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Lowest nonzero eigenvalue of the diffusion equation for a Brownian particle in a symmetric double well with low friction

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Abstract
In this work a particle undergoing Brownian motion in a symmetric double well is considered, in the limit of low frictional forces, and small temperature. It is assumed that the particle fluctuations over equilibrium are governed by a second-order diffusion equation, in which the drift velocity solves a HJY equation, while the diffusion coefficient is determined from the stationary condition. The excited state is constructed by imposing suitable boundary conditions at the saddle point by means of an integral equation which is solved to a first approximation by iteration, in the limit of high barrier. The result is a complex eigenvalue for the relaxation of the fluctuation, which is interpreted as a damped stochastic resonance. The relation to Kramer's rate is discussed.

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1. Introduction

This work aims at the calculation of the longest relaxation time for a probability density fluctuation over the equilibrium state of a Brownian particle in a symmetric double well, in the low-friction limit and small temperature. This problem had been considered previously in [1, 2] by approximate methods, which proceed by expansion of the potential energy function in powers of the inverse of the distance between the wells. By the approximate procedure it was found that a canonical distribution of probability density satisfies the equilibrium condition over the whole range of parameters, from high to low values of frictional coefficient β (for that particular model potential).

In the present calculation we assume that the transition probability density distribution of the system satisfies a second-order diffusion equation, and therefore the diffusion coefficient is evaluated from the given drift velocity and the assumed canonical configurational equilibrium

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distribution. From this assumed equilibrium distribution the lowest nonvanishing eigenvalue is obtained in the limit of small temperature by imposing suitable conditions at the boundary between the two wells, following an integral equation method introduced by us in previous work [3–6]. The boundary conditions at the saddle point correspond to an antisymmetric eigenfunction. Consequently, this probability density function (pdf) separates into two equilibrium distributions with opposite signs in the limit of high barrier, and infinite separation. The eigenvalue obtained in this way is the upper value resulting from the splitting of the equilibrium one-well distribution into a symmetric and an antisymmetric probability distribution function.

The expansion of the drift velocity was obtained in [7] in powers of β, for the singular solution [8] to the Hamilton–Jacobi–Yasue (HJY) equation, which is independent of time (see also [2]). The HJY is the low-temperature limit of the Hamilton–Jacobi–Yasue–Riccati (HJYR) equation. This is the Hamilton–Jacobi equation of classical mechanics, supplemented with two terms which take into account frictional effects (Yasue), and an average interaction energy with the random field (Riccati). This term is temperature-dependent and vanishes in the limit of zero temperature, thus yielding a sort of BKW (Brillouin–Kramers–Wentzel) approximation to the problem. The interest of such an approximation is in reducing the order of the equation from second or higher order, to the first.

It has been proved by the present author (see [7] and references therein) that the drift velocity of a general stochastic process is bound to satisfy some kind of a HJYR equation. Therefore, in order to compute the drift velocity of a one-dimensional system, we are left with the problem of calculating the solutions to a first-order partial differential equation in two variables, coordinate and time. The solution is here calculated for that value of the energy E, measured from the well bottom, which makes the frictionless term of the expansion singular with respect to t_0 and E, in the sense that both derivatives of the action with respect to E and t_0 vanish. This solution has the property that the momentum in the well bottom vanishes. It is proved, using the results of [2], that this property can be extended under general hypothesis to some finite range of values of β and consequently to the whole region where the β-series applies.

The choice of the solution to the HJY equation to describe the diffusion process is, it has been shown, arbitrary, in the sense that the two-time transition probability density, from some initial configuration onwards, is independent of this choice [9]. However, the asymptotic equation for large time will be strongly dependent upon this choice, and therefore the asymptotic description of fluctuations over the equilibrium state will be different, according to different choices. Consequently, boundary conditions must be chosen in conformity with the drift velocity [9]. If this requirement is fulfilled, the asymptotic equation has the meaning explained in [9].

It has been shown there that the diffusion operator obtained by using the singular solution is free from initial data (for appropriate choice of boundary conditions); consequently, the asymptotic equation properly describes the evolution of fluctuations over the equilibrium state [7], in the asymptotic regime [7, 9]. It manifests the fact that, being independent of initial parameters, the asymptotic equation is most suitable to describe statistical ensembles of randomly distributed particles.

This paper is organized as follows. Section 2 derives the parameters of the diffusion equation of second order which governs the evolution of the physical process. Section 3 shows how the stationary equilibrium distribution function can be modified so as to satisfy the required conditions at the boundary. Section 4 shows that the eigenvalue of the pdf modified through boundary conditions is independent of the relevant integration parameter of the associated integral equation. This allows us (see section 6) to obtain the best choice of that parameter in order to optimize the convergence of the expanded solution of the integral equation. Section 5 shows how an expression for the eigenvalue k is obtained from boundary conditions applied to the integral equation for the pdf. Section 6 shows how to select the leading terms of the eigenvalue k in the limit of low temperature, and evaluates this result, in terms of the zeroth-order action $\varphi^{(0)}$. The nontrivial statement is proved which warrants that the action $\varphi(q_m)$, where $\varphi(q)$ is a singular solution to the HJY equation, vanishes at a minimum point of the potential energy, from which the energy is computed. This allows us to obtain an explicit expression for the complex eigenvalue k, valid in the limit of small temperature, which is the main result of this paper. Section 7 compares this result with the Kramer rate, which shows a different temperature dependence in the prefactor, and moreover comparison is made with results obtained by the flux-over-population method, which are similar to the present ones. These calculations are reproduced in detail in the appendix.

