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Heat distribution function for motion in a general potential at low temperature

Hans C Fogedby[1,2] **and Alberto Imparato**[1]

[1] Department of Physics and Astronomy, University of Aarhus, Ny Munkegade, 8000, Aarhus C, Denmark
[2] Niels Bohr Institute, Blegdamsvej 17, 2100, Copenhagen Ø, Denmark

E-mail: fogedby@phys.au.dk and imparato@phys.au.dk

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Abstract
We consider the 1D motion of an over-damped Brownian particle in a general potential in the low temperature limit. We derive an explicit expression for the probability distribution for the heat transferred to the particle. We find that the local minima in the potential yield divergent side bands in the heat distribution in addition to the divergent central peak. The positions of the bands are determined by the potential gaps. We, moreover, determine the tails of the heat distribution.

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(Some figures in this article are in colour only in the electronic version)

There is a strong current interest in the thermodynamics and statistical mechanics of small fluctuating systems in contact with a heat reservoir and driven by external forces. The strong interest stems from the recent possibility of the direct manipulation of nano systems and biomolecules. These techniques permit direct experimental access to the probability distribution functions (PDFs) for the work or for the heat exchanged with the environment [1–9]. These techniques have also opened the way to the experimental verification of the fluctuation theorems, which relate the probability of observing entropy-generating trajectories with that of observing entropy-consuming trajectories [10–27]. Interestingly, the unfolding of biopolymers [1, 2, 28] or the motion of colloidal particles in optical tweezers [4–9] can be described to a large extent as a one-dimensional Brownian motion. However, from a theoretical point of view the time evolution of the work and heat PDFs for a Brownian particle in an external potential is governed by a complex partial differential equation [6, 27] whose explicit solution is available only for simple potentials. It is therefore of interest to extract some general properties regarding the motion of a Brownian particle.

In the present paper we consider a Brownian particle in a general static potential. We show that an explicit asymptotic expression for the heat PDF can be obtained in the low

temperature–long time limit. As a starting point we consider the stochastic motion in 1D of an overdamped Brownian particle in the general static potential $U(x)$. This simplification is justified by the fact that nano systems and biomolecules in aqueous solutions typically behave as overdamped systems. Within a conventional Langevin description the equation description of motion is given by

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -\frac{\partial U}{\partial x} + \xi, \tag{1}$$

where the noise characterizing the fluctuations imparted by the heat bath at a temperature T is correlated according to

$$\langle \xi(t)\xi(0)\rangle = 2T\delta(t). \tag{2}$$

We are setting $k_{\mathrm{B}} = 1$ and the kinetic coefficient $\Gamma = 1$; note that for the motion in a viscous medium we have according to Stokes theorem $\Gamma = 1/6\pi\eta R$, where R is the radius of the particle and η the viscosity.

The kinetics of a particle moving in a general potential is complex. On the one hand, the particle can be trapped in local minima on a time scale given by the inverse spring constant in a local harmonic approximation; on the other hand, the particle can also make a Kramers transition across potential barriers separating local minima. These transitions are typically dominated by the Arrhenius factor $\exp(-\Delta U/T)$, where ΔU is the potential barrier. However, in the long time limit, i.e. at times larger than the largest relaxation time, the particle samples the full potential profile and the stationary distribution is given by the Boltzmann expression

$$P_0(x) = \frac{\mathrm{e}^{-\beta U(x)}}{Z(\beta)}, \tag{3}$$

where $Z(\beta)$ is the partition function

$$Z(\beta) = \int \mathrm{d}x\, \mathrm{e}^{-\beta U(x)}, \tag{4}$$

and $\beta = 1/T$ (the inverse temperature).

