \frac{a^2}{4Dt}\left(\frac{x^2}{2Dt} - 1\right) + \cdots\right]. \tag{10}$$

We note that $P_{\rm image}$ is *not* normalized to unity $[\int_{-\infty}^{\infty} P_{\rm image}(x,t)dx = q]$. We also note that, up to a multiplicative constant, the nth term ($n = 0, 1, 2, \ldots$) in this expansion of $G(x-a,t)$ has the form

$$P_n(x,t) = G(x,t)\left(\frac{a}{\sqrt{2Dt}}\right)^n H_n\left(\frac{x}{\sqrt{2Dt}}\right), \tag{11}$$

where H_n is the nth probabilists' Hermite polynomial $[H_0(y) = 1;\ H_1(y) = y;\ H_2(y) = y^2 - 1;\ H_3(y) = y^3 - 3y;\ \ldots]$. Equation (10) is essentially a multipole expansion. The leading term P_0 is the fundamental solution of a "monopole," namely a Brownian particle starting at the origin. The next term ($n = 1$) describes the PDF of a dipole, i.e., two opposite images located symmetrically with respect to the origin. Then the following terms correspond to a linear quadrupole setting ($n = 2$), octupole ($n = 3$), etc. From the linearity of the free-diffusion equation it follows that each function $P_n(x,t)$ (11) is itself a solution of this equation. Therefore, a linear combination of $P_n(x,t)$,

$$P(x,t) = G(x,t)\sum_{n=0}^{\infty}\left(\frac{c_n}{\sqrt{2Dt}}\right)^n H_n\left(\frac{x}{\sqrt{2Dt}}\right), \tag{12}$$

where c_n are constants with dimensionality of length, is also a solution of the free-diffusion equation [23].

With the above in mind, we return to the escape problem from the square well, subject to delta-function initial conditions $P(x,0) = \delta(x)$. We note the following: (i) Because of the symmetry of the problem with respect to reflection around the origin, we must have that $P(x,t) = P(-x,t)$, which means that we only need to solve the PDF for $x > 0$. Symmetry also implies that the PDF inside the well, $P_<(x,t)$, is an even function and, thus, when expressed as in Eq. (12), it contains only the even terms. This ensures that the probability flux at the origin vanishes $[\partial_x P_<(0,t) = 0]$. (ii) As we will see

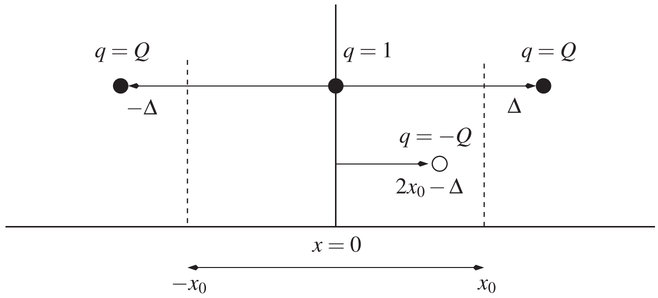

FIG. 1. A schematic explaining the solution by the method of images. The diffusing particle is represented by the solid circle at the origin and has a size $q = 1$. In order to derive the PDF inside the well ($x < x_0$), we place two images of size $q = Q$ at $x = \pm\Delta$, where $\Delta > x_0$. These images are also represented by solid circles. For the calculation of the PDF in the region to the right of the well ($x > x_0$), we replace the image at $x = \Delta$ with an opposite image of size $-Q$ which is placed at $2x_0 - \Delta$ (depicted with an open circle).

later in Sec. III, the asymptotic thermodynamic behavior is captured by the terms up to order $1/t^{3/2}$, which means that we only need to calculate the first three moments in Eq. (12) or, equivalently, express the PDF as the sum of the PDFs of three particles. These are located as shown in Fig. 1. The central particle of size $q = 1$, which is located at the origin, represents the diffusing Brownian particle. Since $P_<(x,t)$ has no dipole term, we place two image particles of size $q = Q$ at $\pm\Delta$. We require that $\Delta > x_0$, i.e., put these images outside the potential well in order to guarantee that the delta-function initial condition is satisfied (even though we are interested in the behavior at asymptotically large times). For $P_>(x,t)$, we keep the particles at $x = 0$ and $x = -\Delta$, and replace the image at $\Delta > x_0$ with an opposite image of size $-Q$ located symmetrically with respect to the boundary at x_0, i.e., at $x = x_0 - (\Delta - x_0) = 2x_0 - \Delta$ (depicted with an open circle in Fig. 1). With this replacement we accomplish two things: First, the fact $P_>(x,t)$ is represented as the sum of the PDFs of three particles, none of which is located at $x > x_0$, ensures that the delta-function initial boundary condition is satisfied. Second, the exchange of the image Q with an opposite image $-Q$ locate symmetrically with respect to the boundary ensures that the flux is continuous at $x = x_0$, which means that BC (7) is satisfied.

