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Properties of diffusive systems near a saddle point: application to a quartic double well

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Abstract

This paper aims at the analysis of diffusive properties of unidimensional mechanical systems in the environment of maxima and minima of the potential. It begins with a study of the properties of the singular solutions of the Hamilton–Jacobi–Yasue equation in the above-mentioned environment, in both strong or very small frictional forces.

For the quartic symmetrical double-well potential, approximate solutions are found for local validity and the diffusion operator is then calculated in the limits of deep wells and small temperature, the regime being supposed to be aperiodic, with high or moderate values of frictional coefficient. This equation is proved to be nonunique. This operator is then reduced to second order by imposing suitable boundary conditions. Thus an appropriate eigenvalue equation is obtained to describe stationary states in the environment of extremal points of the potential energy function. The main interest of this work relies upon the fact that transition times between wells mainly depend upon fluctuations near the saddle point.

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1. Introduction

In the past there has been wide interest in the study of diffusion in markedly nonlinear oscillators. These systems exhibit profiles of the potential energy function which are characterized by more or less deep wells separated by barriers which are saddle points of the potential.

Much effort was devoted to the study of the relaxation time of the system for jumping from one well to the neighbouring one [1–11], or to the oscillation frequency of the probability density for alternating among different adjacent sites [3, 10, 11]. Related quantities of interest for applications are the mean first-passage time (MFPT) for reaching the barrier top from a situation of confinement inside a single well, or the relaxation time (the eigenvalue) of the corresponding probability density [5, 9, 10].

Most earlier work, however, was limited to systems that experience strong frictional forces, which therefore can be described by a simple Smoluchowski equation for diffusion in configuration space [6, 8]. Actually the evaluation of diffusion parameters or time constants of strongly nonlinear systems, such as double wells, necessitates an accurate description of diffusive behaviour up to the saddle point.

Configurational diffusion equations yielding the time evolution of the two-time transition probability density are suitable for computing either eigenvalues or averages of properties which only depend upon the system coordinates. It is, therefore, tempting to apply the technical apparatus developed by this author in previous papers [12–18] in order to evaluate the diffusion parameters of dynamical systems, to the description of these systems in the neighbourhood of saddle points, taking nonlinearity into account.

The diffusion operator obtained in this way describes the evolution of the system from the given initial preparation and, therefore, admits a unique solution as a transition probability density, provided the initial data are conveniently specified. For this same reason this operator has a high degree of arbitrariness, because it has the form of a linear combination of derivatives of a unique function, which add up to zero [19]. In order to specify this operator further one has to add supplementary conditions requiring the coefficients of derivatives to be independent of initial data. It has been proved (actually for a quadratic potential) that in the long time limit this operator becomes adequate to describe arbitrary fluctuations over the stationary state [18, 19]. It is this limiting equation that will be deduced here, which admits the projected canonical distribution as an equilibrium solution. It is expected that this operator should be unique, because it is required to describe the time evolution of arbitrary fluctuations.

For these reasons it will be convenient to represent the drift velocity by the singular solutions to the Hamilton–Jacobi–Yasue–Riccati (HJYR) equation, which represent the limiting form of the velocity field after the transients because the initial conditions have faded out [14]. In the overdamped regime, these solutions and the path integrals involved in the calculations are localized so that it will be possible to calculate diffusion parameters separately for the regions of convexity or concavity of the potential profile.

Therefore, for any given average current, such as the singular solution to the HJYR equation, the diffusion coefficient results to be determined univocally by the equilibrium probability density, if the equation itself is supposed to be second order. This paper is organized as follows: In section 2, a classification of the solutions to the HJY equation (without the Riccati term) is given. They belong to two classes, according to their behaviour in the vicinity of stationary points of the potential energy function.

In section 3, the properties of the singular solutions are analysed, in the environment of stationary points of the potential energy, separately either for high and moderate values of the frictional coefficient β, or in the limit of low values of β. The stationarity of singular solutions is especially discussed. Actually, where stationarity is not realized, the diffusion coefficient is divergent.

In section 4, the basic formulae for the evaluation of the diffusion operator are reproduced from previous work by this author, by focusing especially upon systems with high or moderate values of frictional coefficient. For these systems the diffusion operator may be evaluated separately around different regions of the potential.

In section 5, we consider the special model described by a symmetric quartic potential, and the diffusion operator is evaluated for the region around the midpoint, which can be either a saddle point or a well, according to the sign of the parameters. The calculations are performed by expanding in powers of the inverse distance between the two wells (or saddle points). The result is an approximate fourth-order diffusion operator for the transition probability density.

In section 6, this evolution operator is compared with the analogue which was obtained previously by expansion in powers of $\frac{1}{\beta}$. The two equations turn out to be different.

In section 7, the equation obtained here is reduced to second order by imposing suitable boundary conditions on the solutions.

2. General properties of singular solutions of the HJY equation near extremal points of the potential energy

The singular solution to the HJY equation related to a one-dimensional dynamical system evolving in the potential $U(q)$ with frictional coefficient β and mass m satisfies the following equation [12, 17, 18]:

$$\frac{1}{2m}\phi'(q)^2 + U(q) + \beta\phi(q) = 0 \tag{2.1}$$

obtained from equation (2.4) of [18] by equating to zero the time derivative of the action ϕ. The prime denotes derivatives over spatial coordinate q, t is the time coordinate and t_0 is the initial time of preparation of the system.

