Regularized Boltzmann-Gibbs statistics for a non-confining field

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In nature, a system coupled to a thermal environment may attain a quasi-equilibrium (QE) state which is very long lived. 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 related to the fact that the Coulomb potential is asymptotically flat, and hence non-binding in a thermal setting. Moreover, 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 [4,5,6], where the system can stay for a very long time in a QE condition, 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 BG statistical mechanics even if the system appears to be in a thermal steady state [7,11]. Here our goal is first to regularize the divergent partition function in order to calculate observables of interest, and then provide a complete toolbox for this case.

To be more specific, 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 Fokker-Planck equation (FPE) [12, 13] with the force field $F(x) = -\partial_x V(x)$, namely $\partial_t P(x,t) = D(\partial^2_x - \partial_x \frac{F(x)}{k_B T}) P(x,t)$, 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 it is assumed to be an even function. The key feature is that $\lim_{x \to \infty} V(x) = 0$, 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

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

with $U_0 > 0$. After suitably scaling variables (namely, $x/x_0 \to x$, $D t / x_0^2 \to t$, $V(x)/U_0 \to v(x)$), the FPE assumes the non-dimensional form

$$\partial P(x,t)/\partial t = \partial^2_x P(x,t) + \frac{1}{\xi} \partial_x \left( \partial v(x) \partial_x P(x,t) \right),$$

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

Qualitatively, 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. (ii) When the trap is deep compared to the temperature ($\xi \ll 1$), the system attains QE at intermediate timescales. 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 $t^{-1/2}$, 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 time scale, where the particles attain a QE state. This is found, for example, when we plot the mean squared displacement (MSD) $\langle x^2(t) \rangle$ versus time, as shown in Fig. 1, obtained by numerically solving the FPE, Eq. 2. In particular, notice the plateau of $\langle x^2(t) \rangle$, which is a clear indication of QE. As we increase $\xi$ (by increasing the temperature or reducing the trap deepness), the QE effect clearly diminishes in strength. Such plots describe a wide variety of models and systems, for example a particle in a cage, in a glassy system [14,16].

As we will see, similar long-lived quasi-stationary regimes are found for other observables, like the energy and the entropy. Then, a first question is whether we can somehow apply concepts of equilibrium thermodynamics to these states, relating the microscopic dynamics to thermodynamics, through some kind of partition...
function. However, the BG prescription does not work, since the partition function $Z = 2 \int_{0}^{\infty} e^{-v(x)/\xi} dx$ is divergent, because $\lim_{x \to \infty} e^{-v(x)/\xi} = 1$. We can still ask if it is possible to regularize the Boltzmann-Gibbs prescription, and how to do it. This is the problem we address in this letter, and the answer has possible applications to a vast number of systems.

Concerning the definition of quasi-equilibrium, thermodynamics is defined with 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. Thus, mathematically, while equilibrium is defined through minimization of a thermodynamic potential, the vanishing of the second derivative of the observable defines QE. The final goal of this letter is to show how to formalize statistical physics for the calculation of relevant QE averages in non-confining fields.

**Time-dependent solution approach.** In Fig. 2 we show the numerical solutions of the FPE (2), starting from a Dirac delta 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 that the time it takes the particle to explore the local minimum.

If the potential were binding, $P(x, t) = \text{const} e^{-v(x)/\xi}$ would be a steady state solution and the constant would be the inverse partition function. In our nonbinding case, we must replace that constant by noting that the force vanishes at large distances and hence the density must...
obey a free diffusion equation. Matching these two limits yields

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

where \( C \) is a constant and \text{erfc} is the complementary error function \[17\]. To obtain the factor \( C \), we split the normalization condition for the PDF defined in Eq. \( 4 \) in terms of an intermediate length scale \( \ell \) such that

\[
\frac{1}{2C} \simeq \int_0^\ell (e^{-v(x)/\xi} - 1)dx + \int_\ell^\infty \text{erfc}\left(\frac{x}{\sqrt{4t}}\right)dx
\]

\[
\simeq \int_0^\infty (e^{-v(x)/\xi} - 1)dx - \int_\infty^{\infty} (e^{-v(x)/\xi} - 1)dx
\]

\[
\frac{Z_0/2}{R} + \int_0^\infty \text{erfc}\left(\frac{x}{\sqrt{4t}}\right)dx \simeq Z_0/2 + O(\sqrt{t}) ,
\]

where we have assumed that the potential decays faster than \( 1/x \). The integral denoted \( Z_0/2 \) is the predominant term in Eq. \( 4 \), it is time independent and of order \( e^{1/\xi} \). Its integrand is essentially the Mayer \( f \)-function and \( Z_0 \) is proportional to the second virial coefficient from the theory of gases \[18\]. The term \( R \) scales as \( 1/\xi \), so that it becomes increasingly negligible compared to \( Z_0 \). The \text{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 theory of infinite ergodic theory applies \[2,8\].

To summarize, if the potential field decays faster than \( 1/x \), the PDF is given by \( P(x, t) \simeq e^{-v(x)/\xi} \text{erfc}(x/\sqrt{4t})/Z_0 \), 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), and we have

\[ P_{\text{QE}}(x) \simeq \frac{e^{-v(x)/\xi}}{Z_0} , \]

which resembles the canonical BG law (see Fig. 2).

When the potential decays slower than \( 1/x \), namely as \( 1/x^\mu \), with \( 0 < \mu \leq 1 \), \( Z_0 \) in Eq. \( 4 \) diverges, and a technical modification of the basic formula is required. By adding and subtracting terms in Eq. \( 4 \), we obtain the generalized normalization

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

where \( \sigma_K(x; \xi) \equiv \sum_{k=0}^K (-v(x)/\xi)^k/k! \), with \( K = [1/\mu] \) (where \( [ \ ] \) means floor function), ensuring a non-divergent integral.