The values of Q and Δ can be now found by writing both $P_<(x,t)$ and $P_>(x,t)$ in the form of Eq. (12), and imposing BC (8) [with the partition coefficient σ defined in Eq. (9)] to order $1/t^{3/2}$. Comparing the terms proportional to $1/t^{1/2}$ yields $Q = (1-\sigma)/(2\sigma)$, and from the terms proportional to $1/t^{3/2}$ we find that $\Delta = 2x_0/\sigma$. Since we demand that $\Delta > x_0$, we must restrict the discussion in what follows to $0 < \sigma < 2$. Notice that for $\sigma > 1$, we consider a potential step rather than a potential well. With the above values of Q and Δ, the PDFs are given by

$$P_<(x,t) = G(x,t)\left[\frac{1}{\sigma} - \left(\frac{1-\sigma}{\sigma^3}\right)\frac{x_0^2}{Dt} + O\left(\frac{1}{t^2}\right)\right], \tag{13}$$

$$P_>(x,t) = G(x,t)\left[1 - \frac{1-\sigma}{\sigma}\frac{xx_0}{2Dt} + \frac{(1-\sigma)(2-\sigma)}{\sigma^2}\frac{x_0^2}{2Dt}\left(\frac{x^2}{2Dt} - 1\right) + O\left(\frac{1}{t^{3/2}}\right)\right]. \tag{14}$$

The scaling behavior of x with t is $x \sim x_0 \sim t^0$ in $P_<$, and $x \sim \sqrt{Dt} \sim t^{1/2}$ in $P_>$. Also, recall that $G(x,t) \sim 1/t^{1/2}$. Thus, in Eq. (14) the terms scale as $1/t^{1/2}, 1/t, 1/t^{3/2} \ldots$, while in Eq. (13) the terms with scaling $\sim 1/t^n$, where n is an integer, are missing because $P_<$ is even. If we keep only the leading terms in Eqs. (13) and (14), we get

$$P_<(x,t) \simeq \frac{G(x,t)}{\sigma}, \tag{15}$$

$$P_>(x,t) \simeq G(x,t), \tag{16}$$

which is the asymptotic solution Eq. (3).

Omitting in Eqs. (13) and (14) the terms $\sim 1/t^{3/2}$, whose contributions at large times to the PDF are extremely small and fall below the resolution of the computer simulations, we write

$$P_<(x,t) \simeq \frac{G(x,t)}{\sigma}, \tag{17}$$

$$P_>(x,t) \simeq G(x,t)\left[1 - \frac{1-\sigma}{\sigma}\frac{xx_0}{2Dt}\right]. \tag{18}$$

Figure 2(a) shows results for $P(x,t)$ based on 10^8 Langevin dynamics trajectories starting at $x = 0$, that were generated with the algorithm presented in Ref. [24]. [See also Ref. [25]: The algorithm is an extension to discontinuous potentials of the Grønbech-Jensen and Farago (GJF) integrator for inertial Langevin dynamics [26]. The friction coefficient in the simulations is set to $\alpha = k_BT/D$.] The system parameters are $D = 0.01$ and $x_0 = 2$. The black curve shows the PDF for $\sigma = 0.9$ at $t = 2500$; the other curves correspond to $t = 10^4$ with $\sigma = 0.9$ (red), $\sigma = 0.8$ (blue), and $\sigma = 1.1$ (green). Noticeably, the last three curves look nearly identical for $x > x_0$, which is consistent with Eq. (18) where the asymptotically leading term in $P_>(x,t)$ is the fundamental Gaussian solution. To better test the accuracy of Eqs. (17) and (18), we plot the function $Q(x,t) \equiv P(x,t)/G(x,t) - 1$ and compare the computational data with the analytical expressions. This is done in Fig. 2(b), showing the computational results at $t = 10^4$ for $\sigma = 0.9$ (black) and $\sigma = 1.1$ (green), along with the corresponding predictions of Eqs. (17) and (18) (dashed red and blue lines, respectively). The agreement is, clearly, excellent.

B. The free energy

In the spirit of the equilibrium canonical ensemble, we define the time-dependent Helmholtz free energy $F(t) = E(t) -$