The solutions of the HJY equation obtained by equating to zero the time derivative, are singular solutions in the sense that [18]

$$\frac{\partial\phi}{\partial t} = -\frac{\partial\phi}{\partial t_0} = 0 \tag{2.1$'$}$$

if $U(q)$ is independent of time. There is left, however, the dependence upon a second constant representing initial conditions, which fades out as $O(\mathrm{e}^{-\beta(t-t_0)})$ [12]. These solutions are expected to match, in the limit $\beta \to 0$, the singular solution to the HJ equation with $\beta = 0$ (which is obtained by equating to zero the derivatives of the complete integral with respect to both parameters), because this solution is tangent to every integral surface of the HJ equation. Actually, one may think of a damped trajectory as one which is following a particular undamped characteristic trajectory during an infinitesimal time interval, and later prosecutes through the contiguous trajectory with a slightly lower value of the energy, during the next infinitesimal time interval. In the limit of infinitesimal frictional coefficient, it is therefore tangent to every undamped trajectory and consequently to every integral surface which is tangent to it.

We consider solutions to equation (2.1) $\varphi(q) = \phi(q)$, in the vicinity of extremal points of the potential $U(q)$, that is points $\hat{q}$ where

$$U'(\hat{q}) = 0. \tag{2.2}$$

By differentiation of equation (2.1) and using (2.2), putting $p(q) = \phi'(q)$ follows

$$p(\hat{q})\left[\frac{1}{m}p'(\hat{q}) + \beta\right] = 0 \tag{2.3}$$

from which one of the two alternatives follows, or both:

$$p(\hat{q}) = 0 \tag{2.4}$$

$$p'(\hat{q}) = -m\beta. \tag{2.5}$$

From the above equations we can argue the following:

(i) suppose that (2.4) is true, then upon substitution into equation (2.1),

$$U(\hat{q}) + \beta\varphi(\hat{q}) = 0. \tag{2.6}$$

Expanding around $\hat{q}$

$$U(q) = U(\hat{q}) + \Delta U(q) \tag{2.7}$$

$$\varphi(q) = \varphi(\hat{q}) + \Delta\varphi(q) \tag{2.8}$$

$$p(q) = p(\hat{q}) + \Delta p(q) \tag{2.9}$$

there follows

$$\frac{1}{2m}(\Delta p)^2 + \Delta U(q) + \beta\Delta\varphi(q) = 0 \tag{2.6$'$}$$

which to second order gives

$$\left[\frac{1}{2m}\varphi''(\hat{q})^2 + \frac{1}{2}U''(\hat{q}) + \frac{1}{2}\beta\varphi''(\hat{q})\right](q-\hat{q})^2 = 0 \tag{2.10}$$

from which $\varphi''(\hat{q})$ can be calculated, as well as derivatives of higher orders, from similar equations. The important fact is that equations (2.6′) and (2.10) hold true for every stationary point of the potential where equation (2.4) is satisfied.

(ii) Equation (2.5) gives in the place of (2.6), (2.6′) and (2.10)

$$\frac{1}{2m}p(\hat{q})^2 + U(\hat{q}) + \beta\varphi(\hat{q}) = 0 \tag{2.11}$$

$$\frac{1}{2m}\Delta p(q)^2 + \frac{1}{m}p(\hat{q})\Delta p(q) + \Delta U(q) + \beta\Delta\varphi(q) = 0 \tag{2.11$'$}$$

$$\left[\frac{1}{2m}p(\hat{q})p''(\hat{q}) + \frac{1}{2}U''(\hat{q})\right](q-\hat{q})^2 = 0 \tag{2.12}$$

which yields $p''(\hat{q})$, etc. The expansion of $\varphi(q)$ around $\hat{q}$ as follows:

$$\varphi(q) = \varphi(\hat{q}) + p(\hat{q})(q-\hat{q}) - \frac{1}{2}m\beta(q-\hat{q})^2 - \frac{1}{3!}\frac{mU''(\hat{q})}{p(\hat{q})}(q-\hat{q})^3 + \text{h.o.t.} \tag{2.13}$$

If $U(q)$ is symmetric around $\hat{q}$, it can be proved that equations (2.4) and (2.9) with $\beta > 0$ yield $\varphi(q)$ symmetric around $\hat{q}$, while equations (2.5) and (2.9) with $\beta > 0$ yield $\varphi(q)$ without definite symmetry.

Equations (2.4) and (2.9) with $\beta = 0$ yield $\Delta\varphi(q)$ symmetric or antisymmetric around $\hat{q}$, but, if equation (2.4) is not true, equations (2.5) and (2.9) with $\beta = 0$ yield $\Delta\varphi(q)$ necessarily antisymmetric around $\hat{q}$.

3. Analysis of the singular solutions of the HJY equation in the proximity of stationary points of the potential energy

3.1. High values of β

The singular solutions of the HJY equation for high or moderate values of frictional coefficient have been classified and discussed in [13, 18]. The first singular solution may be expanded

$$\phi(q) = -\frac{m}{2}\beta(q-Q)^2 + c(q-Q) + \frac{d}{\beta} + \frac{q-Q}{\beta}\int^q \mathrm{d}\eta \frac{U(\eta)}{(\eta-Q)^2} + O\left(\frac{1}{\beta^2}\right) \tag{3.1}$$

where c, d and Q are constants. If $U(q) = 0$ there results

$$p(q) = -m\beta(q-Q) + c + O\left(\frac{1}{\beta^2}\right) \tag{3.2}$$

so that from equation (2.1) follows upon substitution, by redefining Q:

$$d = \frac{-c^2}{2m} \qquad O\left(\frac{1}{\beta^2}\right) = 0 \tag{3.3}$$

$$\phi(q) = -\tfrac{1}{2}m\beta(q-Q)^2 + \text{const.} \tag{3.3$'$}$$

This solution is of type (2.5), that is kinetic type, except for $q = Q$, where equation (2.4) is also true.

