Regularized Boltzmann-Gibbs statistics for a Brownian particle in a nonconfining field

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(Received 8 April 2020; revised 25 June 2020; accepted 28 September 2020; published 16 October 2020)

We consider an overdamped Brownian particle subject to an asymptotically flat potential with a trap of depth U_0 around the origin. When the temperature is small compared to the trap depth ($\xi = k_B T / U_0 \ll 1$), there exists a range of timescales over which physical observables remain practically constant. This range can be very long, of the order of the Arrhenius factor $e^{1/\xi}$. For these quasiequilibrium states, the usual Boltzmann-Gibbs recipe does not work since the partition function is divergent due to the flatness of the potential at long distances. However, we show that the standard Boltzmann-Gibbs statistical framework and thermodynamic relations can still be applied through proper regularization. This can be a valuable tool for the analysis of metastability in the nonconfining potential fields that characterize a vast number of systems.

DOI: [10.1103/PhysRevResearch.2.043088](https://doi.org/10.1103/PhysRevResearch.2.043088)

I. INTRODUCTION

In nature, a system coupled to a thermal environment may not be confined indefinitely. A well-known example is the hydrogen atom coupled to a thermal bath at temperature T . As noted by Fermi [1], the partition function of the hydrogen atom diverges [2]. This is due to the fact that the Coulomb potential is asymptotically flat, and hence nonbinding in a thermal setting. Similarly, the barometric formula is an excellent practical approximation to describe the density of particles in the atmosphere, at least in the vicinity of Earth [3]. However, as in the Coulomb case, the gravitational field of the Earth is not sufficient to maintain an atmosphere in equilibrium for an infinite time. Another well-known example is when a Kramers reaction coordinate is in the vicinity of a metastable state [4–6], where the system can stay for a very long time, although it is eventually destined to escape. In all these examples, the partition function of the single particle is divergent, and hence we cannot apply the usual toolbox of equilibrium Boltzmann-Gibbs (BG) statistical mechanics even if the system appears to be in a thermal steady state [7–11]. On the other hand, as we shall see, if the potential has a deep minimum when compared to the temperature, the system may attain a quasiequilibrium (QE) state, in the sense that thermodynamic observables, such as the energy and the entropy, are almost time independent. Then, the question arises whether we can somehow apply concepts of equilibrium thermodynamics to these states, relating the microscopic dynamics to thermodynamics, through some kind of partition

function. In doing so, however, we cannot simply use the BG prescription since the partition function, as usually defined, is divergent. We can still ask if it is possible to regularize the Boltzmann-Gibbs prescription and how to do it.

Here our goal is first to show that by regularizing the divergent partition function, we are able to calculate the values of observables in these QE states, and hence provide a complete toolbox for nonconfining potentials. For that aim, we investigate the overdamped dynamics of a single classical particle coupled to a thermal heat bath with temperature T . The particle starts at the minimum of the potential field, and then, due to the separation of timescales, one sees that the physical observables appear stationary for long times. The first theoretical challenge is to define this quasiequilibrium state precisely. This is done with an inflection-point technique, which can be viewed as an extension of extremum principles found for ordinary equilibrium. Second, what are the values of the observables in quasiequilibrium? How can one obtain them given that the partition function is infinite? One way is to solve the Fokker-Planck equation (FPE); however, this is hard and we wish to find solutions which are nearly time independent. So, we seek a method that does not consider time explicitly, invoking principles of ordinary equilibrium statistical mechanics. Finally, we ask the following: Is the structure of thermodynamics still maintained even in the absence of true equilibrium? For this question, we show that a regularized partition function is useful in the evaluation of free energy, entropy, and energy, just like in the usual textbooks, but with a new partition function which we call Z_K .

The paper is organized as follows. In Sec. II, we describe the kind of systems considered, which exhibit QE states as defined in Sec. III. In Sec. IV, we show how to regularize QE states when the standard partition function is non-normalizable in the unbounded space. An alternative, finite-size approach is presented in Sec. V and final comments are given in Sec. VI.

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II. THE SYSTEM

Consider a Brownian particle in one dimension coupled to a thermal heat bath. The concepts we will discuss are not modified in higher dimensions. We assume that the motion is overdamped and that the Einstein relation between diffusivity and damping holds. The density $P(x, t)$ is then described by the FPE [12,13], with the force field $F(x) = -\partial_x V(x)$, namely, $\partial_t P(x, t) = D[\partial_{xx}^2 - \partial_x \frac{F(x)}{k_B T}]P(x, t)$, where D is the diffusion coefficient, T the temperature, and k_B the Boltzmann constant. The potential field $V(x)$ has a local minimum at $x = 0$ and is assumed to be an even function. The key feature is that $\lim_{x \rightarrow \infty} V(x) = 0$ and that the field is bounded from below. A family of potentials that fulfill these conditions, and hence will be used to exemplify the problem, is

$$V_\mu(x) = -\frac{U_0}{[1 + (x/x_0)^2]^{\mu/2}}, \quad (1)$$

with $U_0, \mu > 0$. After suitably scaling variables [namely, $x/x_0 \rightarrow x$, $Dt/x_0^2 \rightarrow t$, $V(x)/U_0 \rightarrow v(x)$], the FPE assumes the nondimensional form

$$\frac{\partial P(x, t)}{\partial t} = \frac{\partial^2}{\partial x^2} P(x, t) + \frac{1}{\xi} \frac{\partial}{\partial x} \left[\frac{\partial v(x)}{\partial x} P(x, t) \right], \quad (2)$$

where the only free parameter for a given μ is the reduced temperature $\xi = k_B T/U_0$.