2. Solving the equations of motion for low values of frictional coefficient

The HJY equation for a classical Newtonian particle evolving in a potential $U(q)$, with energy E, is written [7, 10]

$$\frac{1}{2m}\left(\frac{\partial\varphi}{\partial q}\right)^2 + U(q) + \beta\varphi(q) = E \tag{2.1}$$

where q denotes the spatial coordinate, m the mass, β the frictional coefficient and $\varphi(q, E)$ is the action. The energy E has been split from the additional constant in $\varphi(q)$ because it remains finite in equation (2.1) when $\beta \to 0$. It is the energy evaluated at those points where $\beta\varphi(q)$ vanishes.

Since it is assumed that $\varphi(q)$ has no poles as $\beta \to 0$, equation (2.1) can be solved by a power expansion in β. By the change of variables

$$\frac{\partial\varphi}{\partial q} = \frac{1}{z} \tag{2.2}$$

the two leading terms of the expansion are [7]

$$z_0(q) + \beta z_1(q) = \frac{\pm 1}{\sqrt{2m(E - U(q))}} + \frac{\beta}{2(E - U(q))^{3/2}} \int^q \mathrm{d}\eta (E - U(\eta))^{1/2}. \tag{2.3}$$

For $\beta = 0$, equation (2.3) represents in implicit form the law of the motion, since it yields the momentum $p = m\dot{q}$ as a function of coordinate q, for a fixed value of energy E. For small values of β, it expands around that trajectory by adding the small corrections due to frictional forces.

For particular values of initial conditions (here represented by E and the corresponding coordinate t_0, see equations (6.4)–(6.4′)) the first term of equation (2.3) yields a singular solution, which has a characteristic curve in common with every integral surface.

By taking the inverse of equation (2.3) it is obtained

$$\begin{aligned}\frac{1}{m}p(q) &= \frac{1}{mz_0(q)} - \frac{\beta}{m}\frac{z_1(q)}{z_0(q)^2} + O(\beta^2)\\ &= \pm\sqrt{\frac{2}{m}(E - U(q))} - \frac{\beta}{(E - U(q))^{1/2}} \int^q \mathrm{d}\eta (E - U(\eta))^{1/2} + O(\beta^2).\end{aligned} \tag{2.4}$$

The second term of this expansion yields precisely that modification of the first one which results from the variation of energy due to dissipation to first order in β. Higher corrections may be evaluated in the same way. Consequently, the solution modified by addition of these frictional terms will reproduce the whole damped trajectory.

The diffusion equation follows from the choice of a particular *p(q)*

$$\left[\frac{\partial^2}{\partial q^2}D(q) - \frac{1}{m}\frac{\partial}{\partial q}p(q)\right]P(q,t) = \frac{\partial P}{\partial t} \tag{2.5}$$

for the two-time transition probability density. Equation (2.5) is an asymptotic equation, valid in the limit $t - t_0 \to \infty$, where t_0 is the initial time of preparation [7, 9]. Here we assume, besides the validity of (2.5), that the stationary equilibrium distribution of probability density is

$$P_e(q) \propto \exp\left\{-\frac{U(q)}{T}\right\} \tag{2.6}$$

where T is the temperature. This yields

$$D(q) = \mathrm{e}^{U(q)/T}\int^q \mathrm{d}\eta \frac{1}{m}p(\eta)\,\mathrm{e}^{-U(\eta)/T} \cong -\frac{1}{m}\left[\frac{Tp(q)}{U'(q)} + \frac{T^2p'(q)}{U'(q)^2}\right] \tag{2.7}$$

where the prime denotes derivatives over the spatial coordinates.

The calculation of the diffusion coefficient from the equations of motion has been carried out in [2] according to our procedure [11], by splitting the velocity into a drift plus a diffusive component. That calculation was only applicable to systems with high or moderate values of frictional coefficient. A more extended calculation including small frictional forces was made in [1], for a similar model potential, to first order in the parameters of nonlinearity only, and the results were found consistent with equation (2.7).

The separation of the velocity into two components is in principle arbitrary, as explained in previous [2, 7, 9], except that the drift must satisfy a Hamilton–Jacobi–Yasue–Riccati equation, in order to eliminate the memory term in the averaged diffusion equation. The choice of the singular solution of the above-mentioned equation is motivated by the following arguments:

(i) the singular solution is the natural extension of the usual drift term which is admitted in the most common forms of diffusion equations. See, for this purpose, [2], section 1, 3.
(ii) The singular solution allows the asymptotic form of the diffusion operator to retain a physical significance, as a generator of the 2-point transition probability density in the asymptotic state, for appropriate initial conditions. See, for example, [9], section 5.
(iii) Supposing the supersystem composed by particle plus bath to be in a stationary time-invariant state (which requires that the eigenvalue of the corresponding phase-space density is zero), then the phase average of any function of particle variables is time-independent. This requires that the diffusion operator is independent of time. This meets also the requirements of point (ii).

