Exact path-integral evaluation of the heat distribution function of a trapped Brownian oscillator

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Using path integrals, we derive an exact expression—valid at all times t—for the distribution $P(Q,t)$ of the heat fluctuations Q of a Brownian particle trapped in a stationary harmonic well. We find that $P(Q,t)$ can be expressed in terms of a modified Bessel function of zeroth order that in the limit $t\to\infty$ exactly recovers the heat distribution function obtained recently by Imparato *et al.* [Phys. Rev. E **76**, 050101(R) (2007)] from the approximate solution to a Fokker-Planck equation. This long-time result is in very good agreement with experimental measurements carried out by the same group on the heat effects produced by single micron-sized polystyrene beads in a stationary optical trap. An earlier exact calculation of the heat distribution function of a trapped particle moving at a constant speed v was carried out by van Zon and Cohen [Phys. Rev. E **69**, 056121 (2004)]; however, this calculation does not provide an expression for $P(Q,t)$ itself, but only its Fourier transform (which cannot be analytically inverted), nor can it be used to obtain $P(Q,t)$ for the case $v=0$.

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I. INTRODUCTION

Developments in spectroscopy and imaging over the last several years [1] have greatly increased our ability to test theoretical models of single-particle dynamics in the condensed phase. Among the theoretical predictions that can now be compared with experimental data are those related to the theorems that govern the statistics of fluctuating thermodynamic variables [2]. Models of the distribution of the work delivered to or by small systems [3], such as colloidal particles in optical traps [4], to name a common example, are especially amenable to theoretical treatment and experimental verification.

That is generally not the case with other thermodynamic variables, however. Fluctuations in the heat Q, for instance, are much less easily studied because they are often nonlinear functionals of the particle trajectories that define a system's temporal evolution [5]. But recently, Imparato *et al.* [6] have not only obtained accurate long-time estimates of the heat generated by the random fluctuations of single micron-sized polystyrene beads in stationary and moving harmonic traps, they have also derived a closed-form expression for its heat distribution function, $P(Q,t)$, which fits the data semiquantitatively. However, their expression is only approximate and only applies in the limit $t\to\infty$.

Unfortunately, it is not always possible to experimentally track the behavior of small systems for arbitrarily long periods of time. This circumstance underscores the importance of and the need for *exact* solutions to problems in single-molecule thermodynamics. An exact expression for the heat distribution function of a Brownian oscillator moving at a constant speed v (a model of the system probed by Imparato *et al.* [6]) was, in fact, obtained by van Zon and Cohen [7], but their result is expressed in terms of a Fourier transform with respect to the variable Q that cannot be analytically inverted. Nor can it be extended to the limit $v\to 0$ [8] (corresponding to a stationary trap), where a comparison with the corresponding experimental result would have been possible.

So, as far as we are aware, the exact heat distribution function for a model of even stationary optical trap experiments has presently not been reported in closed form [9]. As of now, approximate theory of Imparato *et al.*, which predicts that $P(Q,t\to\infty)$ is proportional to a modified Bessel function of zeroth order, K_0, provides the best description of this function. Later analytical calculations by Fogedby and Imparato [10] suggest that zeroth-order modified Bessel functions also describe the heat distributions of particles in *general* potentials U (and not just harmonic potentials), but these results, too, are only approximate and apply only in the long-time low-temperature limit.

It is in this context that we show, in this paper, that the calculation of the heat distribution function of a Brownian particle in a stationary harmonic potential can, in fact, be carried out exactly using path integrals, along the lines of the approach based on the Onsager-Machlup functional [11]. Furthermore, our calculated $P(Q,t)$ coincides exactly with the result of Imparato *et al.* [6] when we pass to the limit $t\to\infty$.

Sections II and III lay out the details of our calculations. The first of these is a short account of how the dynamics of a particle in a deterministic time-dependent potential and acted on by delta-correlated random forces can be represented in path-integral form. The expression we derive here is not new and has been obtained by Minh and Adib [12], but the present derivation shows how it may be obtained directly from the Langevin equation, without appealing to the equivalent Fokker-Planck and Schrodinger-like equations. Section III discusses the application of this path integral to the exact evaluation of the heat distribution function, and Sec. IV analyzes its structure in various limits.