If now $U(q) = \frac{1}{2}m\omega_0^2(q-Q)^2$
then

$$\phi(q) = -\frac{1}{2}m\beta(q-Q)^2 + c(q-Q) + \frac{d}{\beta} + \frac{q-Q}{\beta}\frac{1}{2}m\omega_0^2(q-Z) + O\left(\frac{1}{\beta^2}\right). \tag{3.4}$$

Substituting now into equation (2.1) there follows

$$c = d = 0 \qquad Q = Z. \tag{3.5}$$

Consequently, this solution is of coordinate type. Therefore, the first singular solution can be either of kinetic type or of coordinate type, or both.

The second singular solution has an expansion in powers of $\frac{1}{\beta}$ whose first term is precisely $O\left(\frac{1}{\beta}\right)$. Therefore

$$p'(q) \neq -m\beta \qquad \text{if} \quad \beta > 0. \tag{3.6}$$

Consequently, this solution is of coordinate type, that is every stationary point of the potential energy is a point of equilibrium. This can also be proved by the solution of the recursive equations for the coefficients of the expansion in powers of $\frac{1}{\beta}$ (see, for instance, [18] equation (3.11)). Actually it can be proved that if $p_{-\lambda}(q)$ is proportional to $U'(q)$ for $1 \leqslant \lambda \leqslant n$, then $p_{-n-1}(q)$ also bears the factor $U'(q)$.

3.2. *Low values of β*

For low values of the frictional coefficient β, the HJY equation may be expanded conveniently in powers of β. The first term of the expansion corresponding to $\beta = 0$ yields

$$p^{(0)}(q) = \pm\sqrt{2m(E - U(q))} \tag{3.7}$$

so that $p^{(0)}(q)$ vanishes if and only if

$$E = U(q) \tag{3.8}$$

while

$$p^{(0)\prime}(q) = \mp\frac{1}{2}\sqrt{2m}\frac{U'(q)}{\sqrt{E - U(q)}} \tag{3.9}$$

is always zero in a stationary point $\hat{q}$ of the potential energy function, where $p^{(0)}(\hat{q}) \neq 0$. There follows that the zeroth-order solution $p^{(0)}(q)$ is always of kinetic type, as might be expected, except for points where $E = U(\hat{q})$. Now, if $p^{(0)}(\hat{q}) \neq 0$, it is also nonzero $p(\hat{q})$ for sufficiently small values of β, therefore the stationary point is of kinetic type, in the whole range of values of β.

From the above arguments there follows that since the second singular solution is always of coordinate type in every stationary point of the potential energy function (in the zone of high values or moderate values of frictional coefficient), while every solution of equation (2.1) in the limit of small β can be of coordinate type only at those points where equation (3.8) is satisfied, then the kinetic character of the singular solution cannot be conserved at every stationary point, if the potential energy function has more than a single point of stationarity (except for $U(q)$ identically zero). Actually, with the exception of these special forms of the potential there is no solution which is entirely of coordinate type for $\beta \to 0$.

In the arguments developed above, we have assumed that the series in $\frac{1}{\beta}$ represents the solution at least in an asymptotic sense in a suitable environment of $\beta = \infty$. This assumption is of course implicit in the common guess that stipulates

$$p(q) \cong -\frac{U'(q)}{\beta} \tag{3.12}$$

in all the interval of definition. The results presented here are therefore an extension of the rather trivial ones that follow from equation (3.12), which proves that singular solutions have been customarily considered, in a heuristic way, the most appropriate to the description of diffusion phenomena. This can be understood by considering that equation (3.12) represents the limiting value of velocity for every trajectory for $t - t_0 \gg \frac{1}{\beta}$, when the initial kinetic energy has been consumed by frictional forces.

Actually, the singular solutions are usually defined through the condition of stationarity of the complete integral of the full HJYR equation, with respect to the parameters, which allows for the determination of these parameters (see for instance [18]). Consequently, they are solutions to the equations of motion independent of initial conditions specifying any particular trajectory, thus being well suited to describe the diffusive motion in the asymptotic regime, where the memory of initial data has faded out. It is precisely this condition of elimination of a memory term which forces the drift velocity to obey a HJYR equation, thus adding corrections to the leading term proportional to $\frac{1}{\beta}$ (equation (3.12)).

The fundamental character of singular solutions for description of diffusion has been discussed in [18, 19].

4. Diffusion equation in the neighbourhood of stationary points of the potential energy for moderate or high values of frictional coefficient

The second singular solution for the HJY equation can be worked out explicitly in the environment of the stationary points of the potential energy by expansion in powers of the coordinate difference from the point of stationarity and using equations (3.6), (2.4) and (2.10). Then the diffusion operator may be calculated from this approximate solution, in the limit of zero temperature, and very small deviations from a parabolic potential profile. The procedure follows from [14–18] and requires an expansion of the response functions in powers of fluctuations of fast variables, with the evaluation of the relevant correlation functions, which is here needed to leading order only.