The choice of the singular solution of the HJYR equation to represent the drift is not invalidated by the fact that this function of position is often complex-valued. In fact the total velocity, given by the sum of two components, is generally real-valued, at least in the asymptotic regime, because the force is real. It follows that the two-point transition pdf is real-valued. See for this purpose the explicit calculations in [9].

The use of a second-order diffusion operator should not introduce any additional constraint on the process under study, since it has been proved in [2] that higher-order operators are not uniquely defined.

We stress the fact that, although the resulting equations strongly resemble the quantum-mechanical evolution equations for the two-point transition probability density, the stochastic process under study is purely classical. The low-temperature limit has the advantage of making the calculations more expedient, and of making the comparison easier with earlier results of numerous authors [16]. This comparison shows that the present equations lead to results in agreement with those obtained by conventional methods based upon classical assumptions.

The main difference with a quantum-mechanical diffusion process is, in my opinion, the strong dependence of the diffusion coefficient (2.7) upon the potential energy function, which is necessary in order that the equilibrium pdf should be a projected canonical distribution, given by equation (2.6).

3. Satisfying boundary conditions through an integral equation

The solution to equation (2.5) given by equation (2.6) generates new solutions to the eigenvalue problem through the integral equation [4]

$$P_k(q) = P_e(q) - k\int_a^q \mathrm{d}\eta \frac{P_e(q)}{D(\eta)P_e(\eta)}\int_b^\eta \mathrm{d}\varsigma\ P_k(\varsigma) \tag{3.1}$$

which satisfy

$$\frac{\partial P_k}{\partial t} = -kP_k(q,t). \tag{3.2}$$

The constants a and b are chosen so as to satisfy the proper boundary conditions at the points $q = a$ and $q = b$. Varying the constant a merely changes normalization, while b is related to the derivative at the point $q = a$. The value of the function $P_k\,(q)$ at any point $q = c$ allows us to transform equation (3.1) into an equation for the eigenvalue k. Putting $c = \hat{q}$ we find

$$P_k(\hat{q}) = P_e(\hat{q}) - k\int_a^{\hat{q}} \mathrm{d}\eta \frac{P_e(\hat{q})}{D(\eta)P_e(\eta)}\int_b^\eta \mathrm{d}\varsigma\ P_k(\varsigma) \tag{3.3}$$

from which k may be evaluated as a function of boundary conditions at the point $\hat{q}$. Putting $b = -\infty$ implies that the flux of particles vanishes for $q \to -\infty$.

4. The effect of the variation of the constant *a* on the eigenvalue

Equation (3.3) may be expanded yielding the identity

$$\begin{aligned}
P_k(\hat{q}) = {}& P_e(\hat{q})\left[1 - k\int_a^{\hat{q}} \frac{\mathrm{d}\eta}{D(\eta)P_e(\eta)}\int_{-\infty}^\eta \mathrm{d}\varsigma\ P_e(\varsigma) + k^2\int_a^{\hat{q}} \frac{\mathrm{d}\eta}{D(\eta)P_e(\eta)}\int_{-\infty}^\eta \mathrm{d}\varsigma\ P_e(\varsigma)\right.\\
&\left.\times\int_a^{\varsigma} \frac{\mathrm{d}\eta_1}{D(\eta_1)P_e(\eta_1)}\int_{-\infty}^{\eta_1} \mathrm{d}\varsigma_1\ P_e(\varsigma_1) - \cdots\right]\\
= {}& P_e(\hat{q})\left[1 - k\int_d^{\hat{q}} \frac{\mathrm{d}\eta}{D(\eta)P_e(\eta)}\int_{-\infty}^\eta \mathrm{d}\varsigma\ P_e(\varsigma) + k^2\int_d^{\hat{q}} \frac{\mathrm{d}\eta}{D(\eta)P_e(\eta)}\right.\\
&\left.\times\int_{-\infty}^{\eta} \mathrm{d}\varsigma\ P_e(\varsigma)\int_d^{\varsigma} \frac{\mathrm{d}\eta_1}{D(\eta_1)P_e(\eta_1)}\int_{-\infty}^{\eta_1} \mathrm{d}\varsigma_1\ P_e(\varsigma_1) - \cdots\right]\\
&\times\left[1 - k\int_a^d \frac{\mathrm{d}\eta}{D(\eta)P_e(\eta)}\int_{-\infty}^\eta \mathrm{d}\varsigma\ P_k(\varsigma)\right].
\end{aligned} \tag{4.1}$$

Equating the above expression to zero, and putting $\hat{q} \neq d$, it follows that

$$\begin{aligned}
&P_e(\hat{q})\left[1 - k\int_a^{\hat{q}} \frac{\mathrm{d}\eta}{D(\eta)P_e(\eta)}\int_{-\infty}^\eta \mathrm{d}\varsigma\ P_{k,a}(\varsigma)\right]\\
&\quad = P_e(\hat{q})\left[1 - k\int_d^{\hat{q}} \frac{\mathrm{d}\eta}{D(\eta)P_e(\eta)}\int_{-\infty}^\eta \mathrm{d}\varsigma\ P_{k,d}(\varsigma)\right] = 0
\end{aligned} \tag{4.2}$$

where the additional subscript in the distribution function P_k denotes the lower limit of the integral in the integral equation (3.1), which defines $P_k\,(q)$.