II. PATH INTEGRAL OF A BROWNIAN PARTICLE IN A GENERAL POTENTIAL

Consider a point particle moving in one dimension under conditions of high friction in the presence of both a time-dependent potential and random thermal fluctuations. If $x(t)$

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denotes the particle's position at time t, its equation of motion is given by

$$\zeta \frac{dx(t)}{dt} = -\frac{\partial U(x,t)}{\partial x} + \theta(t), \tag{1}$$

where ζ is the friction coefficient of the particle, $U(x,t)$ is the time-dependent potential that acts on it, and $\theta(t)$ is a white-noise variable that is defined completely by its first and second moments,

$$\langle \theta(t) \rangle = 0, \tag{2a}$$

$$\langle \theta(t)\theta(t') \rangle = 2\zeta k_B T \delta(t-t'), \tag{2b}$$

with k_B as Boltzmann's constant and T as the temperature. From the structure of these moments, the distribution of $\theta(t)$ is seen to be given by the functional

$$P[\theta] \propto \exp\left[-\frac{1}{4\zeta k_B T} \int_0^t dt' \, \theta^2(t') \right]. \tag{3}$$

This means that by virtue of Eqs. (1) and (3), the distribution of particle positions can be written as

$$P[x] = J[x] \exp\left[-\frac{1}{4\zeta k_B T} \int_0^t dt' \{ \zeta \dot{x}(t) + U'(x(t'),t') \}^2 \right], \tag{4}$$

where $J[x]$ is the Jacobian of the transformation from $\theta(t)$ to $x(t)$ [which, in general, is a functional of $x(t)$], the dot on $x(t)$ denotes a time derivative, and the prime on $U(x,t)$ denotes a derivative with respect to x. An expression for the Jacobian is easily obtained from Eq. (1) after first rewriting it in the discrete form [13],

$$\frac{\zeta(x_i - x_{i-1})}{\Delta t} = -\frac{U'(x_i,t_i) + U'(x_{i-1},t_{i-1})}{2} + \theta_i, \quad i = 1,2,\ldots,n. \tag{5}$$

Here, t_i stands for $i\Delta t$, Δt being a small but finite interval of time, and x_i and θ_i stand, respectively, for $x(t_i)$ and $\theta(t_i)$. The original Langevin equation [Eq. (1)] can be thought of as arising from Eq. (5) in the limits $\Delta t \to 0$, $n \to \infty$, and $n\Delta t \to t$. In terms of the above discrete representation, the Jacobian is given by the following determinant:

$$J = \begin{vmatrix} \frac{\partial \theta_1}{\partial x_1} & \frac{\partial \theta_1}{\partial x_2} & \cdots & \frac{\partial \theta_1}{\partial x_n} \\ \frac{\partial \theta_2}{\partial x_1} & \frac{\partial \theta_2}{\partial x_2} & \cdots & \frac{\partial \theta_2}{\partial x_n} \\ \vdots & \vdots & & \vdots \\ \frac{\partial \theta_n}{\partial x_1} & \frac{\partial \theta_n}{\partial x_2} & \cdots & \frac{\partial \theta_n}{\partial x_n} \end{vmatrix}, \tag{6}$$

whose elements can be found from Eq. (5). Thus, $\partial\theta_1/\partial x_1 = (\zeta/\Delta t)[1 + \Delta t U''(x_1,t_1)/2\zeta]$, while $\partial\theta_1/\partial x_2 = \partial\theta_1/\partial x_3 = \cdots = 0$. Similarly, $\partial\theta_2/\partial x_1 = -(\zeta/\Delta t)[1 - \Delta t U''(x_1,t_1)/2\zeta]$ and $\partial\theta_2/\partial x_2 = (\zeta/\Delta t)[1 + \Delta t U''(x_2,t_2)/2\zeta]$, while $\partial\theta_2/\partial x_3 = \partial\theta_2/\partial x_4 = \cdots = 0$. From these results, one sees that J has a lower triangular form, and it follows therefore that

$$J = \prod_{i=1}^{n} \frac{\zeta}{\Delta t}\left(1 + \frac{\Delta t}{2\zeta} U''(x_i,t_i)\right) \approx \left(\frac{\zeta}{\Delta t}\right)^n \exp\left[\sum_{i=1}^{n} \frac{\Delta t}{2\zeta} U''(x_i,t_i) \right]. \tag{7}$$