III. QUASIEQUILIBRIUM

Qualitatively, as seen in Fig. 1(a) showing the mean-squared displacement (MSD) $\langle x^2(t) \rangle$ vs time from a direct numerical integration of the FPE, given by Eq. (2), the dynamics of a packet of particles all starting at $x = 0$ follows three stages: (i) For very short times, the particles spread diffusively and the force is not yet felt. Hence, here, $\langle x^2 \rangle \sim 2t$. (ii) When the potential well is deep compared to the temperature ($\xi \ll 1$), the system stagnates at intermediate timescales and then $\langle x^2 \rangle$ is roughly a constant. Importantly, these timescales can be exponentially long, proportional to $e^{1/\xi}$, the Arrhenius factor. (iii) Finally, for very long times, the density of particles within the trap will decay to zero as $t^{-1/2}$ [7,8], and the particles will diffuse to large distances since there are not, in principle, external boundaries to block the diffusion.

We are interested in the intermediate timescale, where there is stagnation of the dynamics, as seen in the plateau in Fig. 1, which we denominate a QE state. In other contexts, QE has alternative definitions [14,15] or the system is described as being in a long-lived metastable state [16]. Notice in Fig. 1(a) that when we increase ξ (by increasing the temperature or reducing the well deepness), the QE effect signaled by the stagnation clearly diminishes in strength. Similar plots have been reported for systems of particles with Lennard-Jones interactions [17,18], particles diffusing in porous media [19], and are also found in single-molecule experiments [20,21]. Note, however, that we do not treat many-body effects found in glasses, or anomalous diffusion found in single-molecule experiments. Moreover, as we will see, similar long-lived quasistationary regimes also occur for thermodynamic observables, such as the energy and the entropy.

FIG. 1. (a) MSD $\langle x^2(t) \rangle$ vs time t , obtained from the numerical solutions of the FPE (2), starting from a Dirac δ at the origin, with the potential field $v_4(x) = -1/(1+x^2)^2$, for different values of the scaled temperature $\xi = k_B T/U_0$ indicated in the legend. At short and long times, particles move almost in free diffusion, but, at intermediate scales, they are in a QE state, whose lifetime is longer the smaller is ξ . We highlight the log-inflection point in the plateau region (open circle), defined by Eq. (3), which was numerically calculated. Dotted horizontal lines (in both panels) are the theoretical prediction based on QE, given by Eq. (18), which perfectly match the MSD when stagnation is long lived. (b) MSD $\langle x^2(L) \rangle$ vs L , given by Eq. (20), for particles subject to the field $v_4(x)$ in a finite box $[-L, L]$. The (log L)-inflection point (open triangle) is given by Eq. (27).

With regard to a more precise definition of quasiequilibrium, we note that thermodynamics is formulated via extremum principles, and similarly here the inflection points of observables can be useful to define a characteristic QE value, as shown for the MSD in Fig. 1(a). More precisely, since usually metastability involves timescales over many orders of magnitude, and hence it is analyzed on a logarithmic scale, we define the *log-inflection* point through

$$d^2 \langle x^2 \rangle / d(\ln t)^2 = 0. \quad (3)$$

The value of $\langle x^2 \rangle$, and similarly for other observables, satisfying this equation at the inflection time is what we use as the QE value of the observable (see Fig. 1 and further discussion in Sec. V). This useful definition will soon be explored. The main idea behind the inflection point is that instead of relying on an intuitive definition of QE, that is, when observables “nearly” do not change over time, the inflection point is clearly well defined and lies within the stagnation region. Importantly, as shown in Fig. 1, this definition allows us to go from a low-temperature phase, where stagnation lasts a few

orders of magnitude over time, to higher temperatures where we still have an inflection point, but the stagnation is not so long lived. We take the system state at the inflection point as the definition of the QE state. Thus, mathematically, while equilibrium is defined through extremization (vanishing of the first derivative) of a thermodynamic potential, the vanishing of a second derivative defines QE.