Consequently, by expanding the two alternative expressions (4.2), it follows that the difference between the two first-order approximants obtained by substituting P_e either for $P_{k,a}$ or $P_{k,d}$, is removed into the higher-order terms.

5. Evaluation of the eigenvalue *k*

It is supposed from now on that $U(q) - E \geqslant 0$ in the whole interval of definition in which we are interested. Then from equations (2.3), (2.6), (4.2) it is obtained, using (2.7) in the small temperature limit,

$$
\begin{aligned}
k^{-1} = -m \int_d^{\hat{q}} \mathrm{d}y \frac{U'(y)}{Tp(y)} \exp(U(y)/T) \int_{-\infty}^{y} \mathrm{d}z \exp(-U(z)/T) \\
&= \pm \mathrm{i}\sqrt{\frac{m}{2\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \int_d^{\hat{q}} \mathrm{d}y \frac{U'(y)}{T} \exp((U(y) - E)(1 - Tx^2)/T) \\
&\quad \times \int_{-\infty}^{y} \mathrm{d}z \exp(-(U(z) - E)/T) \\
&\quad + \frac{m\beta}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \int_d^{\hat{q}} \mathrm{d}y \frac{U'(y)}{T} x^2 \exp((U(y) - E)(1 - Tx^2)/T) \\
&\quad \times \int_d^{y} \mathrm{d}z\, (U(z) - E)^{1/2} \int_{-\infty}^{y} \mathrm{d}w \exp(-(U(w) - E)/T) \\
&= \pm \mathrm{i}\sqrt{\frac{m}{2\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \frac{\exp((U(\hat{q}) - E)(1 - Tx^2)/T)}{1 - Tx^2} \int_{-\infty}^{\hat{q}} \mathrm{d}z \exp(-(U(z) - E)/T) \\
&\quad \mp \mathrm{i}\sqrt{\frac{m}{2\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \frac{\exp((U(d) - E)(1 - Tx^2)/T)}{1 - Tx^2} \int_{-\infty}^{d} \mathrm{d}z \exp(-(U(z) - E)/T) \\
&\quad \mp \mathrm{i}\sqrt{\frac{m}{2\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \int_d^{\hat{q}} \mathrm{d}y \frac{\exp(-(U(y) - E)x^2)}{1 - Tx^2} \\
&\quad + \frac{m\beta}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \frac{x^2 \exp((U(\hat{q}) - E)(1 - Tx^2)/T)}{1 - Tx^2} \\
&\quad \times \int_d^{\hat{q}} \mathrm{d}z (U(z) - E)^{1/2} \int_{-\infty}^{\hat{q}} \mathrm{d}w \exp(-(U(w) - E)/T) - \frac{m\beta}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \\
&\quad \times \int_d^{\hat{q}} \mathrm{d}y \frac{x^2 \exp((U(y) - E)(1 - Tx^2)/T)}{1 - Tx^2} (U(y) - E)^{1/2} \\
&\quad \times \int_{-\infty}^{y} \mathrm{d}w \exp(-(U(w) - E)/T) \\
&\quad - \frac{m\beta}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \int_d^{\hat{q}} \mathrm{d}y \frac{x^2 \exp(-(U(y) - E)x^2)}{1 - Tx^2} \int_d^{y} \mathrm{d}z (U(z) - E)^{1/2}. \qquad (5.1)
\end{aligned}
$$

In the above equation we interpret the integral over dx as the principal part.

6. Symmetric double well

Consider now a symmetric double well of any shape whatsoever with boundaries where $U(q)$ goes to infinity. Take as $q = \hat{q}$ the coordinate of the saddle point. Then the boundary condition (4.2) defines that probability distribution function which is antisymmetric around the midpoint of coordinate $\hat{q}$. From equation (5.1) it is clear that

$$
\begin{aligned}
k^{-1} \cong \pm \mathrm{i}\sqrt{\frac{m}{2\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \frac{\exp((U(\hat{q}) - E)(1 - Tx^2)/T)}{1 - Tx^2} \int_{-\infty}^{\hat{q}} \mathrm{d}z \exp(-(U(z) - E)/T) \\
+ \frac{m\beta}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \frac{x^2}{1 - Tx^2} \exp((U(\hat{q}) - E)(1 - Tx^2)/T) \int_d^{\hat{q}} \mathrm{d}z (U(z) - E)^{1/2}
\end{aligned}
$$

$$\times \int_{-\infty}^{\hat{q}} \mathrm{d}w \exp(-(U(w)-E)/T) - \frac{m\beta}{\sqrt{\pi}} \int_{-\infty}^{+\infty} \mathrm{d}x \frac{x^2}{1-Tx^2}$$
$$\times \int_{d}^{\hat{q}} \mathrm{d}y \exp((U(y)-E)(1-Tx^2)/T)(U(y)-E)^{1/2}$$
$$\times \int_{-\infty}^{y} \mathrm{d}w \exp(-(U(w)-E)/T) \tag{6.1}$$

the omitted terms being $O(\exp(-U(\hat{q})/T))$ with respect to those which are retained. Now, if $U(y) < U(\hat{q})$ for $d \leqslant y < \hat{q}$, it can also be ascertained that the last term in equation (6.1) can be neglected in the limit of small temperature, with respect to the remaining two terms.