At low temperature, $\beta \to \infty$, a steepest descent argument applied to the partition function (4) implies that only the local minima in U contribute. The particle is trapped in the local minima and only rarely makes Kramers transitions to neighboring wells. Expanding the potential to quadratic order about the well at a position x_i with gap U_i and second derivative k_i (spring constant) we obtain the local contribution

$$U(x) \sim U_i + \tfrac{1}{2}k_i(x - x_i)^2, \tag{5}$$

and for the partition function, performing the Gaussian integral, $\int \mathrm{d}x \exp(-\alpha x^2) = \sqrt{\pi/\alpha}$,

$$Z(\beta) \sim \sum_i \left(\frac{2\pi}{\beta k_i}\right)^{1/2} \mathrm{e}^{-\beta U_i}. \tag{6}$$

In the present paper we wish to focus on the distribution of the heat exchange $Q(t)$ with the reservoir in the long time–low temperature limit. For the Brownian motion of a particle in a potential the heat $Q(t)$ sampled up to time t is a fluctuating quantity characterized by a time-dependent probability distribution $P(Q, t)$. In the long time limit the distribution $P(Q, t)$ approaches a stationary distribution $P_0(Q)$ which we proceed to analyze.

The heat delivered by the heat bath in the time span t is in general given by expression [6, 22, 29]

$$Q(t) = \int_{x_0}^{x(t)} \mathrm{d}x \frac{\mathrm{d}U}{\mathrm{d}x} = \int_0^t \mathrm{d}t' \left(\frac{\mathrm{d}U}{\mathrm{d}x}\right)_{x(t')} \frac{\mathrm{d}x(t')}{\mathrm{d}t'}. \tag{7}$$

The first integral in (7) is a stochastic integral [30] and thus one has to choose an integration scheme. By choosing the Stratonovich integration scheme the second equality in (7) holds, otherwise, additional boundary terms appear on its rhs, see, e.g. [31]. In (7), one simply samples the energy change associated with the fluctuating position of the particle; x_0 is the initial position and $x(t)$ the position at time t. The expression (7) can, of course, in principle be evaluated by the insertion of (1). However, this more cumbersome procedure can be circumvented by noting that simple quadrature yields

$$Q(t) = U(x(t)) - U(x_0). \tag{8}$$

Note that this result only holds for a static potential. In the case of a prescribed dynamic potential doing work on the particle according to a given protocol, the expression (8) does not hold and one is faced with the more intractable problem of handling (7).

Introducing the characteristic function the heat distribution is given by

$$P(Q,t) = \int \frac{\mathrm{d}p}{2\pi}\, \mathrm{e}^{\mathrm{i}pQ} \langle \mathrm{e}^{-\mathrm{i}pQ(t)} \rangle, \tag{9}$$

where the average $\langle \cdots \rangle$ in the characteristic function is over both the initial position x_0 and the final position $x(t)$. At $t = 0$ the heat distribution $P(Q,0) = \delta(Q)$. After a transient period of order the inverse spring constants and Kramers rates the heat distribution function becomes stationary. The particle is at all times in thermal equilibrium characterized by the Boltzmann distribution (3). Accordingly, averaging at long times over x_0 and $x(\infty)$ using (3) we obtain for the characteristic function

$$\langle \mathrm{e}^{-\mathrm{i}pQ(\infty)} \rangle = \int \mathrm{d}x_0\, \mathrm{d}x\, P_0(x_0)\, P_0(x)\, \mathrm{e}^{-\mathrm{i}pU(x)+\mathrm{i}pU(x_0)}. \tag{10}$$

Finally, extending the partition function (4) to complex inverse temperature we obtain in a compact manner a general long time expression for the characteristic function

$$\langle \mathrm{e}^{-\mathrm{i}pQ(\infty)} \rangle = \frac{|Z(\beta + \mathrm{i}p)|^2}{Z(\beta)^2}; \tag{11}$$

note that $\langle \mathrm{e}^{-\mathrm{i}pQ(\infty)} \rangle_{p=0} = 1$ ensuring the normalization condition $\int \mathrm{d}Q\, P(Q,\infty) = 1$.