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

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

where \( Z_K \) is given by Eq. \( 8 \). 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 such as 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. \( 8 \) explicitly becomes

\[ u_{\text{QE}} = \frac{1}{Z_K} \int_0^\infty e^{-v(x)/\xi}dx \equiv -\frac{1}{Z_0} \frac{\partial}{\partial \xi} \ln Z_0 , \]

It is noteworthy that the QE mean energy obeys the familiar statistical mechanics relation with the (regularized) partition function \[10\].

![Figure 3](image-url) (Color online) Energy \( E \) and entropy \( S \) vs. time \( t \) (left) and box size \( L \) (right), in the field \( v_4(x) \), for different values of \( \xi \) indicated in the legend. The time evolution was obtained by integration of the FPE 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 QE values. These are computed with Eq. \( 8 \) for the energy, and, interestingly, for the entropy are well described by the equilibrium relation \( F/U_0 \equiv f = u - \xi s = \xi \ln Z_0 \), where \( f \) is the free energy. The symbols indicate the respective (log)inflection points.
From the integration of the FPE (for \(v_4(x)\) and for different values of \(\xi\)), we show in Fig. 8 that the stagnation phenomenon occurs for the energy \(u(t) = E(t)/U_0 = \int_{-\infty}^{\infty} v(x)P(x,t)dx\), as well as for another basic thermodynamic quantity, the entropy, \(s(t) \equiv S(t)/k_B = -\int_{-\infty}^{\infty} \log(P(x,t))P(x,t)dx\). The comparison between theory and numerics for QE states is also depicted in Fig. 8, showing excellent agreement between time-dependent simulations and QE statistical physics proposed here.

The moment observables \(\langle O(x) \rangle = \langle x^n \rangle\) 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. (9), obtaining

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

where \(K' = [(n+1)/\mu]\) and the function \(\sigma_{K'}\) regularizes the numerator. In the particular case of the MSD presented in Fig. 1 \(n = 2\), and so, for \(\mu = 4\), \(K' = K = 1\). Then, Eq. (10) yields the explicit form

\[
\langle x^2 \rangle_{\text{QE}} = \frac{2F_2\left(\frac{1}{2} + \frac{1}{2}; \frac{3}{2}; \frac{3}{2}; \frac{1}{2}; \frac{1}{2}; \frac{1}{2}; \frac{1}{2}; \frac{1}{2}\right)}{2F_2\left(\frac{1}{2} + \frac{1}{2}; \frac{3}{2}; \frac{3}{2}; \frac{3}{2}; \frac{1}{2}; \frac{1}{2}; \frac{1}{2}; \frac{1}{2}\right)} ,
\]

plotted by horizontal lines in Fig. 1, in good agreement with numerical results. We note that this theory greatly improves a harmonic approximation of the minimum of the potential, therefore the nonlinearity of the force field cannot be neglected.

Thus we have represented a statistical theory with which we may obtain time independent averages in QE. 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. (9) depending only on the behavior of the potential at long distances, while the regularization of the numerator in Eqs. 8-9 depends on the asymptotics of both the potential field and the observable.

**Bounded domain approach.** So far we addressed 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 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. This allows us to add a tool for the calculation of thermodynamic observables in QE, and, more importantly, to show the generally of the developed concepts.

Up till now 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 \(t \to \infty\) is considered. We start by computing the partition function

\[
Z(L) = 2 \int_0^L e^{-v(x)/\xi} dx ,
\]

(11)

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

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

(12)

This is plotted as a function of \(L\) in Fig. 10, for several values of \(\xi\). 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 semi-analytically without evolving the system in time. Moreover, Eq. (12) allows to obtain theoretically the inflection point in the stagnation region, also plotted in Fig. 10.

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

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

(13)

Then, we split \(Z(L)\) as

\[
Z(L) = Z_K + Z_K^>(L) + Z_K^<\left(L\right) ,
\]

(14)

where

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

(15)

\[
Z_K^>(L) = -2 \int_0^L \left( e^{-v(x)/\xi} - \sigma_K(x;\xi) \right) dx ,
\]

(16)

\[
Z_K^<\left(L\right) = 2 \int_0^L \sigma_K(x;\xi) dx .
\]

(17)

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 \(\xi\) and take \(L \to \infty\), 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. With analogous treatment of the integral in Eq. (12), we arrive at Eq. (9) for \(n = 2\), which is \(L\)-independent.
Then, when $\xi$ is small enough, we observe that 
\[ \langle x^2 \rangle_{\text{QE}} \simeq \langle x^2(L^*) \rangle \simeq \langle x^2(t^*) \rangle, \]
where the $\dagger$ stands for the (log)inflection point characterizing the stagnation zone (see Fig. 1). More generally, we have
\[ \langle O \rangle_{\text{QE}} \simeq \langle O(L^*) \rangle \simeq \langle O(t^*) \rangle. \] (18)

Thus, we can use the finite size system expression, obtain $L^*$ and then infer the stagnation value. For example: in Fig. 1 we use Eq. (12) for the MSD to semi-analytically determine $L^*$. We then compare the result with the time dependent solutions of the FPE showing good agreement between them. 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.

**Final remarks.** We have shown that long-lived QE states emerge when particles are subject to an external field which has a well at the origin and is asymptotically flat. Despite the divergent character of the standard partition function due to the non-confining 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.

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