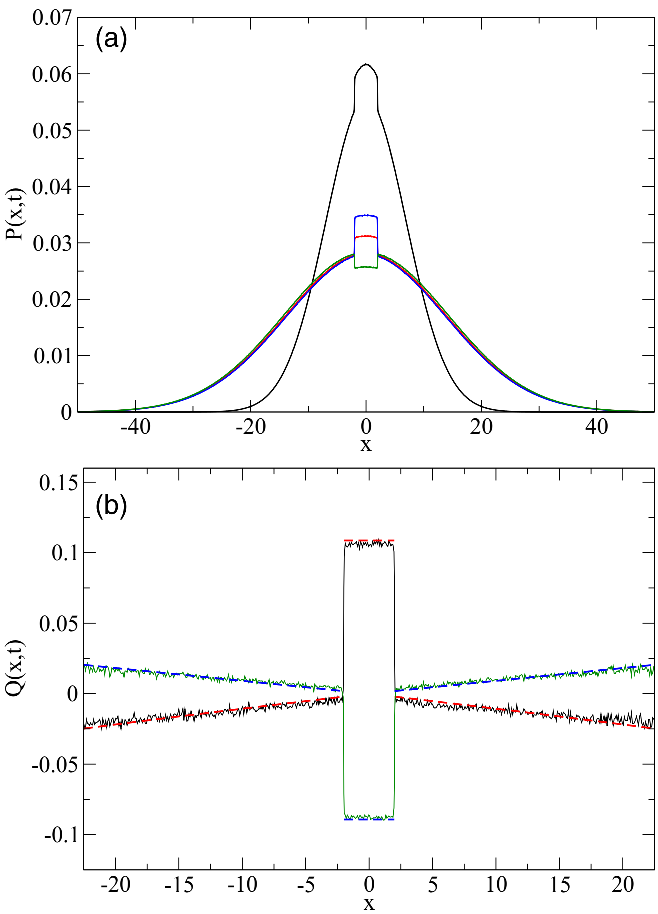

FIG. 2. (a) The PDF of a particle diffusing in a square-well potential of size $2x_0 = 4$ with $D = 0.01$. The black curve presents the results for $\sigma = 0.9$ at $t = 2500$. The other curves correspond to $t = 10^4$ with $\sigma = 0.9$ (red), $\sigma = 0.8$ (blue), and $\sigma = 1.1$ (green). (b) The function $Q(x,t)$ (see definition in the text) for $\sigma = 0.9$ (black) and $\sigma = 1.1$ (green) at $t = 10^4$. Dashed red and blue lines depict the corresponding predictions of Eqs. (17) and (18).

$TS(t)$, where the entropy is given by

$$S(t) = -k_B \int_{-\infty}^{\infty} P(x,t) \ln P(x,t) dx$$
$$= -2k_B \left\{ \int_0^{x_0} P_<(x,t) \ln [P_<(x,t)] dx + \int_{x_0}^{\infty} P_>(x,t) \ln [P_>(x,t)] \right\}, \quad (19)$$

and the energy

$$E(t) = \int_{-\infty}^{\infty} U(x) P(x,t) dx = -2U \int_0^{x_0} P_<(x,t) dx. \quad (20)$$

Inserting expressions (17) and (18) into Eqs. (19) and (20), we arrive after some calculations at

$$-TS(t) = -TS_0(t) + \frac{2Ux_0}{\sigma Z^*} + O(1/t), \quad (21)$$

$$E(t) = E_0 - \frac{2Ux_0}{\sigma Z^*} + O(1/t^{3/2}), \quad (22)$$

where Z^* is the partition coefficient defined in (4), while $E_0 = 0$ and S_0 are the energy and entropy of a freely diffusing particle in a flat potential $U = 0$ [see, respectively, Eqs. (5) and (6)]. From Eqs. (21) and (22) we conclude that, at large times, the excess (with respect to free diffusion) energy and entropy diminishes as $1/Z^* \sim 1/t^{1/2}$, while the excess free energy, $\delta F = (E - E_0) - T(S - S_0)$, diminishes at a faster rate: $\delta F \sim 1/t$. From a dimensional analysis we can rewrite the above result as

$$\frac{\delta F}{k_B T} \simeq \frac{A^2}{2Dt} = \frac{A^2}{\langle x^2 \rangle_{U=0}}, \quad (23)$$

where A is a constant with dimensionality of length, and $\langle x^2 \rangle_{U=0} = 2Dt$ is the mean-square displacement of a free particle. In the following section, we consider single-particle diffusion in a general nonconfining potential field and show that A is comparable to the (finite) range of the potential well. Another way to write Eq. (23) is in the form resembling that of Einstein's relation $k_B T = D/\mu$, where μ is the mobility of the particle. Introducing the time-dependent diffusion coefficient $\tilde{D}(t) = A^2/2t$, we can write

$$\delta F(t) = \frac{\tilde{D}(t)}{\mu}, \quad (24)$$

which constitutes a linear response (Einstein) relation for nonconfining potentials [27].

III. THE GENERAL CASE

For a general nonconfining potential $U(x)$, it has been shown in Ref. [8] [cf. Eq. (48)] that *for large* x *and* t, the PDF is well approximated by

$$P(x,t) = G\left(1 - \frac{l_0|x|}{2Dt} + d_2 \frac{x^2 - 2Dt}{4D^2 t^2} + \cdots\right), \quad (25)$$

where $G = G(x,t)$ for brevity,

$$l_0 = \int_0^{\infty} [e^{-\beta U(x)} - 1] dx \quad (26)$$

is related to the second virial coefficient, and d_2 is a constant with dimensionality of [length]^2. For the square-well example in Sec. II, $l_0 = (1-\sigma)x_0/\sigma$, and so the leading correction (dipole) term in Eq. (14) for $P_>(x,t)$ is simply a special case of the corresponding term in Eq. (25). The constant d_2 in the next correction (quadrupole) term in Eq. (25) depends on the initial distribution of the particle. In the case of a square-well potential with $P(x, t = 0) = \delta(x)$, we have from the comparison of Eqs. (25) and (14) that $d_2 = (1-\sigma)(2-\sigma)x_0^2 = 2l_0^2 + l_0 x_0$. One may thus speculate that for the problem of diffusion in a general symmetric potential $U(x)$ subject to a δ-function initial condition at the origin,

$$d_2 = 2\left\{l_0^2 + \int_0^{\infty} x[e^{-\beta U(x)} - 1] dx\right\}. \quad (27)$$