At low temperature the partition function predominantly samples the local minima in U and we obtain inserting the asymptotic expression (6) generalized to complex inverse temperature the low temperature–long time expression for the characteristic function

$$\langle \mathrm{e}^{-\mathrm{i}pQ(\infty)} \rangle = \left[\frac{\beta^2}{\beta^2 + p^2} \right]^{1/2} \frac{\sum_{ij} (k_i k_j)^{-1/2} \exp(-\beta(U_i + U_j)) \exp(-\mathrm{i}p(U_i - U_j))}{\sum_{nm} (k_n k_m)^{-1/2} \exp(-\beta(U_n + U_m))}. \tag{12}$$

First, we note again that $\langle \mathrm{e}^{-\mathrm{i}pQ(\infty)} \rangle_{p=0} = 1$ yielding the normalization of $P(Q,\infty)$, moreover, the phase factors $\exp(-\mathrm{i}p(U_i - U_j))$ can according to (9) be absorbed in a shift of Q. The interesting aspect resides in the prefactor $(\beta^2 + p^2)^{-1/2}$ which has branch points in the complex p plane at $p = \pm\, \mathrm{i}\beta$.

By inspection of (9) and (12) we note that for small Q relative to $U_i - U_j$ the integral in (9) is logarithmically divergent for large p since $(\beta^2 + p^2)^{-1/2} \sim p^{-1}$, implying a logarithmically divergent contribution to $P(Q,\infty) \equiv P_0(Q)$, i.e. $P_0(Q) \sim -\log|Q - (U_i - U_j)|$. For large $|Q|$, i.e. the tails of the distribution $P_0(Q)$, we sample the small p region in (9) and (12), and closing the contour in the upper half plane (lower half plane) for $Q > 0$ ($Q < 0$) and picking up the branch point contribution $p = \mathrm{i}\beta$ ($p = -\mathrm{i}\beta$) we obtain the dominant exponential tails $P_0(Q) \sim \exp(-\beta|Q|)$.

However, using the well-known identity [32]

$$\int_0^\infty \mathrm{d}x \frac{\cos ax}{(b^2 + x^2)^{1/2}} = K_0(ab), \tag{13}$$

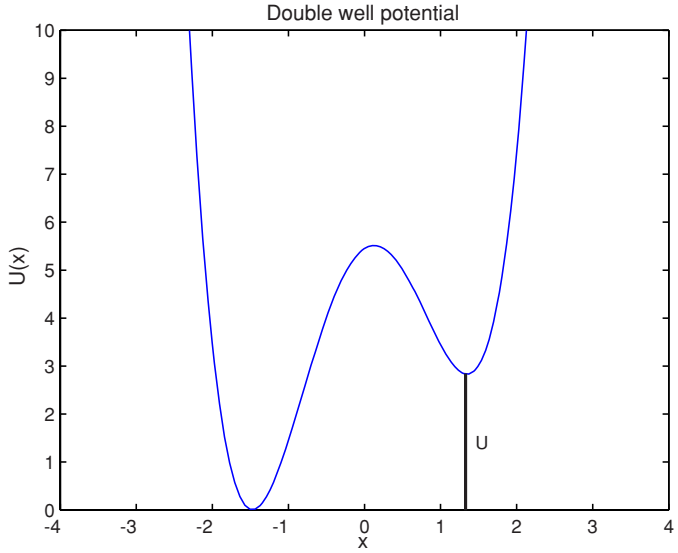

Figure 1. Double well potential with gap U (arbitrary units).

where $K_0(x)$ is a Bessel function of the second kind, it is easy to derive an explicit expression for the heat distribution function. We have

$$P_0(Q) = \frac{\beta}{\pi} \frac{\sum_{ij} (k_i k_j)^{-1/2} \, \mathrm{e}^{-\beta(U_i+U_j)} K_0(\beta|Q-(U_i-U_j)|)}{\sum_{nm} (k_n k_m)^{-1/2} \, \mathrm{e}^{-\beta(U_n+U_m)}}. \tag{14}$$