Proof.

$$\left|\int_{d}^{\hat{q}} \mathrm{d}y \frac{\exp((U(y)-E)(1-Tx^2)/T)}{1-Tx^2}(U(y)-E)^{1/2} \int_{-\infty}^{y} \mathrm{d}w \exp(-(U(w)-E)/T)\right|$$
$$< \left|\frac{\exp((U(\hat{q})-E)(1-Tx^2)/T)}{1-Tx^2}\right.$$
$$\times \int_{d}^{\hat{q}} \mathrm{d}y \exp((U(y)-U(\hat{q}))(1-Tx^2)/T)(U(y)-E)^{1/2}$$
$$\left.\times \int_{-\infty}^{\hat{q}} \mathrm{d}w \exp(-(U(w)-E)/T)\right| \tag{6.2}$$

where the first integral on the rhs is infinitesimal with $T \to 0$ and $|x| < \frac{1}{\sqrt{T}}$. By comparing this result with the second term on the rhs of equation (6.1), it follows that the expression above can be safely neglected for T sufficiently small and $|x| < \frac{1}{\sqrt{T}}$. Consequently, also the integral over $\mathrm{d}x$ of the same expression can be neglected as $T \to 0$, because the major contribution to the integral over $\mathrm{d}x$ comes from the region where $|x| < \frac{1}{\sqrt{T}}$, for both expressions in the second row and in the third row of the rhs of equation (6.1).

In the case that $U(y) - U(\hat{q})$ is a smooth function which can be conveniently expanded around $\hat{q}$ in powers of $y - \hat{q}$, the assertion follows by analytical calculation. Thus after collecting terms it is obtained

$$k^{-1} \cong \pm \mathrm{i}\sqrt{\frac{m}{2}} \int_{-\infty}^{\hat{q}} \mathrm{d}z \exp(-(U(z)-E)/T) \frac{\exp((U(\hat{q})-E)/T)}{\sqrt{U(\hat{q})-E}}$$
$$\times \left[1 - \frac{\beta}{2} \frac{\varphi^{(0)}(\hat{q}) - \varphi^{(0)}(d)}{U(\hat{q})-E}\right] \tag{6.3}$$

where

$$\varphi^{(0)}(q) = \pm\sqrt{2m} \int^{q} \mathrm{d}\eta \sqrt{E-U(\eta)} \tag{6.3$'$}$$

is the coordinate part of the action evaluated in the limit of zero frictional forces. The expression which has been calculated is exact to leading order in the low-temperature limit.

There remain to be defined the values of the constants E and d which appear in the equations (6.3), (6.3$'$). The two following equations will make sure that $f(q, t - t_0, E)$ is a singular solution with respect to both parameters E and t_0:

$$\frac{\partial f}{\partial t_0} = E \exp(-\beta(t-t_0)) = 0 \tag{6.4}$$

$$\frac{\partial f}{\partial E} = \pm\sqrt{\frac{m}{2}} \int_{d}^{q} \frac{\mathrm{d}\eta}{\sqrt{E-U(\eta)}} + \frac{\exp(-\beta(t-t_0)) - 1}{\beta} + O(\beta) = 0 \tag{6.4$'$}$$

or

$$t - t_0 = -\frac{1}{\beta}\ln\left[1 \mp \beta\sqrt{\frac{m}{2}}\int_d^q \frac{\mathrm{d}\eta}{\sqrt{E - U(\eta)}}\right] + O(\beta). \tag{6.4$''$}$$

In the above equations $f(q, t - t_0, E)$ is the action:

$$f(q, t - t_0, E) = \varphi(q, E) - E\frac{1 - \exp(-\beta(t - t_0))}{\beta}. \tag{6.5}$$

Therefore, making $E \to 0$, it follows that $d \to q_m$ also (see equations (6.6), (6.7)). Consequently, provided that $U(q)$ is smooth around q_m endowed with nonvanishing second derivative, and β sufficiently small, $t - t_0 \to \mp\mathrm{i}\infty$. This extends to general unidimensional systems the result proved in [7] for linear systems with vanishing friction.

We now prove the assertion made above.

Fixing the zero of the energy scale in the well bottom with coordinate q_m yields

$$U(q_m) = 0 \tag{6.6}$$

which, together with (6.4), bears to the consequence that $\varphi(q, 0)$ is a solution of the coordinate type [2] at the point q_m, because

$$p'(q_m) = \mp\sqrt{\frac{m}{2}}\frac{U'(q_m)}{\sqrt{-U(q_m)}} + O(\beta) \neq -m\beta. \tag{6.7}$$

This inequality results, provided the first term on the rhs is nonzero as a limiting value for $q \to q_m$. Property (6.7) obviously holds in the whole domain of convergence of the series. It follows that $p(q_m) = 0$, and consequently, $\varphi(q_m) = 0$ by (2.1), (6.4), (6.6). Therefore we must put $d = q_m$ in equation (5.1), as the lower limit of the integral over dz. The integral over dy in the same equation has been proved to a large extent to be insensitive its lower limit, but it can be proved that the best choice is $d \cong q_m$, because it makes $P_k(q) = P_e(q)$ at the point where this function attains its maximum value, thus optimizing the integral of normalization in the first iteration. It follows

$$k \cong \mp\mathrm{i}\sqrt{\frac{2U(\hat{q})}{m}}\exp(-U(\hat{q})/T)\frac{1 + \beta\varphi^{(0)}(\hat{q})/2U(\hat{q})}{\int_{-\infty}^{\hat{q}}\mathrm{d}z\exp(-U(z)/T)}. \tag{6.8}$$

Equation (6.8) yields the eigenvalue of the diffusion equation (2.5), (2.7), belonging to an eigenfunction of the same equation which describes a fluctuation over the equilibrium state (2.6) [7, 9]. The first term represents a sharp resonance frequency which however describes the oscillations of the probability density, not of the particle itself, which undergoes a stochastic motion. It is expected therefore that the frequency of jumps would match the theoretical mean value after averaging over a large number of jumps, or over an ensemble of many particles non-interacting between them. The second term which is linear in β represents the rate at which the given fluctuation over the stationary equilibrium state fades while oscillating between the two wells.