Equation (27) can be also written as

$$d_2 = 2l_0(l_0 + l_1), \quad (28)$$

where the length l_1 is defined as

$$l_1 = \frac{\int_0^\infty x[e^{-\beta U(x)} - 1]dx}{\int_0^\infty [e^{-\beta U(x)} - 1]dx}. \quad (29)$$

We note the following regarding Eqs. (26)–(29):

(1) The lengths l_0 and l_1 scale as t^0 since the integrands in Eqs. (26) and (29) are nonzero only within the limited range of the potential well.

(2) Depending on $\beta U(x)$, l_0 and l_1 can have either positive or negative values. Generally speaking, l_0 serves as a measure for whether the potential is "effectively" attractive ($l_0 > 0$) or repulsive ($l_0 < 0$).

(3) Writing $U(x) = U(x=0)f(x)$, with $f(x=0) = 1$ and $f(x \to \infty) \to 0$, we see that if $f(x)$ does not change a sign, then l_1 has the same sign as l_0.

(4) Furthermore, if $|\beta U(x=0)| \ll 1$ (weak potential) then, from Eqs. (26) and (29), we readily see that $l_0 \sim |\beta U(x=0)|^1$, but $l_1 \sim |\beta U(x=0)|^0 \gg l_0$. Therefore, in this limit,

$$d_2 \simeq 2l_0 l_1, \quad \text{for } |\beta U(x)| \ll 1. \quad (30)$$

(5) Finally, we note that l_0 and l_1 can be associated with the *quasiprobability distribution*, with statistical weights that are given by $w(x) = \exp[-\beta U(x) - 1]$ and, thus, may also assume negative values. In this statistics, $l_0 = \int_0^\infty w_1(x)dx$ plays the role similar to the partition function, while $l_1 = \langle x \rangle$ is the average displacement.

To check the accuracy of Eq. (25), we consider a different example of a Gaussian potential,

$$U(x) = Ue^{-(x/x_0)^2}. \quad (31)$$

We set $x_0 = 1$, $D = 0.01$, and compute $P(x,t)$ from 10^8 Langevin dynamics trajectories starting at $x = 0$. Figure 3(a) shows the PDF at $t = 10^4$ for $U = -0.2$ (black) and $U = +0.2$ (red). Figure 3(b) shows the function $Q(x,t) = P(x,t)\exp[+\beta U(x)]/G(x,t) - 1$ which, supposedly, is well approximated by the (piecewise) linear form $Q(x,t) \simeq -l_0|x|/2Dt$ since the quadrupole term is negligibly small. For the examples considered in the figure, we have $l_0 = 0.190$ ($U = -0.2$) and $l_0 = -0.165$ ($U = +0.2$). The dashed red and blue lines in Fig. 3(b) depict these linear functions and demonstrate that, indeed, they nicely fit to the function Q.

We now switch to the free-energy calculation, while keeping only those contributions that decay either as $\sim 1/t^{1/2}$ or $\sim 1/t$. Taking Eq. (25) and using it in Eq. (20) yields the following expression for the time-dependent energy:

$$E(t) = 2\int_0^\infty U(x)Ge^{-\beta U(x)}\left[1 - \frac{l_0 x}{2Dt} + \cdots\right]dx. \quad (32)$$

Taking advantage of the fact that contribution to this integral comes from a finite limited region, we can write that in the limit $t \to \infty$, $G \simeq 1/\sqrt{4\pi Dt} = 1/Z^*$. This also allows us to drop the dipole term in the square brackets. Thus [7,8],

$$E(t) = \delta E(t) \simeq 2\int_0^\infty U(x)e^{-\beta U(x)}G\,dx = \frac{2\int_0^\infty U(x)e^{-\beta U(x)}dx}{Z^*} + O\left(\frac{1}{t^{3/2}}\right), \quad (33)$$