Using the identity $\int \mathrm{d}x \, K_0(x) = \pi$ following from (13) we confirm the normalization condition $\int \mathrm{d}Q \, P_0(Q) = 1$. For small argument $K_0(x) \sim -\log(x)$ and we obtain for $Q \sim U_i - U_j$

$$P_0(Q) \approx -\frac{\beta}{\pi} \frac{(k_i k_j)^{-1/2} \, \mathrm{e}^{-\beta(U_i+U_j)}}{\sum_{nm} (k_n k_m)^{-1/2} \, \mathrm{e}^{-\beta(U_n+U_m)}} \log|Q-(U_i-U_j)|, \tag{15}$$

showing that $P_0(Q)$ exhibits a multi-band structure of log divergent peaks at $Q = U_i - U_j$ in agreement with our qualitative discussion. For large argument $K_0(x) \sim (\pi/2x)^{1/2} \exp(-x)$, and we obtain the exponential tails $P_0(Q) \sim Q^{-1/2} \exp(-\beta|Q|)$, including the prefactor $Q^{-1/2}$.

Equation (14) is the main result of this paper. Now we apply (14) to a specific case. In the case of the double-well potential depicted in figure 1 with two minima, the second minimum with gap U, we obtain from (12) the characteristic function

$$\langle \mathrm{e}^{-\mathrm{i}pQ(\infty)} \rangle = \left[\frac{\beta^2}{\beta^2+p^2} \right]^{1/2} \left[1 + 2 \left(\frac{k_1}{k_2} \right)^{1/2} \mathrm{e}^{-\beta U} (\cos pU - 1) \right], \tag{16}$$

yielding the heat distribution function

$$\begin{aligned} P_0(Q) = {} & \frac{\beta}{\pi} \left[1 - 2 \left(\frac{k_1}{k_2} \right)^{1/2} \mathrm{e}^{-\beta U} \right] K_0(\beta|Q|) \\ & + \frac{\beta}{\pi} \left(\frac{k_1}{k_2} \right)^{1/2} \mathrm{e}^{-\beta U} (K_0(\beta|Q-U|) + K_0(\beta|Q+U|)). \end{aligned} \tag{17}$$

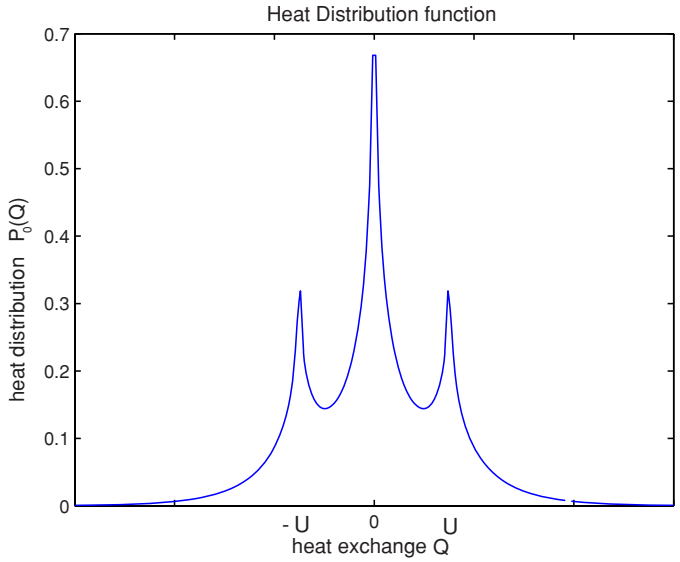

Figure 2. Heat distribution function pertaining to a double well potential with gap U. The spectrum shows a central peak at $Q = 0$ and two side bands at $Q = \pm U$ (arbitrary units).

In figure 2 we have shown the heat distribution function $P_0(Q)$ as a function of heat transfer Q for the parameter values $k_1 = k_2 = 1$, $\beta = 1$ and $U = 1.5$.