7. Comments

7.1. Prior results

In [1] the same problem was treated for a particular model potential, where the drift and diffusion terms were evaluated up to first order in the parameter of nonlinearity, thus obtaining the result

$$k = \frac{1}{\pi}\left(\frac{19}{18}\beta - \frac{5}{3}\mathrm{i}\omega_0\right)\exp(-U(\hat{q})/T) \tag{7.1}$$

where the transmission factor is seen to depend uniquely upon the parameters β and the frequency ω_0 in the well bottom. The present result considerably modifies the previous one, by introducing the action $\varphi^{(0)}(\hat{q})$ which, to a quadratic approximation, is equal to $\pm\frac{\mathrm{i}}{2\pi}I(\hat{q})$, where $I(\hat{q})$ is the action as defined, for instance, in [12]. The result obtained in [12] for the rate, which is however a different problem [13], may be written in the present notation

$$k^{(\mathrm{Kr})} \cong \mp\frac{\mathrm{i}}{2}\beta\varphi^{(0)}(\hat{q})\frac{\omega_0}{T}\exp(-U(\hat{q})/T) \tag{7.2}$$

where the superscript refers to Kramer's rate. Thus, evaluating the integral in (6.8) gives the result

$$\mathrm{Re}(k) \cong k^{(\mathrm{Kr})}\sqrt{\frac{T}{4\pi U(\hat{q})}}. \tag{7.3}$$

Kramer's rate may be evaluated in the present context by the flux-over-population method [16], by assuming that it is equally applicable to systems in the underdamped regime, provided the stationary solution of the diffusion equation, which carries a constant flux, is known. The result is similar in form to equation (5.1), except for boundary conditions, which, generally speaking, only affect the result by a numerical factor. It is remarkable that essentially the same result is obtained by making use of Adelman and Garrison's equation in the asymptotic form for large time ([17], equation (3.3), see also [9]): in order to compare the results the phases of the trigonometric functions must increase monotonically with time (see the appendix). Consequently, we suggest that the different form of the pre-exponential factors (transmission coefficients) obtained through the energy-diffusion-limited rate theory, is due to the assumption that the pdf depends only upon the energy, or the action, being independent of the angle. This neglects the asymmetry of the pdf about the well bottom, which is caused by depletion of particles in the escaping region neighbouring the saddle point. This depletion is more pronounced at low temperature and thus causes the decrease in the transmission factor (equation (7.3)).

7.2. *Quantum effects*

The low-temperature limit is here understood in a purely classical fashion. Quantum effects would produce discretization of the levels in the potential well around $q_{m,}$ due to the semiclassical condition that the action $I(q)$ should be an integer multiple of $2\pi\hbar$, the quantum of action. This would produce a departure from the stationary equilibrium distribution (2.6). It is therefore expected that quantum effects would become easily detectable as soon as discretization of the levels was important near the barrier top, that is as the condition

$$I(\hat{q}) \gg 2\pi\hbar \tag{7.4}$$

breaks down. However, since it has been assumed throughout this work that $T \ll U(\hat{q})$, the validity of (2.6) requires the more stringent condition

$$\frac{I(\hat{q})}{2\pi} \gg \frac{T}{\omega_0} \gg \hbar \tag{7.5}$$

where $2\pi T/\omega_0$ is the action of a level of energy T, having assumed that $U(q)$ is smooth around q_m, and $\omega_0 = \sqrt{U''(q_m)/m}$.

In the framework of the interpretation of quantum mechanics as a (classical) diffusion process [14, 15], inequality (7.5) also acquires the following significance: the absolute value of the diffusion coefficient of the quantum diffusion process should be negligible versus the absolute value of the diffusion coefficient, given by equation (2.7), of the diffusive Brownian stochastic process of a particle in a bath at temperature T. In the proximity of the barrier top this requirement yields in the place of (7.5):

$$\frac{T}{\omega(\hat{q})} \gg \hbar \tag{7.6}$$

where use has been made of equation (2.7), and

$$\omega(\hat{q}) = \sqrt{-\frac{U''(\hat{q})}{m}}. \tag{7.7}$$

The equality in equation (7.6) defines the quantum crossover temperature in the low friction limit [16].

7.3. Interpretation

According to our interpretation of the asymptotic diffusion operator [7, 9, 16], the associated propagator represents the transition probability of a pseudo-Markov process whose initial conditions in the remote past are determined from the data at the present instant. It is therefore possible to guess the evolution of a fluctuation over the equilibrium state which is monitored by these data. The eigenvalue that has been computed here yields the time evolution of such a fluctuation, which is shaped so as to make the decaying law purely exponential. Since the diffusion operator conserves the norm, this must vanish at all times. There follows that the physical solution for the normalized probability density must be the linear combination of the equilibrium state probability density, with norm equal to 1, and the given fluctuation.