So we have

$$\mathscr{D}^{(0)}(t, t_0) = \frac{1}{m^2}\int_{t_0}^{t} \mathrm{d}\tau\, \mathrm{e}^{-\beta(t-\tau)} \int_{-\infty}^{\tau} \mathrm{d}\sigma \int_{-\infty}^{t} \mathrm{d}s\, g(\tau, \sigma) g(\tau, s)\langle k(s)k(\sigma)\rangle \tag{4.1}$$

$$\begin{aligned}\mathscr{D}^{(1)}(t, t_0) = &-\frac{1}{m^3}\int_{-\infty}^{t} \mathrm{d}s \int_{t_0}^{t} \mathrm{d}\tau \int_{-\infty}^{\tau} \mathrm{d}\xi \int_{t_0}^{\xi} \mathrm{d}\eta \int_{-\infty}^{\eta} \mathrm{d}\sigma\, g(t, s)\\ &\times \exp\left\{\frac{1}{m}\int_{\tau}^{t} p'(q(\mu))\,\mathrm{d}\mu\right\} g(\tau, \xi)\left[\frac{1}{m}p''(q(\xi))\tilde{p}(\xi) + \mathsf{g}'(q(\xi))\right]\\ &\times \exp\left\{\frac{1}{m}\int_{\eta}^{\xi} p'(q(\mu))\,\mathrm{d}\mu\right\} g(\eta, \sigma)\langle k(s)k(\sigma)\rangle\end{aligned} \tag{4.1$'$}$$

with the following [17, 18]

$$\mathscr{D}(t, t_0) = \mathscr{D}^{(0)}(t, t_0) + \mathscr{D}^{(1)}(t, t_0) + \cdots \tag{4.2}$$

$$\hat{D}_q(t, t_0)\langle\delta(q(t) - q)\rangle = \langle\delta(q(t) - q)\mathscr{D}(t, t_0)\rangle. \tag{4.2$'$}$$

In the above formulae, the hat over an uppercase letter denotes an operator and the brackets stochastic averages over the realizations $\{k(s), -\infty < s < +\infty\}$ of the random Gaussian force with zero mean [20], where

$$\langle k(t)k(s)\rangle = 2m\beta T\delta(t - s) \qquad \forall\, t, s \tag{4.3}$$

where T is the temperature. Moreover δ denotes a Dirac δ-function and the functions g and g are defined as follows [14–18]:

$$g(t, s) = \exp\left\{-\frac{1}{m}\int_s^t p'(q(\alpha))\,\mathrm{d}\alpha\right\} \tag{4.4}$$

$$\mathsf{g}(q) = -\hat{D}_q^{\mathrm{tr}} p''(q). \tag{4.4$'$}$$

The diffusion equation then follows

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial q}\frac{1}{m}p(q)P(q, t) + \frac{\partial}{\partial q}\hat{D}_q(t, t_0)P(q, t) \tag{4.5}$$

where $P(q, t) = P(q, t/q_0, t_0)$ is the two-time conditional transition probability density. The memory term [16–18] in equation (4.5) has been omitted, consistent with the present approximations (see below).

5. Specific models and calculations

5.1. Position of the problem

The calculations have been carried out along these lines (see section 4) for a cubic potential energy profile, by expanding the solution to the HJY equation in the central region of the potential well, and the results were reported in [10].

Hereafter we shall examine in some detail a quartic potential, which can be represented analytically by the function

$$U(q) = \frac{1}{2}m\frac{\omega_0^2}{R^2}(q^2 - Rq)^2. \tag{5.1}$$

By defining

$$q - \frac{R}{2} = r \tag{5.2}$$

there follows

$$U(r) = \frac{1}{2}m\frac{\omega_0^2}{R^2}\left(\left(\frac{R}{2}\right)^2 - r^2\right)^2 \tag{5.1$'$}$$

so that the potential is manifestly symmetric about the midpoint $r = 0$. This point is a maximum or a minimum point according to the sign of ω_0^2. In the range of values of β where the asymptotic expansion in powers of $\frac{1}{\beta}$ is valid for the second singular solution, and therefore equation (3.6) holds, the expansion of the solution in powers of the coordinate is given by equations (2.9) and (2.10) and the equations which follow.

However, since it has been shown in section 3 that the second singular solution cannot be of coordinate type in every stationary point of the potential energy, there follows that the range of validity of the expansion does not cover all values of β. Note, however, that $p(q)$ is exactly solvable in the limit $\beta \to 0$ and small temperature (equation (3.7)).

The solution to the HJY equation which has been calculated and used in this work is the following:

$$\frac{1}{m}p(r) = \frac{1}{m}p'(0)r + \frac{1}{6m}p'''(0)r^3 + \text{h.o.t.} \tag{5.3}$$

where

$$\frac{1}{m}p'(0) = -\left(\frac{1}{2}\beta - \sqrt{\frac{1}{4}\beta^2 - \frac{U''(0)}{m}}\right) \tag{5.4}$$

$$\frac{1}{m}p'''(0) = \frac{U''''(0)}{\beta - 4\sqrt{\frac{1}{4}\beta^2 - \frac{U''(0)}{m}}}. \tag{5.4$'$}$$

The formulae above allow us to evaluate the coefficients of the diffusion equation (4.5) to the desired order of approximation through the calculation of the relevant stochastic averages which appear in equations (4.1) and (4.1′) and in the higher orders of approximation.