The interpretation of the log divergent multi-band structure in the heat distribution function in the low temperature–long time limit is easy. From the work of Imparato *et al* [6], see also the work of van Zon *et al* [23], it is well-known that the heat distribution function for a static harmonic potential is given by the Bessel function $K_0(\beta|Q|)$ exhibiting a log divergence at zero heat transfer $Q \sim 0$; for large Q the distribution falls off according to the Boltzmann factor $\exp(-\beta|Q|)$. For a general potential possessing several minima these features seem to persist. Each minima in the potential acts like a local reservoir where the particle at low temperature can be trapped for a long time before making a Kramers transition to another well. Since the transfer between the potential well with gap U_i to the well with gap U_j involves the energy difference $U_i - U_j$, the divergent band appear at heat transfer $Q = U_i - U_j$. It also follows from (15) that the contributions are weighted with the corresponding Boltzmann factors.

In the case of the double well potential depicted in figure 1 with a well with zero gap and a well with gap U the discussion is particularly transparent. At low temperature the particle is for most of the time trapped in the zero gap well yielding the log divergent behavior for zero heat transfer. Occasionally, the particle makes a Kramers transition to the well with gap U and becomes trapped yielding log divergent peaks at $Q \sim \pm U$. The side bands originating from the well with the gap are down by the Boltzmann factor $\exp(-\beta U)$. The sum rule (normalization) $\int \mathrm{d}Q\, P_0(q) = 1$ implies that the total integrated strength is constant. We also note that for the case of a vanishing gap $U = 0$, i.e. for two gapless wells, we recover the result $P_0(Q) = (\beta/\pi)K_0(\beta|Q|)$, independent of the spring constant [6].

In order to model a double well potential in more detail we have used the fourth-order polynomial

$$U(x) = \mathrm{d}x^4 + 4Ux^3 + \left(\frac{9U^2}{2d} - \frac{d}{2}\right)x^2, \tag{18}$$

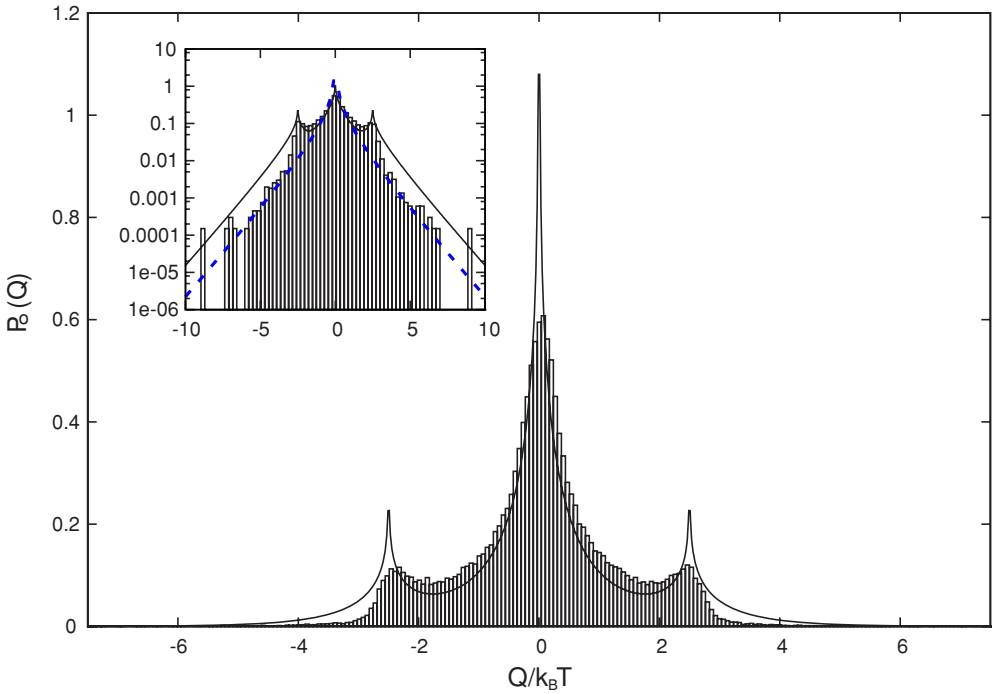

Figure 3. Analytical solution (17) (full line), and heat distribution (histogram) as obtained by numerical solution of the Langevin equation (10^5 independent trajectories, with $t_0 = 0$, $t = 10$), for the potential in (18) with $d = 15$, $U = 2.5$, $\beta = 1$. Inset: heat distribution in a log-linear scale. Dashed lines: $|Q|^{-3/4} \exp(-\beta|Q|)$.