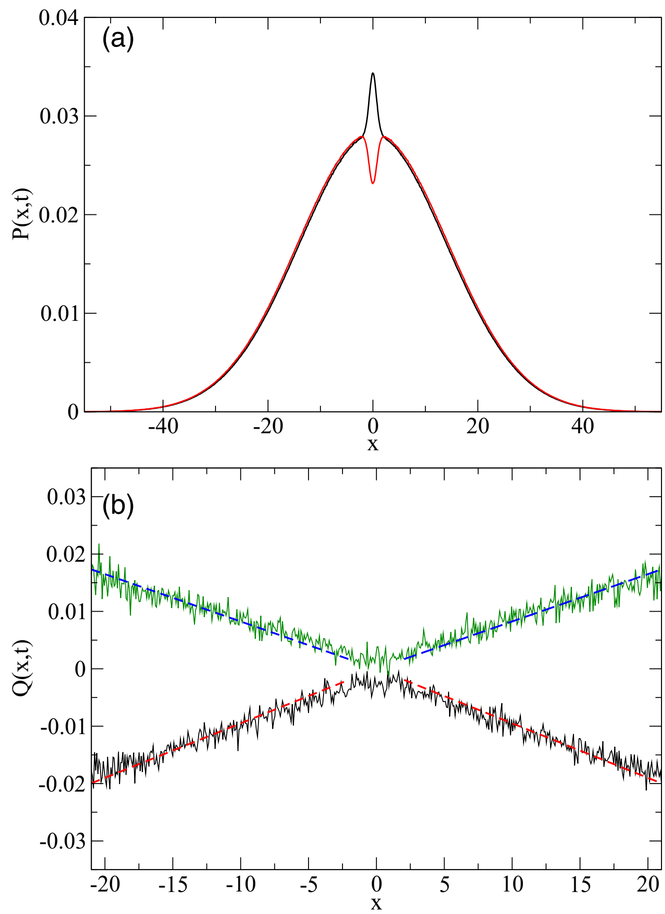

FIG. 3. (a) The PDF of a particle diffusing ($D = 0.01$) in a Gaussian potential (31) of size $x_0 = 1$ with $U = -0.2$ (black) and $U = +0.2$ (red) at $t = 10^4$. (b) The function $Q(x,t)$ (see definition in the text) for $U = -0.2$ (black) and $U = +0.2$ (green) at $t = 10^4$. Dashed red and blue lines depict the corresponding predictions of Eq. (25) with $l_0 = 0.190$ and $l_0 = -0.165$, respectively.

which generalizes Eq. (22) for the energy of a Brownian particle is a square potential. Equation (33), which can also be written as $\lim_{t\to\infty} Z^*E(t) = \int_{-\infty}^{\infty} U(x)\exp[-\beta U(x)]dx$, is yet another demonstration that Z^* plays a role similar to a partition function and that the Boltzmann factor is an infinite invariant density.

For the entropy calculation in the general case, we insert Eq. (25) into Eq. (19), which gives

$$-TS(t) \simeq 2k_BT\int_0^\infty Ge^{-\beta U(x)}\left[1 - \frac{l_0 x}{2Dt} + d_2\frac{x^2 - 2Dt}{4D^2t^2}\right] \times \left[\ln G - \beta U(x) - \frac{l_0 x}{2Dt} - \frac{(l_0 x)^2}{8(Dt)^2} + d_2\frac{x^2 - 2Dt}{4D^2t^2}\right]dx. \quad (34)$$

Note that because we are not interested in the contributions to S diminishing faster than $\sim 1/t$, we can (i) truncate the general solution (25) after the quadrupole correction term, (ii) use the Taylor expansion $\ln[1+\epsilon] \simeq \epsilon - \epsilon^2/2$, and (iii) omit in the integrand any terms featuring products of l_0 and d_2 having dimensionality of (length)^k with $k > 2$. Rearranging Eq. (34), we write

$$-TS(t) \simeq 2k_BT\int_0^\infty \bigg\{G\ln G - \beta U(x)Ge^{-\beta U(x)} + G\ln G[e^{-\beta U(x)}-1] - Ge^{-\beta U(x)}\frac{xl_0}{2Dt}[\ln G - \beta U(x)+1]$$
$$+ Ge^{-\beta U(x)}\frac{(l_0x)^2}{8(Dt)^2} + d_2\, Ge^{-\beta U(x)}\frac{x^2-2Dt}{4D^2t^2}[\ln G - \beta U(x)+1]+\bigg\}dx. \quad (35)$$

There are six terms in Eq. (35), to be henceforth denoted by $-TS_i$ ($i = 1,\dots,6$). The first one is simply

$$-TS_1 = -TS_0, \quad (36)$$

where S_0 is the entropy of the free particle [see Eq. (6)]. The second term is identical to Eq. (33), except for the minus sign; thus,

$$-TS_2 \simeq -E(t) = -2\int_0^\infty U(x)Ge^{-\beta U(x)}dx \simeq -\frac{2\int_0^\infty U(x)e^{-\beta U(x)}dx}{Z^*}. \quad (37)$$

In the third term, we explicitly write that

$$\ln G = -\frac{x^2}{4Dt} - \frac{1}{2}\ln(4\pi Dt), \quad (38)$$

which gives

$$-TS_3 = 2k_BT\int_0^\infty G\bigg[-\frac{x^2}{4Dt} - \frac{1}{2}\ln(4\pi Dt)\bigg][e^{-\beta U(x)}-1]dx. \quad (39)$$

However, the contribution to this integral is limited to a finite range, which means that the first term in (38) can be omitted from (39). Further taking the limit $t\to\infty$ where $G\to 1/Z^*$, we arrive at

$$-TS_3 \simeq -\frac{k_BT\ln(4\pi Dt)}{Z^*}\int_0^\infty [e^{-\beta U(x)}-1]dx = -\frac{k_BTl_0}{Z^*}\ln(4\pi Dt). \quad (40)$$