5.2. *Evaluation of* $\mathscr{D}^{(0)}(t, t_0)$

From equations (4.1), (4.3) and (5.3), we obtain

$$\begin{aligned}
\langle \delta(r(t)-r)\mathscr{D}^{(0)}(t,t_0)\rangle &= \frac{2m\beta T}{m^2}\int_{t_0}^{t} \mathrm{d}\tau\, \mathrm{e}^{-\beta(t-\tau)} \int_{-\infty}^{\tau} \mathrm{d}\sigma\, \mathrm{e}^{-2(\frac{1}{m}p'(0)+\beta)(\tau-\sigma)} \\
&\quad\times \left[\langle \delta(r(t)-r)\rangle - \frac{1}{m}p'''(0)\int_{\sigma}^{\tau} \mathrm{d}\alpha \langle \delta(r(t)-r)r(\alpha)^2\rangle\right] + \text{h.o.t.} \\
&= \frac{2\beta T}{m}\langle \delta(r(t)-r)\rangle \frac{1}{2\beta\left(\frac{1}{m}p'(0)+\beta\right)} - \frac{2\beta T}{m}\int_{t_0}^{t}\mathrm{d}\tau\, \mathrm{e}^{-\beta(t-\tau)}\frac{1}{m}p'''(0) \\
&\quad\times \int_{-\infty}^{\tau}\mathrm{d}\alpha \langle \delta(r(t)-r)r(\alpha)^2\rangle \int_{-\infty}^{\alpha}\mathrm{d}\sigma\, \mathrm{e}^{-2(\frac{1}{m}p'(0)+\beta)(\tau-\sigma)} + \text{h.o.t.}
\end{aligned} \tag{5.5}$$

In equation (5.5), the Eulerian component of momentum has been expanded up to cubic terms, according to equation (5.3), and subsequently the exponentials have been expanded to the next lowest order in powers of $\frac{1}{R}$(i.e. to $O(\frac{1}{R^2})$).

The next step appears to be the evaluation of the correlation functions appearing in equation (5.5): application of Novikov' theorem yields [21–26]

$$\begin{aligned}
\langle \delta(r(t)-r)r(\alpha)^2\rangle &= \langle \delta(r(t)-r)r(\alpha)\rangle\langle r(\alpha)\rangle \\
&\quad+ \int_{-\infty}^{t}\mathrm{d}s\left\langle \frac{\delta}{\delta k(s)}[\delta(r(t)-r)r(\alpha)]\right\rangle \int_{-\infty}^{\alpha}\mathrm{d}\sigma\left\langle\frac{\delta r(\alpha)}{\delta k(\sigma)}\right\rangle \langle k(s)k(\sigma)\rangle \\
&= \int_{-\infty}^{t}\mathrm{d}s\int_{-\infty}^{\alpha}\mathrm{d}\sigma\left\langle \delta'(r(t)-r)\frac{\delta r(t)}{\delta k(s)}r(\alpha)\right\rangle\left\langle\frac{\delta r(\alpha)}{\delta k(\sigma)}\right\rangle\langle k(s)k(\sigma)\rangle \\
&\quad+ \int_{-\infty}^{t}\mathrm{d}s\int_{-\infty}^{\alpha}\mathrm{d}\sigma\left\langle \delta(r(t)-r)\frac{\delta r(\alpha)}{\delta k(s)}\right\rangle\left\langle\frac{\delta r(\alpha)}{\delta k(\sigma)}\right\rangle\langle k(s)k(\sigma)\rangle \\
&= 2m\beta T\int_{-\infty}^{\alpha}\mathrm{d}\sigma\left\langle \delta'(r(t)-r)\frac{\delta r(t)}{\delta k(\sigma)}r(\alpha)\right\rangle\left\langle\frac{\delta r(\alpha)}{\delta k(\sigma)}\right\rangle \\
&\quad+ 2m\beta T\int_{-\infty}^{\alpha}\mathrm{d}\sigma\left\langle \delta(r(t)-r)\frac{\delta r(\alpha)}{\delta k(\sigma)}\right\rangle\left\langle\frac{\delta r(\alpha)}{\delta k(\sigma)}\right\rangle
\end{aligned}$$

$$= 2m\beta T \left\{ \int_{-\infty}^{\alpha} \mathrm{d}\sigma \langle \delta'(r(t)-r)r(\alpha)\rangle \left\langle \frac{\delta r(t)}{\delta k(\sigma)} \right\rangle \left\langle \frac{\delta r(\alpha)}{\delta k(\sigma)} \right\rangle \right.$$
$$+ \int_{-\infty}^{\alpha} \mathrm{d}\sigma \langle \delta(r(t)-r)\rangle \left\langle \frac{\delta r(\alpha)}{\delta k(\sigma)} \right\rangle^2$$
$$+ \int_{-\infty}^{\alpha} \mathrm{d}\sigma \left\langle \frac{\delta r(\alpha)}{\delta k(\sigma)} \right\rangle \int_{-\infty}^{t} \mathrm{d}s' \int_{-\infty}^{t} \mathrm{d}\sigma'$$
$$\times \left[\left\langle \frac{\delta}{\delta k(s')} \delta'(r(t)-r)r(\alpha) \right\rangle \left\langle \frac{\delta}{\delta k(\sigma')} \frac{\delta r(t)}{\delta k(\sigma)} \right\rangle \right.$$
$$\left.\left. + \left\langle \frac{\delta}{\delta k(s')} \delta(r(t)-r) \right\rangle \left\langle \frac{\delta}{\delta k(\sigma')} \frac{\delta r(\alpha)}{\delta k(\sigma)} \right\rangle \right] \langle k(s')k(\sigma')\rangle \right\} \tag{5.6}$$