Passing to the limits $n \to \infty$, $\Delta t \to 0$, and $n\Delta t \to t$ in this equation and incorporating the result into Eq. (4), we now have

$$P[x] \propto \exp\left[\frac{1}{2\zeta} \int_0^t dt' \, U''(x(t'),t') - \frac{\beta}{4} \int_0^t dt' \times \left\{ \zeta \dot{x}(t')^2 + \frac{1}{\zeta} U'(x(t'),t')^2 + 2\dot{x}(t') U'(x(t'),t') \right\} \right], \tag{8}$$

where the factor of ∞ coming from $\lim_{n\to\infty,\Delta t\to 0}(\zeta/\Delta t)^n$ is absorbed into the proportionality constant, which will be defined later through a normalization constraint. This equation may be simplified as follows: recalling that the potential is a function of x and t, we can write an infinitesimal change in its value, dU, in terms of similar changes in these variables. That is, $dU = (\partial U/\partial x)dx + (\partial U/\partial t)dt$, which itself can be written as $dU = (\partial U/\partial x)\dot{x}(t)dt + (\partial U/\partial t)dt$. Hence, $U'(x(t),t)\dot{x}(t)dt = dU - \dot{U}(x(t),t)dt$. Therefore,

$$\int_0^t dt' \dot{x}(t') U'(x(t'),t') = U(x(t),t) - U(x(0),0) - \int_0^t dt' \frac{\partial U(x(t'),t')}{\partial t'}. \tag{9}$$

If the value of the variable $x(t)$ at t is denoted as x_f and its value at $t=0$ is denoted as x_0, we can now use Eq. (8) to define the probability that a particle starting from x_0 at time $t=0$ is at the point x_f at time t in terms of the propagator

$$G(x_f,t|x_0,0) = \exp(-\beta\Delta U/2) \int_{x(0)=x_0}^{x(t)=x_f} \mathcal{D}[x] \times \exp\left[-\int_0^t dt' \left\{ \frac{\dot{x}(t')^2}{4D} + V - \frac{\beta}{2}\frac{\partial U}{\partial t'} \right\} \right]. \tag{10}$$

Here, $\beta = 1/k_B T$, $\Delta U = U(x_f,t) - U(x_0,0)$, $D = k_B T/\zeta$, $V = D[(\beta U'/2)^2 - \beta U''/2]$, and $\mathcal{D}[x]$ is a measure on the space of functions (incorporating the factor of infinity referred to earlier) that ensures that the propagator is suitably normalized. This expression for the propagator is identical to the one derived by Minh and Adib [12] via the Fokker-Planck and Schrodinger-like equations that Eq. (1) is equivalent to. The present derivation strikes us as somewhat more direct and transparent than this earlier approach.

III. HEAT DISTRIBUTION FUNCTION AND ITS EVALUATION

Given a particle whose dynamics are governed by Eq. (1), it now remains to establish how the heat that it dissipates by virtue of its thermal fluctuations in a deterministic (possibly time-dependent) external potential is distributed. To this end, we first recall the relation between the heat (which we shall denote Q) and the stochastic trajectory $x(t)$ that determines its value at the end of an interval of time t; this relation is [6,14,15]

$$Q(t) = \int_0^t dt' \dot{x}(t') U'(x(t'),t'). \tag{11}$$

The probability density $P(Q,t)$ that the stochastic variable $Q(t)$ has the value Q at time t can be written, in general, in the following form:

$$P(Q,t) = \langle \delta[Q - Q(t)] \rangle, \tag{12}$$

where the angular brackets denote an average over all possible realizations of the trajectory $x(t)$ under a given set of initial conditions. Introducing this average explicitly into Eq. (12), after using the Fourier representation of the delta function, we obtain