which has a gap U, minima located at $x = -(3U/2d) \pm 1/2$ and spring constants $k = 2(d \pm 3U)$. Choosing $\beta = 1$, $U = 2.5$ and $d = 15$ we have in figure 3 depicted the analytical expression (17) together with a numerical solution of the Langevin equation (10^5 independent trajectories, with $t_0 = 0$, $t = 10$).

Finally, we derive a general expression for the large $|Q|$ behavior of the heat distribution function $P_0(Q)$. For large $|Q|$, corresponding to large heat transfer to the heat bath, we sample the wings of the potential. Considering a general potential U behaving like $U \approx Ax^n$, for large $|x|$, and n even, we obtain for the heat distribution function

$$P_0(Q) \propto \int \mathrm{d}x_1 \, \mathrm{d}x_2 \, \mathrm{e}^{-\beta(U_1+U_2)} \delta(|Q| - U_1 + U_2), \tag{19}$$

where $U_1 = U(x_1)$ and $U_2 = U(x_2)$. For large $|Q|$ inserting $U \approx Ax^n$ and introducing polar coordinates $x_1 = r\cos\phi$, $x_2 = r\sin\phi$ we have, using the delta function to eliminate r,

$$P_0(Q) \propto \int r \, \mathrm{d}r \, \mathrm{d}\phi \, \mathrm{e}^{-\beta|Q|F(\phi)} \delta(|Q| - Ar^n(\cos^n\phi - \sin^n\phi)), \tag{20}$$

where $F(\phi) = (1 + \tan^n\phi)/(1 - \tan^n\phi)$. For large Q the integral is dominated by the minima of F for $\phi = 0$ and $\phi = \pi$. Expanding about the minima to second order, $F \approx 1 - 2(\delta\phi)^n$, performing the Gaussian integrals and the r-integration over the delta function in (20) we obtain the distribution function for large $|Q|$

$$P_0(Q) \propto |Q|^{1/n-1} \, \mathrm{e}^{-\beta|Q|}. \tag{21}$$

This is a general result. Here $e^{-\beta|Q|}$ is a Boltzmann factor associated with the heat transfer Q whereas the prefactor $|Q|^{1/n-1}$ is a 'density of states' contribution. For $n = 2$ we obtain the previous Bessel result, $P_0(Q) \approx |Q|^{-1/2} \exp(-\beta|Q|)$, pertaining to the harmonic approximation, and for $n = 4$, corresponding to the double well model potential (18), we have $P_0(Q) \approx |Q|^{-3/4} \exp(-\beta|Q|)$. In the inset in figure 3 we have depicted the heat distribution in a log-linear scale. The dashed line corresponds to $P_0(Q) \propto |Q|^{-3/4} \exp(-\beta|Q|)$.

Regarding the numerical simulation of the double well heat distribution and the comparison with the analytical result, we note that the divergent peak structure in (17) arises from a saddle point analysis only valid in the vicinity of the peaks whereas the simulation samples the whole potential; given the statistics of the simulation we believe that the agreement is good. We, moreover, find a good agreement with the expression (21) for the tails of the distribution (the dashed line in the inset in figure 3).

In this paper we have generalized the result for the heat distribution function for a harmonic potential to the case of a general static potential with several minima in the long time–low temperature limit. Our analysis shows that the gap structure of the potential wells gives rise to a multi-band structure of log divergent peaks in the heat distribution function. We have, moreover, derived a general result for the tails of the heat distribution function.

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