where $\delta A/\delta f(\xi)$ denotes the functional derivative of functional A over the function $f(\xi)$. Now in the limit $T \to 0$ one can write

$$\langle \delta(r(t)-r)r(\alpha)^2\rangle \cong 2m\beta T \int_{-\infty}^{\alpha} \mathrm{d}\sigma \langle \delta'(r(t)-r)r(\alpha)\rangle \left\langle \frac{\delta r(t)}{\delta k(\sigma)} \right\rangle \left\langle \frac{\delta r(\alpha)}{\delta k(\sigma)} \right\rangle$$
$$= (2m\beta T)^2 \int_{-\infty}^{\alpha} \mathrm{d}\sigma \int_{-\infty}^{\alpha} \mathrm{d}\sigma' \left\langle \delta''(r(t)-r) \frac{\delta r(t)}{\delta k(\sigma')} \right\rangle \left\langle \frac{\delta r(t)}{\delta k(\sigma)} \right\rangle \left\langle \frac{\delta r(\alpha)}{\delta k(\sigma)} \right\rangle \left\langle \frac{\delta r(\alpha)}{\delta k(\sigma')} \right\rangle$$
$$\cong (2m\beta T)^2 \int_{-\infty}^{\alpha} \mathrm{d}\sigma \int_{-\infty}^{\alpha} \mathrm{d}\sigma' \langle \delta''(r(t)-r)\rangle \left\langle \frac{\delta r(t)}{\delta k(\sigma)} \right\rangle \left\langle \frac{\delta r(t)}{\delta k(\sigma')} \right\rangle \left\langle \frac{\delta r(\alpha)}{\delta k(\sigma)} \right\rangle \left\langle \frac{\delta r(\alpha)}{\delta k(\sigma')} \right\rangle$$
$$= \langle \delta''(r(t)-r)\rangle \langle r(t)r(\alpha)\rangle_c^2 \tag{5.7}$$

where the subscript c denotes a cumulant average. Continuing along these lines all the leading terms can be obtained in the limit of small temperature, which are proportional to $T^n \langle \delta^{(n)}(r(t)-r)\rangle$ (see equation (5.14)).

5.3. Evaluation of conditional correlation functions

Now the correlation functions, such as (5.7) or (5.24), may be evaluated following different approximate procedures:

(i) The response function in the frozen-trajectory approximation (FTA) can be written as [10–18]

$$\left(\frac{\delta r(t)}{\delta k(s)}\right)^{\mathrm{FTA}} = \frac{1}{m} \int_s^t \mathrm{d}\tau \exp\left\{ \frac{1}{m} \int_\tau^t p'(r(\alpha))\,\mathrm{d}\alpha - \frac{1}{m} \int_s^\tau p'(r(\alpha))\,\mathrm{d}\alpha - \beta(\tau - s) \right\}. \tag{5.8}$$

$p(r)$ is expanded around the equilibrium point $r = -\frac{R}{2}$ (or $q = 0$), so as to make q small with respect to R. This was done in [10], so as to obtain, from equations (4.1) and (4.1′), the diffusion equation for a system in the equilibrium state, in the neighbourhood of the minimum of the potential. This equation can be considered approximately valid up to the saddle point by analytical continuation.

(ii) By computing $\frac{1}{m}p'(r)$ from equation (5.3) with sufficient accuracy, the correlation function of coordinate and, consequently, the diffusion operator can be found to converge. Therefore we expand $\frac{1}{m}p'(r)$ according to equation (5.3), with $p'(0)$, $p'''(0)$ given by equations (5.4) and (5.4′) and

$$\frac{1}{m} p'''''(0) = \frac{\frac{1}{m^2} p'''(0)^2}{\frac{3}{5m} p'(0) + \frac{1}{10}\beta}, \text{ etc.} \tag{5.9}$$

The stationary equilibrium distribution $P_{\mathrm{eq}}(q)$ being supposed to be close to a Gibbs canonical distribution; at small temperature the particle jumps from one potential well to the other, being practically at rest between two jumps. There follows:

$$\langle r(t)^2 \rangle = \frac{R^2}{4} \tag{5.10}$$

$$\langle r(t)^4 \rangle = \frac{R^4}{16} \tag{5.10$'$}$$

and so on. Furthermore

$$\langle r(t)^2 r(s)^2 \rangle = \langle r(t)^2 \rangle \langle r(s)^2 \rangle \tag{5.11}$$

similar relations being valid for higher cumulants. Consequently, it is convenient to put, in the small temperature limit

$$\frac{1}{m}\langle p'(r)\rangle = \frac{1}{m}\sum_{n=0}^{\infty}\frac{1}{2n!}p^{(2n+1)}(0)\left(\frac{R}{2}\right)^{2n} = \frac{1}{m}p'\left(\pm\frac{R}{2}\right) \tag{5.12}$$

and the response functions (5.8) become

$$\left(\frac{\delta r(t)}{\delta k(s)}\right)^{\mathrm{FTA}} = \frac{1}{\frac{2}{m}\langle p'(r)\rangle + \beta}\frac{1}{m}\left(\exp\left\{\frac{1}{m}\langle p'(r)\rangle(t-s)\right\}\right.$$
$$\left. - \exp\left\{-\left[\frac{1}{m}\langle p'(r)\rangle + \beta\right](t-s)\right\}\right). \tag{5.13}$$