$$\begin{aligned} P(Q,t) = &\frac{1}{2\pi}\int_{-\infty}^{\infty} d\lambda \int_{-\infty}^{\infty} dx_f \int_{-\infty}^{\infty} dx_0 P(x_0) \\ &\times \exp(-\beta\Delta U/2) \int_{x(0)=x_0}^{x(t)=x_f} \mathcal{D}[x] \\ &\times \exp\left[-\int_0^t dt' \left\{ \frac{\dot{x}(t')^2}{4D} + V - \frac{\beta}{2}\frac{\partial U(x(t'),t')}{\partial t'} \right\}\right] \\ &\times \exp\left[i\lambda Q - i\lambda \int_0^t dt' \dot{x}(t') U'(x(t'),t') \right]. \end{aligned} \tag{13}$$

Here, $P(x_0)$ is the distribution of initial values of x. Assuming that the particle is initially in thermal equilibrium in the harmonic potential $U = kx_0^2/2$, where k is the force constant of the potential, we see that $P(x_0) = \sqrt{k/2\pi k_B T} e^{-\beta k x_0^2/2}$. We shall also assume that at times $t > 0$, the harmonic potential in which the particle is trapped remains fixed in space, i.e., is stationary. (The case of the uniformly translating trap, where $U = k(x - ut)^2/2$ and u is the uniform speed of translation, is also of considerable interest and has been investigated experimentally and theoretically [6,7,11], but we have not been able to obtain its heat distribution function exactly, so we do not consider it further.) For the stationary trap, $U' = kx$, $V = (D\beta k/2)[\beta k x^2/2 - 1]$, and $\dot{U} = 0$, so Eq. (13) can be written as

$$\begin{aligned} P(Q,t) = &\frac{1}{2\pi}\int_{-\infty}^{\infty} d\lambda \int_{-\infty}^{\infty} dx_f \int_{-\infty}^{\infty} dx_0 P(x_0) \\ &\times e^{-\beta\Delta U/2 + i\lambda Q} G_\lambda(x_f,t|x_0,0), \end{aligned} \tag{14a}$$

where

$$\begin{aligned} G_\lambda(x_f,t|x_0,0) = &\int_{x(0)=x_0}^{x(t)=x_f} \mathcal{D}[x] \exp\left(-\int_0^t dt' \left\{ \frac{1}{4D}\dot{x}(t')^2 \right.\right. \\ &\left.\left. + \frac{1}{4}D\beta^2 k^2 x(t')^2 + i\lambda k x(t')\dot{x}(t') - \frac{1}{2}D\beta k \right\} \right). \end{aligned} \tag{14b}$$

After simplification, $G_\lambda(x_f,t|x_0,0)$ can be reduced to

$$G_\lambda(x_f,t|x_0,0) = \exp\{\beta Dkt/2 - i\lambda k(x_f^2 - x_0^2)/2\} G_0(x_f,t|x_0,0), \tag{15a}$$

where

$$\begin{aligned} G_0(x_f,t|x_0,0) = &\int_{x(0)=x_0}^{x(t)=x_f} \mathcal{D}[x] \exp\left(-\int_0^t dt' \left\{ \frac{1}{4D}\dot{x}(t')^2 \right.\right. \\ &\left.\left. + \frac{1}{4}D\beta^2 k^2 x(t')^2 \right\} \right). \end{aligned} \tag{15b}$$