For the fourth term in Eq. (35), we substitute expression (38) for $\ln G$, which gives

$$-TS_4 = -2k_BT\int_0^\infty Ge^{-\beta U(x)}\frac{xl_0}{2Dt}\bigg\{-\frac{x^2}{4Dt} + \bigg[1-\frac{1}{2}\ln(4\pi Dt)\bigg] - \beta U(x)\bigg\}dx, \quad (41)$$

and which we have separated into three terms to be denoted by $-TS_{4,j}$ ($j = 1, 2, 3$). The third term here,

$$-TS_{4,3} = 2k_BT\int_0^\infty Ge^{-\beta U(x)}\frac{xl_0}{2Dt}\beta U(x)dx \simeq 0, \quad (42)$$

can be neglected because the integral is limited to a finite range. In the first term,

$$-TS_{4,1} = 2k_BT\int_0^\infty Ge^{-\beta U(x)}\frac{xl_0}{2Dt}\frac{x^2}{4Dt}dx, \quad (43)$$

we notice that most of the contribution to the integral comes from the range $x \lesssim \sqrt{Dt}$, which for $t\to\infty$ is much larger than the range of $U(x)$. Therefore, we can set $\exp[-\beta U(x)] \simeq 1$ in the integrand, and have

$$-TS_{4,1} \simeq k_BT\frac{l_0}{4D^2t^2}\int_0^\infty x^3Gdx = \frac{2k_BTl_0}{Z^*}. \quad (44)$$

Similarly, the exchange of $\exp[-\beta U(x)]$ with unity in the second term in Eq. (41) is also allowed, yielding

$$-TS_{4,2} = -2k_BT\int_0^\infty Ge^{-\beta U(x)}\frac{xl_0}{2Dt}\bigg[1-\frac{1}{2}\ln(4\pi Dt)\bigg]dx \simeq -k_BT\frac{l_0}{Dt}\bigg[1-\frac{1}{2}\ln(4\pi Dt)\bigg]\int_0^\infty xGdx$$
$$= -\frac{2k_BTl_0}{Z^*}\bigg[1-\frac{1}{2}\ln(4\pi Dt)\bigg]. \quad (45)$$

Summing Eqs. (42), (44), and (45) gives

$$TS_4 \simeq \frac{k_BTl_0}{Z^*}\ln(4\pi Dt). \quad (46)$$

For the same reasoning as in the above calculation of the fourth entropic term, it is further permissible to replace $\exp[-\beta U(x)]$ with unity in the fifth and the sixth terms in Eq. (35). With this substitution, the fifth term reads

$$-TS_5 \simeq 2k_BT\int_0^\infty G\frac{(l_0x)^2}{8(Dt)^2}dx = k_BT\frac{l_o^2}{4Dt}, \quad (47)$$

and the sixth term is given by

$$-TS_6 \simeq 2k_BT\int_0^\infty d_2\, G\frac{x^2-2Dt}{4D^2t^2}[\ln G-\beta U(x)+1]dx. \tag{48}$$

In Eq. (48) we identify three terms in the square brackets, but the contribution of the second one can be neglected because $U(x)$ has a finite range, and the third one vanishes identically. Thus, we are left with only the first term and, using Eq. (38) for $\ln G$, gives

$$-TS_6 \simeq 2k_BT\int_0^\infty d_2\, G\frac{x^2-2Dt}{4D^2t^2}\left[-\frac{x^2}{4Dt}-\frac{1}{2}\ln(4\pi Dt)\right]dx. \tag{49}$$

The contribution of the second term in square brackets in Eq. (49) vanishes identically, which leaves us with

$$-TS_6 \simeq -2k_BT\int_0^\infty d_2\, G\frac{x^2-2Dt}{4D^2t^2}\left(\frac{x^2}{4Dt}\right) = -d_2\frac{k_BT}{2Dt}. \tag{50}$$

Summing Eqs. (36), (37), (40), (46), (47), and (50) gives

$$-TS(t) = -TS_0(t) - \frac{2\int_0^\infty U(x)e^{-\beta U(x)}dx}{Z^*} - k_BT\frac{2d_2-l_0^2}{4Dt}. \tag{51}$$

From Eqs. (33) and (51), together with Eq. (28), we finally obtain that the excess free energy

$$\delta F = E - T(S-S_0) = -k_BT\frac{3l_0^2+4l_0l_1}{4Dt} + O\left(\frac{1}{t^{3/2}}\right), \tag{52}$$

which generalizes the result of Eq. (23) suggested in Sec. II for the square-well example. In the limit of a weak potential, $l_0 \ll l_1$ [see Eq. (30)], and

$$\delta F = E - T(S-S_0) \simeq -k_BT\frac{l_0l_1}{Dt}. \tag{53}$$

IV. SUMMARY AND DISCUSSION

In this work, we study the problem of a Brownian motion in a nonconfining potential that vanishes at infinity. We start, in Sec. II, by considering a specific example of diffusion in a square-well potential. In this example, the PDFs, both inside and outside the well, satisfy the free-diffusion equation. We use the method of images to arrive at Eqs. (13) and (14), where the PDF is expressed in the form of a multipole expansion with each term decaying $1/t^{1/2}$ faster than the previous one at asymptotically large times. This expansion is generalized in Sec. III to an arbitrary nonconfining (symmetric) potential. The PDF, in the general case, is given by Eq. (25) with the coefficients l_0 and d_2 given by Eqs. (26)–(30).