The possibility of oscillations is a consequence of the fact that the eigenvalue, and therefore the probability density function is complex. The imaginary part of this function determines the subsequent evolution although it is not physically observable [1], like the imaginary part of the voltage in a resonating circuit. In this sense the system has a memory, because its time evolution is not determined uniquely from the real, observable part of its probability density function, but also the imaginary part, which depends upon the evolution in the past, and initial preparation must be taken into account.

The author of this paper, together with Battezzati [1, 2], is confident of having contributed to building up a new approach to the evaluation of the relaxation times of diffusive systems based on the calculation of the lowest eigenvalue of the configurational diffusion equation. This method is equally valuable in the region of small values of frictional coefficient, and in the regions of high or moderate values, and consequently is suitable to explore the turnover region between different regimes. The technique that has been used here, which is based upon an integral equation that allows us to satisfy the prescribed boundary conditions, leads in the first iterate to the evaluation of the mean first-passage time, and is also tightly related to the flux-over-population method. The main interesting feature of this approach is that of using exclusively the configurational diffusive properties of the system, while all the previous approaches were based, as far as we know, on a higher-dimensional diffusion process in phase space including also the velocities, which are important in the low friction limit. The price to pay for this simplification is the extension of the coefficients of evolution equation to the complex domain.

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Appendix. The rate for the truncated harmonic oscillator, by the flux-over-population method

The asymptotic expression for large time of the flux of particles, in Adelman and Garrison's formulation [9, 17] of a diffusion process for a particle in a quadratic potential, is

$$j = -\frac{\omega_0^2 q \sin\omega t}{\frac{1}{2}\beta\sin\omega t + \omega\cos\omega t} P(q,t) - \frac{T}{m}\frac{\sin\omega t}{\frac{1}{2}\beta\sin\omega t + \omega\cos\omega t}\frac{\partial}{\partial q}P(q,t) \tag{A1}$$

from which it is deduced, with the boundary condition $P(\hat{q},t) = 0$ identical with respect to t,

$$P_j(y,t) = -j\frac{\frac{1}{2}\beta\sin\omega t + \omega\cos\omega t}{\sin\omega t}\frac{m}{T}\int_{\hat{q}}^{y} \mathrm{d}q \exp\bigl(m\omega_0^2(q^2 - y^2)/2T\bigr) \tag{A2}$$

where $\omega = \sqrt{\omega_0^2 - \frac{1}{4}\beta^2}$. The fractional slow decrease of $P_j(y,t)$ is therefore calculated from (see [16])

$$\frac{1}{P_j}\frac{\mathrm{d}P_j}{\mathrm{d}t} = -\frac{j}{\int_{-\infty}^{\hat{q}} \mathrm{d}y\, P_j(y,t)} = -k(t) \tag{A3}$$

$$P_j(y,t)^{(t_0)} = P_j(y,t)\exp\left(-\int_{t_0}^{t} k(\tau)\,\mathrm{d}\tau\right). \tag{A4}$$

Therefore

$$k(t) = \frac{T}{m}\frac{\sin\omega t}{\bigl(\frac{1}{2}\beta\sin\omega t + \omega\cos\omega t\bigr)\int_{-\infty}^{\hat{q}}\mathrm{d}y\int_{y}^{\hat{q}}\mathrm{d}q\exp\bigl(m\omega_0^2(q^2 - y^2)/2T\bigr)}. \tag{A5}$$

We now show that, in the limit of vanishing temperature, $k(t) \to k$, a constant number. On putting

$$\frac{\beta}{2\omega_0} = \sin\delta \qquad \frac{\omega}{\omega_0} = \cos\delta \tag{A6}$$

there follows

$$\int_{t_0}^{t}\frac{\sin\omega\tau\,\mathrm{d}\tau}{\frac{1}{2}\beta\sin\omega\tau + \omega\cos\omega\tau} = -\frac{1}{\omega_0^2}\ln\left[\frac{\cos(\omega t - \delta)}{\cos(\omega t_0 - \delta)}\right] + \frac{\beta}{2\omega_0^2}(t - t_0). \tag{A7}$$

Then we compute, to leading order in T

$$\begin{aligned}
&\int_{-\infty}^{\hat{q}}\mathrm{d}q\exp\bigl(m\omega_0^2 q^2/2T\bigr)\int_{-\infty}^{q}\mathrm{d}y\exp\bigl(-m\omega_0^2 y^2/2T\bigr)\\
&\qquad\cong \int_{-\infty}^{\hat{q}}\mathrm{d}q\exp\bigl(m\omega_0^2\hat{q}^2/2T + m\omega_0^2\hat{q}(q - \hat{q})/T\bigr)\sqrt{\frac{2\pi T}{m\omega_0^2}}\\
&\qquad= \sqrt{\frac{2\pi T}{m\omega_0^2}}\frac{T}{m\omega_0^2\hat{q}}\exp\bigl(m\omega_0^2\hat{q}^2/2T\bigr).
\end{aligned} \tag{A8}$$