Let us remark that, in principle, one could consider the inflection point defined through $d^2\langle x^2 \rangle / dt^2 = 0$. This inflection point is always found for the MSD since $\langle x^2 \rangle \sim 2t$ for short times and similarly for very long times. This would imply metastability also for very high temperatures, which is not natural. The log-inflection point defined above exhibits a critical value, as shown in Sec. V. In that sense, it satisfies the intuitive demand that QE states are found for finite times and low temperatures. To summarize, the inflection time and the value of the MSD at this inflection point within the stagnation regime can be found numerically or experimentally, and this useful quantifier of QE is investigated theoretically below.

IV. TIME-DEPENDENT SOLUTION APPROACH

Before presenting an analytical approach to the problem, we show in Fig. 2 the numerical solutions of the FPE (2), starting from a Dirac δ at the origin, after a transient. In order to obtain a QE density $P(x)$, we analyze the FPE at timescales where a QE is reached, namely, times shorter than the Arrhenius timescale, but longer than the time it takes the particle to explore the local minimum. Figure 2(a) demonstrates that $P(x, t)$ times a constant Z_0 is the Boltzmann factor $e^{-v(x)/\xi}$. This holds on spatial scales $x < 1$ and the theoretical challenge is to find Z_0 which is a regularized partition function. Clearly, this implies that BG statistics is still a useful concept even though the normalizing partition function diverges. Examining the figure in more detail, we see that there are two length scales in the problem. The first is the length scale of the potential well, which is unity (x_0 in the original variable). The second is time dependent and associated with the “wings” of the distribution outside the well, which spread out in time. Since the motion in this region is almost purely diffusive, this length scale is the diffusion scale $\sqrt{t}$.

We first notice that for the shorter length scale $x \sim \mathcal{O}(1)$, the time-independent QE solution of the FPE is $P(x, t) \propto \text{const } e^{-v(x)/\xi}$. This is essentially the same as true equilibrium, however, the constant must deviate from the inverse standard normalizable partition function since, as already mentioned, the latter diverges. To determine this constant, we need to find the FPE solution for large distances $x > 1$, and then match it to that of the inner region where the Boltzmann-like solution is valid. Assuming a scaling ansatz for $P(x, t) = t^\alpha g(y)$, with $y \equiv x/\sqrt{t}$, the FPE reads, to leading order in y ,

$$\frac{\alpha}{t}g - \frac{yg'}{2t} = \frac{g''}{t}, \quad (4)$$

as long as $\mu > 1$, so that the potential terms are higher order. Namely, since we deal here with $x \gg 1$, the force is totally negligible. To determine α and g , we have to consider the boundary condition for large y and also match this scaling solution to the solution of the FPE for $1 \ll x \ll \sqrt{t}$. At large y , we have to choose the decaying solution, so

FIG. 2. Numerical solution of FPE (2), with potential $v_4(x)$ and $\xi = 0.05$, vs x (full lines), after a transient regime starting from a Dirac δ at the origin, at different times t indicated in the legend. (a) $Z_0 \times P(x, t)$ vs x shows that the PDF for small x adopts a time-independent shape, corresponding to the non-normalizable Boltzmann factor $e^{-v(x)/\xi}$, represented by dotted lines, while at large x , the erfc-like factor imposes a cutoff. (b) $P(x, t)/e^{-[v(x)-v(0)]/\xi}$ vs $x/\sqrt{4t}$ shows the tail of the density, i.e., the cutoff factor, which tends to the $\text{erfc}(x/\sqrt{4t})$ (black dashed line) for long, but not too long, times, and the inset highlights that this factor is flat in the region of the effective well, all as described by Eq. (7).

$g(y) \sim y^{-2\alpha-1} e^{-y^2/4}$. For small y but large x , we have to match to the quasiequilibrium Gibbs solution, which goes to a time-independent constant. Hence, $\alpha = 0$. Thus, in the scaling regime, we have

$$-\frac{yg'}{2} = g'', \quad (5)$$

which yields the complementary error function [22]

$$g \sim A \text{erfc}(y/2). \quad (6)$$

Thus, for $x \sim \mathcal{O}(1)$, $P(x, t) \sim C e^{-v(x)/\xi}$, and in the diffusive region, $P(x, t) \sim A \text{erfc}(x/\sqrt{4t})$. A uniform approximation which reproduces both behaviors is

$$P(x, t) \simeq C e^{-v(x)/\xi} \text{erfc}(x/\sqrt{4t}), \quad (7)$$

where we used $\lim_{x \rightarrow \infty} V(x) = 0$. We see that the erfc gives an effective cutoff at large distances. To obtain the factor C , we split the normalization condition for the probability density function (PDF) defined in Eq. (7) in terms of an

intermediate length scale ℓ ($1 \ll \ell \ll \sqrt{t}$), such that

$$\begin{aligned} \frac{1}{2C} &\simeq \int_0^\ell e^{-v(x)/\xi} dx + \int_\ell^\infty \operatorname{erfc}\left(\frac{x}{\sqrt{4t}}\right) dx \\ &\simeq \underbrace{\int_0^\infty (e^{-v(x)/\xi} - 1) dx}_{Z_0/2} - \underbrace{\int_\ell^\infty (e^{-v(x)/\xi} - 1) dx}_R \\ &\quad + \int_0^\infty \operatorname{erfc}\left(\frac{x}{\sqrt{4t}}\right) dx \simeq Z_0/2 + \mathcal{O}(\sqrt{t}), \end{aligned} \quad (8)$$