We use the multipole expansion Eq. (25) to calculate the Helmholtz free energy of the particle. We arrive at Eq. (52) which, to order $\sim 1/t$, is the excess free energy with respect to that of a free particle. To better understand this result, it is more instructive to look at the entropy of the particle, or rather the *rate of entropy production*, which can be expressed as a series expansion

$$\dot{S} = \dot{S}_{\rm leading} + \dot{S}_{\rm 1st} + \dot{S}_{\rm 2nd} + \cdots. \tag{54}$$

To leading order [see Eq. (36)], $S_{\rm leading}(t)$ is equal to the entropy of a freely diffusing particle $S_0(t)$, which is given by Eq. (6). The rate of entropy production to this order is therefore

$$\dot{S}_{\rm leading}(t) = \dot{S}_0(t) = \frac{k_B}{t}. \tag{55}$$

The next-order term in the asymptotic expression for the entropy is given by Eq. (37), which can be also written as $S_{\rm 1st}(t) \simeq E(t)/T$. Then, from Eqs. (4) and (33), we find that

$$\dot{S}_{\rm 1st}(t) \simeq -\frac{1}{2t}\frac{E(t)}{T} \sim \frac{1}{t^{3/2}}. \tag{56}$$

Notice the correction $\sim 1/t^{3/2}$ to the energy expression (33). It generates a third-order correction to the $\dot{S}$ that scales as $1/t^{5/2}$ and, therefore, is irrelevant to the present discussion on the zeroth-, first-, and second-order terms in the expansion Eq. (54). Taking this into account, we note that due to global energy conservation, the amount of heat which is transferred to the thermal bath is given by $Q(t) = E(t=0) - E(t)$. The resulting change in the entropy of the bath is $S_{\rm bath}(t) - S_{\rm bath}(t=0) = Q(t)/T = [E(t=0) - E(t)]/T = E(t=0)/T - S_{\rm 1st}(t)$ (plus a third-order correction which is ignored herein). Thus,

$$\dot{S}_{\rm 1st}(t) + \dot{S}_{\rm bath}(t) = 0. \tag{57}$$

The last result can be interpreted as if the first-order correction describes a reversible process. Of course, the spreading of the particle is *not* a reversible process because $\dot{S}_{\rm leading} > 0$, i.e., the total entropy in the universe increases, but the leading correction to this result is simply the negative of the rate of entropy change in the heat bath. In other words, the first correction term (57) represents the total change in the entropy of the particle which is balanced by the change in the entropy of the bath and, therefore, amounts to no net change in the entropy of the universe.

This brings us to the next (second) correction to the entropy, which is given by the sum of the terms in Eqs. (40), (46), (47), and (50). Together, they give

$$S_{2nd} = -\frac{\delta F(t)}{T} = k_B \frac{3l_0^2 + 4l_0 l_1}{4Dt}. \quad (58)$$

This is the residual component after the subtraction of the entropy of a freely spreading particle (zeroth term) and the entropy exchange with the environment (first term). In contrast to these two terms, S_{2nd} depends on the initial distribution of the particle which, throughout this work, has been assumed to be a delta-function distribution at the origin. Typically, the lengths l_0 and l_1 have the same sign [see item No. (3) after Eq. (29)], which means that $S_{2nd}(t) > 0$. Equation (58) can be interpreted as if this excess entropy is localized in the region of the potential and diffuses away with the particle. However, in contrast to S_{1st}, this component is not transferred to the heat bath. It diminishes in time at a rate

$$\dot{S}_{2nd}(t) = -\frac{k_B}{t}\left[\frac{3l_0^2 + 4l_0 l_1}{4Dt}\right] \sim \frac{1}{t^2}, \quad (59)$$

representing a small entropic loss for the universe. This does not imply a violation of the second law of thermodynamics since we are only looking at a correction term which is negligible compared to the entropy gained by the spreading of the particle (55).

ACKNOWLEDGMENTS

I thank Eli Barkai and Erez Aghion for critical comments on the manuscript. The support of the Israel Science Foundation (ISF) Grant No. 991/17 is acknowledged.

[1] J. Crank, *The Mathematics of Diffusion* (Clarendon, Oxford, U.K., 1975).

[2] D. Frenkel and B. Smit, *Understanding Molecular Simulation: From Algorithms to Applications* (Academic, San Diego, 1996).

[3] R. K. Pathria, *Statistical Mechanics* (Pergamon, New York, 1972).

[4] J. C. Chen and A. S. Kim, Adv. Colloid Interface Sci. **112**, 159 (2004).

[5] G. Keller, *Equilibrium States in Ergodic Theory* (Cambridge University Press, Cambridge, U.K., 1998).

[6] M. V. Smoluchowski, Ann. Phys. **48**, 1103 (1915).

[7] E. Aghion, D. A. Kessler, and E. Barkai, Phys. Rev. Lett. **122**, 010601 (2019).