Now the decoupling procedure which has been followed in order to evaluate the lhs of equation (5.6) allows us to evaluate the constrained averages by averaging over equilibrium distribution functions. Since this equilibrium distribution is very small in the zone of interest here, namely the saddle point, it is hopeless to obtain reliable results by using only a few terms of this expansion. Proceeding further in the evaluation of the lhs of (5.7) there results, to leading order in the temperature

$$\langle \delta(r(t)-r)r(\alpha)^2\rangle = 2m\beta T\langle r(t)r(\alpha)\rangle\left[\delta''(r(t)-r)\int_{-\infty}^{\alpha}\mathrm{d}\sigma\left\langle\frac{\delta r(t)}{\delta k(\sigma)}\right\rangle\left\langle\frac{\delta r(\alpha)}{\delta k(\sigma)}\right\rangle\right.$$
$$+\delta'''(r(t)-r)2m\beta T\int_{-\infty}^{t}\mathrm{d}\sigma\int_{-\infty}^{\alpha}\mathrm{d}\tau\left\langle\frac{\delta r(t)}{\delta k(\sigma)}\right\rangle\left\langle\frac{\delta^2 r(t)}{\delta k(\sigma)\delta k(\tau)}\right\rangle\left\langle\frac{\delta r(\alpha)}{\delta k(\tau)}\right\rangle$$
$$+\delta''''(r(t)-r)(2m\beta T)^2\int_{-\infty}^{t}\mathrm{d}\sigma\int_{-\infty}^{t}\mathrm{d}\tau$$
$$\left.\times\int_{-\infty}^{\alpha}\mathrm{d}\xi\left\langle\frac{\delta r(t)}{\delta k(\sigma)}\right\rangle\left\langle\frac{\delta^2 r(t)}{\delta k(\sigma)\delta k(\tau)}\right\rangle\left\langle\frac{\delta^2 r(t)}{\delta k(\tau)\delta k(\xi)}\right\rangle\left\langle\frac{\delta r(\alpha)}{\delta k(\xi)}\right\rangle+\cdots\right]$$
$$=\langle r(t)r(\alpha)\rangle\sum_{n=0}^{\infty}\frac{(-1)^{n+1}}{n!}\langle r(t)^n r(\alpha)\rangle_c\left(\frac{\partial}{\partial r}\right)^{n+1}\langle\delta(r(t)-r)\rangle \tag{5.14}$$

where the cumulant average is defined, for instance, in [27–29] and consists of only those averages which are linked. All the terms of the expansion (5.3) are of the same order in $\frac{1}{R}$, since the most probable values of r are $\pm R/2$.

From equation (5.13) follows

$$\langle r(t)r(\alpha)\rangle_c = \frac{-T}{m\left(\frac{2}{m}\langle p'(r)+\beta\rangle\right)}\left[\frac{\exp\left\{\frac{1}{m}\langle p'(r)\rangle(t-\alpha)\right\}}{\frac{1}{m}\langle p'(r)\rangle}+\frac{\exp\left\{-\frac{1}{m}\langle p'(r)+\beta\rangle(t-\alpha)\right\}}{\frac{1}{m}\langle p'(r)\rangle+\beta}\right] \tag{5.15}$$

$$\langle r(t)^2\rangle = \frac{T}{U''(q=0)} \tag{5.15$'$}$$

because of (5.12). When substituted into the rhs of equation (5.7), equation (5.15′) yields

$$\langle\delta(r(t)-r)r(t)^2\rangle = \langle\delta''(r(t)-r)\rangle\frac{T^2}{[U''(q=0)]^2}$$
$$\cong \frac{[U''(r=0)]^2}{T^2}r^2\frac{T^2}{[U''(q=0)]^2}\langle\delta(r(t)-r)\rangle \qquad (5.16)$$

having assumed $|r| \ll R$ and the distribution of probability density to be canonical [13, 19]. Equation (5.16) shows that the full expansion (5.14) is needed in order to obtain results consistent with the canonical distribution of probability density.

(iii) The same argument proves that the 'correlation function'

$$\langle r(t)r(\alpha)\rangle_c = \frac{-T}{m\left(\frac{2}{m}p'(0)+\beta\right)}\left[\frac{\exp\left\{\frac{1}{m}p'(0)(t-\alpha)\right\}}{\frac{1}{m}p'(0)} + \frac{\exp\left\{-\left(\frac{1}{m}p'(0)+\beta\right)(t-\alpha)\right\}}{\frac{1}{m}p'(0)+\beta}\right] \qquad (5.17)$$

yields the correct result, when substituted into equation (5.7). Equation (5.17) cannot be obtained by direct computation because the response function (5.8) diverges for large *t-s* when $p'(0)$ is substituted for $p'(r)$ into the rhs.