where we have assumed that the potential decays faster than $1/x$. The integral denoted $Z_0/2$ is the dominant term in Eq. (8), and it is time independent and of the order of $e^{1/\xi}$. Its integrand is essentially the Mayer f -function and Z_0 is proportional to the second virial coefficient from the theory of gases [23]. The term R scales as $1/\xi$, so that it becomes increasingly negligible compared to Z_0 . The erfc integral grows with time, but here we assume that this diffusive length scale is small in the sense that $\sqrt{t} \ll Z_0$ and so, as long as t is not exponentially large, the last term can be neglected compared to Z_0 . For times much longer than $e^{1/\xi}$, the widely discussed infinite ergodic theory applies [7,8].

To summarize, if the potential field decays faster than $1/x$, the PDF is given by $P(x, t) \simeq e^{-v(x)/\xi} \operatorname{erfc}(x/\sqrt{4t})/Z_0$, for $x > 0$. The cutoff at large x stems from the pure diffusive process arising from the vanishing of the force at large x . The integral Z_0 in the denominator, playing the role of a partition function, is finite. For large enough time, the cutoff factor is unity for distances within the size of the well [see inset of Fig. 2(b)], and we have

$$P_{\text{QE}}(x) \sim \frac{e^{-v(x)/\xi}}{Z_0}, \quad (9)$$

which resembles the canonical BG law [see Fig. 2(a)]. Here the regularized normalization factor Z_0 is given by Eq. (8), provided that $\mu > 1$. We will soon show that Z_0 is indeed a partition function in the sense that it can be used to find averaged thermodynamic observables such as the energy, when the potential decays faster than $1/x$.

When the potential decays slower than $1/x$, namely, as $1/x^\mu$, with $0 < \mu \leq 1$, Z_0 in Eq. (8) diverges and a technical modification of the basic formula is required. By adding and subtracting terms in Eq. (8), we obtain the generalized normalization

$$Z_K = 2 \int_0^\infty [e^{-v(x)/\xi} - \sigma_K(x; \xi)] dx, \quad (10)$$

where

$$\sigma_K(x; \xi) \equiv \sum_{k=0}^K [-v(x)/\xi]^k / k!, \quad (11)$$

with $K = \lfloor 1/\mu \rfloor$ (where $\lfloor \cdot \rfloor$ means floor function), ensuring a nondivergent integral. In this case, Eq. (9) is still valid, but Z_0 is replaced with Z_K .

We have thus regularized the density replacing the diverging partition function with Z_K , but the regularization process does not end here. As we will soon show, to find the averages of physical observables may require additional regularization

that depends on the potential and the observable. This is the case of the MSD that we are dealing with. Then, before tackling the calculation of its QE value, we start by considering any (symmetric) observable $\mathcal{O}(x)$ that is integrable with respect to the non-normalizable Boltzmann factor. In the QE state, we have

$$\mathcal{O}_{\text{QE}} \equiv \langle \mathcal{O}(x) \rangle_{\text{QE}} = \frac{2}{Z_K} \int_0^\infty \mathcal{O}(x) e^{-v(x)/\xi} dx, \quad (12)$$

where Z_K is given by Eq. (10). This formula is very similar to the usual one for calculating equilibrium averages; the difference is the regularization of the partition function in the denominator. Let us illustrate this procedure by computing an observable of thermodynamic interest, the average energy $u_{\text{QE}} \equiv E_{\text{QE}}/U_0 \equiv \langle v(x) \rangle_{\text{QE}}$. When the potential $v(x)$ decays faster than $1/x$ (hence, $K = 0$), Eq. (12) explicitly becomes

$$u_{\text{QE}} = \frac{\int_0^\infty v(x) e^{-v(x)/\xi} dx}{\int_0^\infty (e^{-v(x)/\xi} - 1) dx} \equiv \xi^2 \frac{\partial \ln Z_0}{\partial \xi}. \quad (13)$$

It is noteworthy that the QE mean energy obeys the familiar statistical mechanics relation with the (regularized) partition function. If the potential decays more slowly than $1/x$, such as $v_\mu(x)$ with $0 < \mu \leq 1$, the computation of the QE energy needs some modification, analogously to Eq. (10), namely,

$$u_{\text{QE}} = \frac{2}{Z_K} \int_0^\infty v(x) [e^{-v(x)/\xi} - \sigma_{K-1}(x; \xi)] dx, \quad (14)$$

which generalizes Eq. (13), obeying $u_{\text{QE}} \equiv \xi^2 \partial_\xi \ln Z_K$.