[8] E. Aghion, D. A. Kessler, and E. Barkai, Chaos, Solitons Fractals **138**, 109890 (2020).

[9] T. Akimoto and T. Miyaguchi, Phys. Rev. E **82**, 030102(R) (2010).

[10] A. Dechant, E. Lutz, E. Barkai, and D. A. Kessler, J. Stat. Phys. **145**, 1524 (2011).

[11] P. Meyer and H. Kantz, Phys. Rev. E **96**, 022217 (2017).

[12] X. Wang, W. Deng, and Y. Chen, J. Chem. Phys. **150**, 164121 (2019).

[13] W. Wang, A. Vezzani, R. Burioni, and E. Barkai, Phys. Rev. Research **1**, 033172 (2019).

[14] T. Akimoto, E. Barkai, and G. Radons, Phys. Rev. E **101**, 052112 (2020).

[15] M. Radice, M. Onofri, R. Artuso, and G. Pozzoli, Phys. Rev. E **101**, 042103 (2020)

[16] The statement that at asymptotically large times a (nonvanishing) function $f(x,t)$ is approximated by another function $g(x,t)$ means that for any x, $[f(x,t) - g(x,t)] \to 0$, and $[f(x,t) - g(x,t)]/f(x,t) \to 0$ for $t \to \infty$. Formally (mathematically) speaking, this is weak convergence.

[17] In the case of a very deep potential well ($\exp[-\beta U(x)] \gg 1$), there is an intermediate-time regime where a quasiequilibrium distribution, $P(x,t) \simeq P_{eq}(x,t) = \exp[-\beta U(x)]/Z$, is established inside the well. See L. Defaveri, C. Anteneodo, D. A. Kessler, and E. Barkai, Phys. Rev. Research **2**, 043088 (2020).

[18] E. J. Carr and W. Turner, Appl. Math. Model. **40**, 7034 (2016).

[19] N. Korabel and E. Barkai, Phys. Rev. E **83**, 051113 (2011).

[20] G. Pontrelli, M. Lauricella, J. A. Ferreira, and G. Pena, Math. Med. Biol. **34**, 559 (2016).

[21] N. E. Sheils, Appl. Math. Model. **46**, 450 (2017).

[22] A standard derivation of Fick's first law is to write the flux $J(x,t) = J^+ - J^-$ as the difference between the currents J^+ and J^- of particles moving to the left and right, respectively. Denoting, respectively, by τ and d the characteristic mean free time and mean free path of the particle, we can write $J^\pm(x,t) = v_0 P(x \mp d, t - \tau)$, where the velocity $v_0 = d/\tau$. The overdamped limit corresponds to $d \to 0$, $\tau \to 0$, and $dv_0 = D/2$, where D is the diffusion coefficient. Then expanding $v_0 P(x \mp d, t-\tau) = v_0 P(x,t) \mp D\partial_x P(x,t)/2 - d\partial_t P(x,t) + \cdots$, and using this expansion to express $J^\pm$, Fick's law that $J = J^+ - J^- = -D\partial_x P$ is immediately recovered. In the presence of a potential jump, only a fraction $\sigma = \exp[-\beta U] < 1$ of the current J^+ represents particles with enough kinetic energy to cross the barrier (based on the overdamped assumption that the momentum is distributed according to the equilibrium Maxwell-Boltzmann distribution). Thus, $J^+ = \sigma v_0 P_<(x - d, t - \tau)$, $J^- = v_0 P_>(x + d, t - \tau)$, and $J = J^+ - J^- = v_0(\sigma P_< - P_>) - D\partial_x P$. This means that in order to comply with the flux continuity BC (7), the PDF must also satisfy $\sigma P_< = P_>$ [BC (8)] at the boundary.

[23] B.-S. Choi, C. Kim, H. Kand, and M. Y. Choi, Physica A **539**, 122914 (2020).

[24] O. Farago, J. Comput. Phys. **423**, 109802 (2020).

[25] O. Farago and G. Pontrelli, Comput. Biol. Med. **124**, 103932 (2020).

[26] N. Grønbech-Jensen and O. Farago, Mol. Phys. **111**, 983 (2013).

[27] One of the referees noted that there is another class of problems with a linear-response (Einstein) relation that involves the system's free energy: In inhomogeneous media, the density-dependent mobility and diffusivity satisfy $D(\rho)/\mu(\rho) = \rho T S''(\rho)$, where ρ is the local density (mea-

sured in units of some reference density ρ^*), and $S(\rho)$ is the equilibrium entropy of a homogeneous system with density ρ. For Boltzmann's entropy $S(\rho) = k_B \rho \ln(\rho)$, the usual Einstein relation $D(\rho)/\mu(\rho) = k_B T$ is locally recovered. See P. H. Chavanis, Entropy **21**, 1006 (2019); D. Andreucci, E. N. M. Cirillo, M. Colangeli, and D. Gabrielli, J. Stat. Phys. **174**, 469 (2019); The relation mentioned by the referee is, of course, completely different than Eq. (24), where the quantity defined as the diffusion coefficient is time dependent and vanishing: $\tilde{D}(t) \sim 1/t$.