Therefore

$$\begin{aligned}
\int_{t_0}^{t} k(\tau)\,\mathrm{d}\tau \cong{}& -\sqrt{\frac{m\omega_0^2 q^2}{2\pi T}}\left[\ln\cos(\omega t - \delta) - \ln\cos(\omega t_0 - \delta) - \frac{1}{2}\beta(t - t_0)\right]\\
&\times\exp\bigl(-m\omega_0^2\hat{q}^2/2T\bigr).
\end{aligned} \tag{A9}$$

Next the limit for vanishing temperature of this expression is evaluated. Writing

$$\cos(\omega t - \delta) = |\cos(\omega t - \delta)|\exp(\mathrm{i}n(t)\pi) \tag{A10}$$

where $n(t)$ is a nondecreasing function of t which assumes integer values only, there follows

$$\lim_{\{T\to 0\}}[|\cos(\omega t-\delta)|\exp(\mathrm{i}n(t)\pi)]\exp\left(-m\omega_0^2\hat{q}^2/2T\right)=1\times\exp(\mathrm{i}n(t))\exp\left(-m\omega_0^2\hat{q}^2/2T\pi\right) \tag{A11}$$

everywhere except for isolated points where $\omega t=\left(n+\frac{1}{2}\right)\pi+\delta$.

As $T\to 0$ the exponent on the rhs of the above equation can be conveniently approximated by a smooth function

$$\omega(t-t_0)\exp\left(-m\omega_0^2\hat{q}^2/2T\right)\approx n(t)\exp\left(-m\omega_0^2\hat{q}^2/2T\right)\pi.$$

It follows

$$\int_{t_0}^{t}k(\tau)\,\mathrm{d}\tau\cong-\sqrt{\frac{m\omega_0^2\hat{q}^2}{2\pi T}}\left(\mathrm{i}\omega-\frac{1}{2}\beta\right)(t-t_0)\exp\left(-m\omega_0^2\hat{q}^2/2T\right)=k(t-t_0) \tag{A12}$$

which is identical with equation (6.8), upper sign (the lower sign can be obtained by reversing the phases).

We clarify now the connection with the procedure adopted in this paper. From Hamilton's principal function for the harmonic oscillator [18]:

$$f(q,q_0,t)=\frac{1}{2}m\left[q^2\left(\omega\cot\omega t-\frac{1}{2}\beta\right)+q_0^2\,\mathrm{e}^{-\beta t}\left(\omega\cot\omega t+\frac{1}{2}\beta\right)-\frac{2\omega qq_0}{\sin\omega t}\,\mathrm{e}^{-\frac{1}{2}\beta t}\right] \tag{A13}$$

the drift velocity (A1) is readily obtained from the stationary condition over q_0, and subsequent elimination of this parameter. The result is

$$f(q,q_0(q,t),t)=-\frac{1}{2}mq^2\frac{\omega_0^2\sin\omega t}{\omega\cos\omega t+\frac{1}{2}\beta\sin\omega t}. \tag{A14}$$

Then the diffusion coefficient follows from equation (2.7).

Consequently, we substitute into (A5) $t=\tau+\mathrm{i}\sigma$, then making $\sigma\to\mp\mathrm{i}\infty$ for stationarity in (A14), it is obtained

$$k(\tau\mp\mathrm{i}\infty)=\frac{1}{\left(\frac{1}{2}\beta\pm\mathrm{i}\omega\right)\int_{-\infty}^{\hat{q}}\mathrm{d}q\int_{-\infty}^{q}\mathrm{d}y\exp\left(m\omega_0^2(q^2-y^2)/2T\right)} \tag{A15}$$

from which, using (A6) and (A8), equation (A12) may be calculated.

References

[1] Battezzati M 1999 *J. Chem. Phys.* **111** 9932
[2] Battezzati M 2003 *J. Phys. A: Math. Gen.* **36** 3725
[3] Battezzati M and Perico A 1981 *J. Chem. Phys.* **75** 886
[4] Perico A and Battezzati M 1981 *J. Chem. Phys.* **75** 4430
[5] Battezzati M and Magnasco V 2001 *J. Chem. Phys.* **114** 3398
[6] Battezzati M and Magnasco V 2002 *J. Phys. A: Math. Gen.* **35** 5653
[7] Battezzati M 1996 *Trends Chem. Phys.* **4** 167
[8] Smirnov V 1981 *Cours de Mathématiques Supérieures* vol 4 (Moscow: Mir) chapter 1
[9] Battezzati M 1996 *J. Chem. Phys.* **105** 6525
[10] Battezzati M 1990 *Can. J. Phys.* **68** 508
[11] Battezzati M 1992 *Phys. Lett.* A **112** 119
[12] Hanggi P, Talkner P and Borkovec M 1990 *Rev. Mod. Phys.* **62** 251
[13] Melnikov V I and Meshkov S V 1986 *J. Chem. Phys.* **85** 1018
[14] Battezzati M 2001 *J. Math. Phys.* **42** 686
[15] de la Peña L and Cetto A M 1996 *The Quantum Dice* (Dordrecht: Kluwer)
[16] Hanggi P and Thomas H 1977 *Z. Phys.* B **26** 85
[17] Adelman S A and Garrison B J 1977 *Mol. Phys.* **33** 1671
[18] Razavy M 1978 *Can. J. Phys.* **56** 311