Equation (15b) is the well-known propagator for the harmonic oscillator [16] and is given by

$$\begin{aligned} G_0(x_f,t|x_0,0) = &\phi(t) \exp\left[-\frac{q}{4D\sinh qt}\{(x_f^2 + x_0^2)\cosh qt \right. \\ &\left. - 2x_f x_0\} \right], \end{aligned} \tag{16}$$

where $\phi(t) = \sqrt{q/4\pi D \sinh qt}$ and $q = D\beta k$. Collecting terms in Eqs. (14b), (15), and (16) and substituting them into Eq. (14a), we now have the heat distribution as being given by

$$\begin{aligned} P(Q,t) = &\frac{\phi(t) e^{qt/2}}{2\pi} \sqrt{\frac{k}{2\pi k_B T}} \int_{-\infty}^{\infty} d\lambda \int_{-\infty}^{\infty} dx_f \int_{-\infty}^{\infty} dx_0 \\ &\times e^{-\beta k(x_f^2 + x_0^2)/4} \exp\left[-\frac{q}{4D}\coth qt\{(x_f - x_0)^2 \right. \\ &\left. + 2x_f x_0(1 - 1/\cosh qt)\} + i\lambda\left\{ Q - \frac{k}{2}(x_f^2 - x_0^2) \right\} \right]. \end{aligned} \tag{17}$$

The integral over λ immediately yields the delta function $2\pi\delta[Q - k(x_f^2 - x_0^2)/2]$, whereupon the integral over x_f can be carried out, and this then leads to the result

$$P(Q,t) = I_1(Q,t) + I_2(Q,t), \tag{18a}$$

where

$$\begin{aligned} I_1(Q,t) = &\frac{\phi(t) e^{qt/2}}{\sqrt{2\pi k k_B T}} \int_{-\infty}^{\infty} dx_0 \frac{1}{|\sqrt{x_0^2 + 2Q/k}|} \\ &\times \exp\left[-\frac{\beta k}{4}x_0^2 - \frac{\beta k}{4}(x_0^2 + 2Q/k) \right. \\ &- \frac{q}{4D}\coth qt\{(\sqrt{x_0^2 + 2Q/k} - x_0)^2 \\ &\left. + 2x_0(1 - 1/\cosh qt)\sqrt{x_0^2 + 2Q/k}\} \right]. \end{aligned} \tag{18b}$$

The integral $I_2(Q,t)$ is identical to $I_1(Q,t)$ except that the term $\sqrt{x_0^2+2Q/k}$ in $I_1(Q,t)$ is replaced by the term $-\sqrt{x_0^2+2Q/k}$. The evaluation of the integral in Eq. (18b) can be carried out by introducing the following change of variable: $y=\sqrt{x_0^2+2Q/k}-x_0$. After also introducing the definition of $\phi(t)$, one can simplify $I_1(Q,t)$ to

$$I_1(Q,t) = \frac{\beta e^{qt/2}}{2\pi\sqrt{2}\sinh qt}\int_0^\infty dy\frac{1}{y}\exp\left[-\mu y^2 - \frac{\sigma}{y^2}\right], \tag{19a}$$

where

$$\mu = \frac{\beta k(1+\cosh qt+\sinh qt)}{8\sinh qt} \tag{19b}$$

and

$$\sigma = \frac{\beta Q^2(\sinh qt+\cosh qt-1)}{2k\sinh qt}. \tag{19c}$$

From the integrals tabulated in Ref. [17], we have the following general result: $\int_0^\infty dz z^{\nu-1}\exp(-\beta x^p-\gamma/x^p)=(2/p)(\gamma/\beta)^{\nu/2p}K_{\nu/p}(2\sqrt{\beta\gamma})$, where $K_a(\cdots)$ is the modified Bessel function of order a. When applied to Eq. (19a), this yields $I_1(Q,t)=(\beta e^{qt/2}/2\pi\sqrt{2}\sinh qt)K_0(2\sqrt{\mu\sigma})$. The integral $I_2(Q,t)$ can be evaluated in exactly the same way by introducing the change of variable $y=\sqrt{x_0^2+2Q/k}+x_0$. One finds then that $I_2(Q,t)=I_1(Q,t)$. Hence, we finally obtain

$$P(Q,t) = \frac{\beta e^{qt/2}}{\pi\sqrt{2}\sinh qt}K_0\left(\beta\sqrt{\frac{Q^2(1+\coth qt)}{2}}\right), \tag{20}$$

which is the principal result of our calculations.