From the integration of the FPE [for $v_4(x)$ and for different values of ξ], we show in Fig. 3 that the stagnation phenomenon occurs for the average energy as a function of time,

$$u(t) \equiv E(t)/U_0 = \int_{-\infty}^\infty v(x) P(x, t) dx, \quad (15)$$

as well as for another basic thermodynamic quantity, the dynamical entropy,

$$s(t) \equiv S(t)/k_B = - \int_{-\infty}^\infty \ln[P(x, t)] P(x, t) dx. \quad (16)$$

The comparison between theory and numerics for QE states is also depicted in Fig. 3, showing excellent agreement between time-dependent simulations and the QE statistical physics proposed here. Interestingly, the QE entropy is computed exactly like in ordinary equilibrium statistical mechanics, $s_{\text{QE}} = u_{\text{QE}}/\xi - \ln Z_0$, where Z_0 is the regularized partition function. This shows how regularized statistical mechanics goes beyond a computation of an effective normalization constant, as thermodynamic identities are maintained in QE.

The moment observables $\langle \mathcal{O}(x) \rangle = \langle x^n \rangle$ require a more careful treatment. The integral over $x^n e^{-v(x)/\xi}$ from zero to infinity diverges, so we need to perform a calculation similar to that of Eq. (10), obtaining

$$\langle x^n \rangle_{\text{QE}} = \frac{2}{Z_K} \int_0^\infty x^n [e^{-v(x)/\xi} - \sigma_{K'}(x; \xi)] dx, \quad (17)$$

where $K' = \lfloor (n+1)/\mu \rfloor$ and the function $\sigma_{K'}$ regularizes the numerator. In the particular case of the MSD presented in

FIG. 3. Dimensionless energy E and entropy S vs time t (top) and box size L (bottom), in the field $v_4(x)$, so $\mu = 4$, for different values of ξ indicated in the legend. The time evolution was obtained by integration of the FPE starting from a Dirac δ at the origin, with free boundary conditions, and L -dependent results from the standard normalized BG state in a box $[-L, L]$. The dashed horizontal lines show the theoretical prediction of the QE values. These are computed with Eq. (13) for the energy, and, interestingly, for the entropy, they are well described by the equilibrium relation $\mathcal{F}/U_0 \equiv f = u - \xi s = \xi \ln Z_0$, where f is the free energy. The symbols indicate the respective log-inflection points for each observable.

Fig. 1, $n = 2$, and so, for $\mu = 4$, $K' = K = 0$. Then, Eq. (17), together with Eq. (1), yields the explicit form (see the Appendix)

$$\langle x^2 \rangle_{\text{QE}} = \frac{2F_2\left(\frac{1}{4}, \frac{3}{4}, \frac{3}{2}, 2; \frac{1}{\xi}\right)}{2F_2\left(\frac{3}{4}, \frac{5}{4}, \frac{3}{2}, 2; \frac{1}{\xi}\right)}, \quad (18)$$

plotted by horizontal lines in Fig. 1(a), in good agreement with numerical results when $\xi \lesssim 0.1$. In this regime, we note that this theory greatly improves a harmonic approximation of the minimum of the potential, as can be observed in Fig. 4, and therefore the nonlinearity of the force field cannot be neglected. However, when $\xi \gtrsim 0.1$, we see deviations. This is hardly surprising as the stagnation is short lived; moreover, the mentioned condition $\sqrt{t} < e^{1/\xi}$ is starting to become questionable. Still, in the next section, we seek a different method to describe the intermediate-temperature regime.

Remark. With numerical simulations of FPE, we cannot prove that log-inflection points vanish beyond a critical value. What we see, however, is that they are impossible to measure precisely when the temperature is $\xi \simeq 0.1$ or higher. In experiments, it would be impossible to detect such log-inflection points at high temperature. In the next section, we will show that a bounded-box method predicts the critical value. This critical temperature separates the low- and high-temperature limits.

FIG. 4. Quasiequilibrium value of the MSD $\langle x^2 \rangle_{\text{QE}}$ as a function of the scaled temperature ξ . We present two theoretical predictions, with the first based on Eq. (18), plotted by a red long-dashed line, and the second one corresponding to the log-inflection point L^* extracted from Eq. (27), plotted by the black solid line. This latter has a terminus point (small black circle) and, beyond this critical value $\xi \simeq 0.194$, the inflection point ceases to exist. It is noteworthy that the log-inflection point in time solutions also presents a critical value $\xi \simeq 0.184$, although different from the first one, also highlighted by a small black filled circle. Black hollow circles correspond to the value at the log-inflection point of $\langle x^2(t) \rangle$, obtained from the FPE temporal solution. The blue short-dashed line represents the harmonic approximation, drawn for comparison.

To summarize, the statistical theory we have presented allows the calculation of time-independent averages in QE, valid below the critical value of ξ . The key is that instead of integration over the BG measure, we perform the ensemble average over regularized states of the observable. The regularization of Z_K , which is similar to the standard partition function, is given by Eq. (10), depending only on the behavior of the potential at long distances, while the regularization of the numerator in Eqs. (13)–(17) depends on the asymptotics of both the potential field and the observable.