IV. DISCUSSION

The expression for $P(Q,t)$ derived in Sec. III [Eq. (20)] is exact and holds at all times t. Earlier, Imparato *et al.* [6], starting from the same Brownian oscillator model used in the present calculations but adopting an approach based on the solution to a Fokker-Planck equation under a ground-state dominance approximation, had derived an expression for the heat distribution that held only for $t\to\infty$. Their result,

$$P_{\text{Imparato}}(Q,t\to\infty) \sim \frac{\beta}{\pi}K_0(\beta|Q|), \tag{21}$$

was found to fit long-time data [6] from experimental measurements of the heat distribution very well. As is easily shown, the result above is exactly recovered from Eq. (20) when t is made very large.

The heat distribution function of Eq. (20) is shown graphically in Fig. 1, where it is plotted as a function of Q at two fixed time values, $t=50$ and $t=0.05$, in units where $k=\zeta=k_BT=1$. The curves are seen to diverge at $Q=0$, a reflection of the logarithmic behavior of the zeroth-order modified Bessel function at small values of its argument [17]. As Fogedy and Imparato have shown in their study of heat distributions of particles moving in potentials of arbitrary (as opposed to harmonic) shape [10], the occurrence of a logarithmic singularity at $Q=0$ can also be understood from a consideration of the characteristic function of $P(Q,t)$, which is the function $\langle\exp[-i\lambda Q(t)]\rangle$, the angular brackets here denoting an average over both the stochastic trajectories of x and their initial distribution. This function is easily obtained from Eq. (17) after performing the simple Gaussian integrals in that expression and may be shown to be of the form $1/\sqrt{\lambda^2+A^2}$, where A is some combination of terms involving the parameters t, D, k_BT, and k. For small values of Q, the integral that now defines $P(Q,t)$, viz., $\int_{-\infty}^{\infty}d\lambda e^{i\lambda Q}/\sqrt{\lambda^2+A^2}$, behaves essentially as $1/\lambda$ for large λ, thereby generating a logarithmic singularity on integration. Despite this singularity, the integral of $P(Q,t)$ over all Q is, in fact, unity as a properly normalized probability density must be. [The proof that $\int_{-\infty}^{\infty}dQP(Q,t)=1$ follows from the identity $\int_0^\infty dxK_0(x)=\pi/2$ applied to Eq. (20).] In the opposite limit of large Q, the function $P(Q,t)$ is characterized by exponential tails, which arise from the asymptotic behavior of the Bessel function, $K_0(z)\sim e^{-z}/\sqrt{z}$.

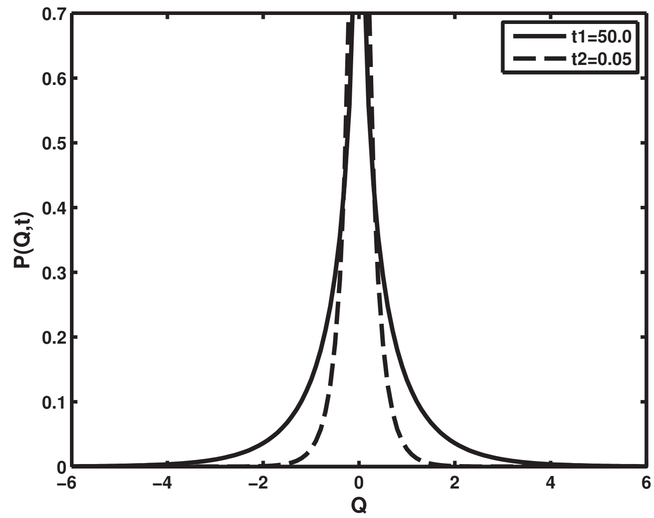

FIG. 1. Graphs of the heat distribution $P(Q,t)$ as a function of Q, as calculated from Eq. (20), at two fixed values of the time: $t=50$ (full line) and $t=0.05$ (dashed line) in units where $k=\zeta=k_BT=1$.

Against the backdrop of the experimental advances that have made it possible to probe thermodynamic entities of ever diminishing size, these exact results are not just interesting in their own right but provide benchmarks for tests of the assumptions that underlie various statistical mechanical theories of small systems.

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