V. BOUNDED DOMAIN APPROACH

So far, we have addressed the QE of a time-dependent process in an unbounded domain. Can the tools developed so far describe an even wider set of problems, in particular systems of finite size? In order to address this issue, we now consider systems confined in a box of size L , larger than the trap size, which attain a BG state. We will show that for the deep asymptotically flat potentials that we are considering herein, the equilibrium state is quasi-independent of L , for $1 \ll L \ll e^{1/\xi}$. Moreover, the equilibrium state is actually the same as the regularized QE of time-dependent systems with free boundary conditions treated so far, for small ξ (see Fig. 4). This allows us to add a tool for the calculation of thermodynamic observables in QE and, more importantly, to show the generality of the developed concepts.

We have seen that there is a cutoff time up to which the observables of interest are practically time independent. This hints that we may alternatively treat the problem as a time-independent one. A step in this direction is to confine the motion to a finite domain, $-L < x < L$. Let us consider the potential field $v(x)$ with reflecting boundaries at $x = \pm L$. We focus on the BG equilibrium properties of the particle, so here $t \rightarrow \infty$ is considered. We start by computing the partition function,

$$Z(L) = 2 \int_0^L e^{-v(x)/\xi} dx, \quad (19)$$

which is, of course, finite for any large but finite L , and then, for the MSD, we find

$$\langle x^2(L) \rangle = \frac{2}{Z(L)} \int_0^L x^2 e^{-v(x)/\xi} dx. \quad (20)$$

This is plotted as a function of L in Fig. 1(b) for several values of ξ . Notice, as we will demonstrate below, that the stagnation values are the same as those found from the time-dependent solution. This is remarkable as it allows us to obtain the QE semianalytically without evolving the system in time. Moreover, Eq. (20) allows one to obtain theoretically the inflection point in the stagnation region, also plotted in Fig. 1(b).

First, we rewrite the integral for $Z(L)$, by adding and subtracting terms, as

$$Z(L) = 2 \int_0^L [e^{-v(x)/\xi} - \sigma_K(x; \xi)] dx + 2 \int_0^L \sigma_K(x; \xi) dx. \quad (21)$$

Then, we split $Z(L)$ as

$$Z(L) = Z_K + Z_K^>(L) + Z_K^<(L), \quad (22)$$

where

$$Z_K = 2 \int_0^\infty [e^{-v(x)/\xi} - \sigma_K(x; \xi)] dx, \quad (23)$$

$$Z_K^>(L) = -2 \int_L^\infty [e^{-v(x)/\xi} - \sigma_K(x; \xi)] dx, \quad (24)$$

$$Z_K^<(L) = 2 \int_0^L \sigma_K(x; \xi) dx. \quad (25)$$

Notice that the convergent integral Z_K is L independent. It is easy to show that $Z_K^>(L)$ is relatively small when $L \gg 1$. Clearly, $Z_K^<(L) \sim 2L$; indeed, when we fix ξ and take $L \rightarrow \infty$, this is the leading contribution. However, if we consider $\xi \ll 1$, with fixed though large L , then $Z_K \propto e^{1/\xi}$ dominates. Since it is L independent, it is well suited for the description of an infinite system, where there is stagnation in time, i.e., those systems modeled by the FPE in QE but with free boundary conditions.

We now perform an analogous splitting of the integral in the numerator of Eq. (20). Namely, we introduce the factor x^2 in the integrands of Eqs. (23)–(25), substitute $K \rightarrow K'$, and perform a split of the numerator of Eq. (20), in the respective integrals $X_{K'}$, $X_{K'}^>$, and $X_{K'}^<$ (note that X in the original units has dimension of a cubic length). In the limit $L \rightarrow \infty$ and fixed ξ , we find the trivial leading term $X_{K'}^< \sim L^3/3$, and this together with the normalization gives $\langle x^2(L) \rangle \propto L^2$ as expected. Meanwhile, $X_{K'}^>$ is small and negligible when $L \gg 1$. Again, since we are interested in the stagnation limit, if L is not too large, the leading term is $X_{K'} = 2 \int_0^\infty x^2 [e^{-v(x)/\xi} - \sigma_{K'}(x; \xi)] dx$, which is also proportional to $e^{1/\xi}$.

Putting all these results together, we arrive at $\langle x^2 \rangle_{\text{QE}} = X_{K'}/Z_K$, that is,

$$\langle x^2 \rangle_{\text{QE}} = \frac{2}{Z_K} \int_0^\infty x^2 [e^{-v(x)/\xi} - \sigma_{K'}(x; \xi)] dx, \quad (26)$$

which is L independent and hence also t independent. Notice that this expression precisely coincides with Eq. (17) for $n = 2$, which was obtained through the time-dependent solution in the unbounded domain, illustrating how both approaches meet.

A. Critical temperature

Still considering the L -dependent expression $\langle x^2(L) \rangle$ in Eq. (20), we can obtain the log-inflection point L^* through $d^2 \langle x^2(L) \rangle / d(\ln L)^2 = 0$, obtaining the transcendental equation

$$2L^2 - (L^2 - \langle x^2 \rangle) \left\{ \frac{4Le^{-v(L)/\xi}}{Z(L)} - \frac{Lf(L)}{\xi} - 1 \right\} \equiv \Delta(L) = 0. \quad (27)$$

We numerically find the solutions of Eq. (27), as the zeros of $\Delta(L)$, which is plotted vs L in Fig. 5 for different values of ξ . Besides the trivial solution ($L^* = 0$, which is nonphysical), there are two solutions for small ξ , which collide at a critical value [$\xi \simeq 0.194$, when $\mu = 4$ in Eq. (1)] and cease to exist above that temperature. Roughly this ξ marks the transition between low- and high-temperature regimes; it is also observable dependent and, in that sense, not universal.

In Fig. 6, we plot the MSD versus time t and box size L on a linear-logarithmic scale (unlike Fig. 1, which is a log-log

FIG. 5. Numerically solving Eq. (27), $\Delta(L) = 0$, for the potential $v_4(x)$ ($\mu = 4$) and different values of the scaled temperature ξ in the legend. Notice that for small ξ , there are two solutions, besides the trivial solution $L = 0$, which collapse at a critical value ($\xi \simeq 0.194$ in the case of the figure) and vanish at higher temperature.

FIG. 6. MSD vs (a) time t and (b) L . The same data of Fig. 1 are plotted in a linear vs logarithmic scale, to display the changes of concavity associated to the inflection points. In (b), the nontrivial inflection points, i.e., the solution of Eq. (27), are highlighted. At low temperature, an inflection point (small symbol) predicts the start of stagnation, while another (large symbol) lies in the stagnation zone. When the temperature ξ increases, these two inflection points meet and disappear above a critical temperature. The black dashed line represents the free-particle case (limit $\xi \rightarrow \infty$), which has no inflection points. It is interesting that similar features are observed in the time evolution, shown in (a).

plot). In this figure, we present the two inflection points, which as mentioned are found only for low enough ξ . At low temperatures, there are two nontrivial inflection points. The first anticipates the start of the stagnation, while the second, which we call L^* , lies in the stagnation region. We take the latter as a signature of the QE state (see Fig. 1). Above a certain temperature, both inflection points merge and disappear in Fig. 6. The line corresponding to the infinite-temperature limit (no potential), where clearly there are no inflection points at all, is also plotted for comparison.

B. Relation between the two approaches

When ξ is small enough, we observe that (see Fig. 4) $\langle x^2 \rangle_{\text{QE}} \simeq \langle x^2(L^*) \rangle \simeq \langle x^2(t^*) \rangle$, where the $*$ stands for the (largest) log-inflection point, which characterizes the stagnation zone (see Fig. 1). Also, the mean energy has two nontrivial inflection points, with the second one in the stagnation region (shown in Fig. 3), while in the case of the entropy, we have a single inflection point in the stagnation region.

Thus, more generally, we postulate that for an observable $\mathcal{O}$, we have, when QE exists,

$$\langle \mathcal{O} \rangle_{\text{QE}} \simeq \langle \mathcal{O}(L^*) \rangle \simeq \langle \mathcal{O}(t^*) \rangle. \quad (28)$$

Thus, we can use the finite-size system expression for the observable, obtain L^* , and then infer the temporal stagnation value. For example, in Fig. 6, we use Eq. (27) for the MSD to determine L^* . We then compare the result with the time-dependent calculation of the MSD, using the FPE, showing good agreement between them, for small ξ . As mentioned, with this method, there is no need to evolve the system in time, which is very important since the escape time is exponentially large.

Figure 4 also reveals that for small ξ , there is excellent agreement between the box method and the theory of QE. This is the regime where we have a clear separation of timescales in the dynamics. When $\xi \gtrsim 0.1$, we observe deviation between the inflection-point and the QE approaches. We see from the figure that the time-dependent simulation results are very close to those obtained by the bounded domain approach given by Eq. (20) even when ξ is relatively large.

VI. FINAL REMARKS

We have shown that long-lived QE states emerge when particles are subject to an external field which has a deep well at the origin and is asymptotically flat. Despite the divergent character of the standard partition function due to the nonconfining potential, a regularization procedure is still possible, allowing one to calculate quantities in the QE states along the lines of the standard recipes of statistical mechanics. The regularization strategy can be applied to a vast number of observables, in particular thermodynamic quantities, e.g., the energy, entropy, and free energy. Experimental proof of these concepts can be made for a single molecule weakly attached to a membrane or a surface embedded in a thermal bath [24–26].

As we increase the temperature, stagnation becomes short lived. We identified a critical temperature that marks the transition between low- and high-temperature states. At that

temperature, two merging inflection points collide. In this sense, the inflection-point method not only defines the QE low-temperature states, but the concept is also very useful far from this limit. Indeed, when departing from the low-temperature regime, we noticed that inflection points based on finite systems are the useful theoretical tool to describe the QE phenomenon.

In general, metastable states emerge in systems with clear separation of timescales, and then observables appear stationary. Eventually, a true equilibrium state can be reached [16,27], for example if the system is finite. While, in our case, there is a transition from a metastable state to a diffusive behavior, the tools developed here will turn out to also be useful in other situations. For example, if we have confinement of the particles in a very large box, the initial QE will not be influenced by finite-size effects, as long as the observation timescale is shorter than the time of escape from the well.

For heterogeneous media, i.e., a spatially dependent diffusion field $D(x)$, several models exist to describe a vast set of diffusion mechanisms [28–33]. One can typically rewrite the FPE to take the form of Eq. (2) with a generalized potential involving the force and diffusivity, in which case our approach will hold for the transformed system. Moreover, as long as the inhomogeneity is weak, the result will remain fundamentally the same.

The investigation of the relaxation properties is important for the dynamical viewpoint of the present problem and preliminary results show that here too the system mimics equilibrium properties on the relevant range of timescales, but this topic deserves a separate careful systematic study. Many other directions to be explored, such as the underdamped dynamics, systems with several metastable states, inhomogeneous diffusion, and interacting systems, are also left for future work.

ACKNOWLEDGMENTS

D.K. and E.B. acknowledge the support of the Israel Science Foundation Grant No. 1898/17. L.D. and C.A. acknowledge partial financial support from Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

APPENDIX

Let us consider the particular case of Eq. (17) in which $n = 2$, corresponding to the MSD, and $\mu = 4$, ($K' = K = 0$) corresponding to the potential field $v_4(x)$. From Eq. (11),

using that $\sigma_0(x; \xi) = 1$, explicitly we have

$$\begin{aligned} \langle x^2 \rangle_{\text{QE}} &= \frac{2}{Z_0} \int_0^\infty (e^{-v_4(x)/\xi} - 1) dx \\ &= \frac{\int_0^\infty x^2 (e^{-v(x)/\xi} - 1) dx}{\int_0^\infty (e^{-v(x)/\xi} - 1) dx}, \end{aligned} \quad (\text{A1})$$

where $v_4(x) = -1/(1+x^2)^2$. We Taylor expand the exponential in the integral in powers of $v_4(x)/\xi$ and integrating term by term.

For the partition function Z_0 , using that

$$\begin{aligned} \int_0^\infty [-v_4(x)/\xi]^k dx &= \int_0^\infty [\xi(1+x^2)^2]^{-k} dx \\ &= \frac{1}{\xi^k} \frac{\sqrt{\pi} \Gamma[2k - 1/2]}{2 \Gamma[2k]}, \end{aligned} \quad (\text{A2})$$

and the Γ function, we obtain

$$\begin{aligned} Z_0 &= 2 \int_0^\infty (e^{-v_4(x)/\xi} - 1) dx \\ &= 2 \sum_{k=1}^\infty \frac{1}{k!} \int_0^\infty [-v_4(x)/\xi]^k dx \\ &= \sum_{k=1}^\infty \frac{1}{k!} \frac{1}{\xi^k} \frac{\sqrt{\pi} \Gamma[2k - 1/2]}{\Gamma[2k]} \\ &= \frac{\pi}{2\xi} {}_2F_2\left(\frac{3}{4}, \frac{5}{4}; \frac{3}{2}, 2; \frac{1}{\xi}\right). \end{aligned}$$

For the denominator, we apply the same procedure, using

$$\begin{aligned} \int_0^\infty x^2 [-v_4(x)/\xi]^k dx &= \int_0^\infty x^2 [\xi(1+x^2)^2]^{-k} dx \\ &= \frac{1}{\xi^k} \frac{\sqrt{\pi} \Gamma[2k - 3/2]}{4 \Gamma[2k]}. \end{aligned} \quad (\text{A3})$$

Then,

$$\begin{aligned} 2 \int_0^\infty [x^2 (e^{-v_4(x)/\xi} - 1)] dx &= 2 \sum_{k=1}^\infty \frac{1}{k!} \int_0^\infty x^2 [-v_4(x)/\xi]^k dx \\ &= \sum_{k=1}^\infty \frac{1}{k!} \frac{1}{\xi^k} \frac{\sqrt{\pi} \Gamma[2k - 3/2]}{2 \Gamma[2k]} = \frac{\pi}{2\xi} {}_2F_2\left(\frac{1}{4}, \frac{3}{4}; \frac{3}{2}, 2; \frac{1}{\xi}\right). \end{aligned}$$

Combining the expression for the numerator and denominator of Eq. (A1), we arrive at Eq. (18).

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