Equation (5.17) can be postulated on the basis of the following arguments. The time evolution of the conditional correlation function of the coordinate in a quadratic potential profile [30] is univocally determined by the two roots of the characteristic equation, which in the present circumstances are precisely the time factors in equation (5.17). This is a consequence of the principle of regression of fluctuations and detailed balance [31–33]. The coefficients of the exponentials may be determined from two further requirements: equation (5.7), putting $\alpha = t$, yields

$$\langle\delta(r(t)-r)\rangle r^2 = \langle\delta''(r(t)-r)\rangle\langle r(t)^2\rangle^2 \qquad (5.18)$$
$$\langle\delta(r(t)-r)\dot{r}(t)\rangle r = \langle\delta''(r(t)-r)\rangle\langle r(t)^2\rangle\langle r(t)\dot{r}(t)\rangle. \qquad (5.18')$$

Now on substituting $P_{\mathrm{eq}}(r)$ for $\langle\delta(r(t)-r)\rangle$ the boundary conditions can be obtained for the 'correlation function'$\langle r(t)r(\alpha)\rangle$ and its first derivative for $\alpha = t$. To this end the lhs of equation (5.18′) must be put equal to zero, because in a stationary state position velocity must be uncorrelated. We recall that the 'correlation function' given by (5.17) has validity only in the proximity of the saddle point, where $|r| \ll R$ and therefore the potential profile is approximately quadratic, and moreover for time intervals which are not much longer than $\frac{1}{\beta}$, as requested by equation (5.5).

The above conditions determine the function (5.17) unequivocally except for the sign, which however results from equation (5.24) below. In the same way all the correlation functions of the form

$$\langle\delta(r(t)-r)r(\alpha)^n\rangle \qquad t \geqslant \alpha \qquad (5.19)$$

where n is a positive integer, are evaluated to leading order in T, and for short time intervals such that $|t-\alpha| < \frac{1}{\beta}$.

The 'correlation function' (5.17), however, has no physical reality, since the mean square value of the coordinate cannot be negative. It can be defined in connection with formulae like (5.7) and (5.24) below, in order to obtain expressions for these correlation functions which have the correct time dependence and fulfil the appropriate boundary conditions for $\alpha = t$, as may be checked by substitution into equations (5.18) and (5.18′).

Finally inserting equation (5.17) into (5.5) and (5.7), we can readily obtain

$$\langle\delta(r(t)-r)\mathscr{D}^{(0)}(t,t_0)\rangle = \frac{T}{U''(0)}\left(\frac{1}{2}\beta - \sqrt{\frac{1}{4}\beta^2 - \frac{U''(0)}{m}}\right)\langle\delta(r(t)-r)\rangle$$
$$- \frac{T^3 p'''(0)}{m^4\left(\frac{2}{m}p'(0)+\beta\right)\left(\frac{1}{m}p'(0)+\beta\right)}\langle\delta''(r(t)-r)\rangle$$
$$\times\left[\frac{1}{\left(\beta-\frac{2}{m}p'(0)\right)\frac{2}{m^2}p'(0)^2} + \frac{\beta}{4\left(\frac{1}{m}p'(0)+\beta\right)^3\left(\frac{2}{m}p'(0)+3\beta\right)}\right.$$
$$\left. + \frac{1}{\frac{1}{m}p'(0)\left(\frac{1}{m}p'(0)+\beta\right)\left(\frac{2}{m}p'(0)+3\beta\right)}\right]. \qquad (5.20)$$

5.4. Evaluation of $\mathscr{D}^{(1)}(t,t_0)$

By expanding the response functions as in section 5.2, it follows that

$$\langle\delta(r(t)-r)\mathscr{D}^{(1)}(t,t_0)\rangle = \frac{-Tp'''(0)}{m^2\left(\frac{1}{m}p'(0)+\beta\right)}$$
$$\times\int_{t_0}^{t}\mathrm{d}\tau\int_{-\infty}^{\tau}\mathrm{d}\xi\,\exp\left\{-\left(\frac{1}{m}p'(0)+\beta\right)(t+\tau-2\xi)+\frac{1}{m}p'(0)(t-\tau)\right\}$$
$$\times\left\langle\delta(r(t)-r)\left[\frac{1}{m}r(\xi)\tilde{p}(\xi)-\hat{D}_r^{\mathrm{tr}}\right]\right\rangle + \text{h.o.t.} \qquad (5.21)$$

Then we write the full expression for $\tilde{p}(\xi)$ and apply the usual decoupling procedure to the fast variables as was done for instance in [18]:

$$\langle\delta(r(t)-r)r(\xi)\tilde{p}(\xi)\rangle = \int_{-\infty}^{\xi}\mathrm{d}s\,\langle\delta(r(t)-r)r(\xi)g(\xi,s)[k(s)-\mathsf{g}(r(s))]\rangle$$
$$= \int_{-\infty}^{\xi}\mathrm{d}s\int_{-\infty}^{t}\mathrm{d}\sigma\left\langle\delta'(r(t)-r)\frac{\delta r(t)}{\delta k(\sigma)}r(\xi)g(\xi,s)\right\rangle\langle k(s)k(\sigma)\rangle$$
$$+\int_{-\infty}^{\xi}\mathrm{d}s\int_{-\infty}^{\xi}\mathrm{d}\sigma\left\langle\delta(r(t)-r)\frac{\delta r(\xi)}{\delta k(\sigma)}g(\xi,s)\right\rangle\langle k(s)k(\sigma)\rangle$$
$$+\int_{-\infty}^{\xi}\mathrm{d}s\int_{-\infty}^{\xi}\mathrm{d}\sigma\left\langle\delta(r(t)-r)r(\xi)\frac{\delta}{\delta k(\sigma)}g(\xi,s)\right\rangle\langle k(s)k(\sigma)\rangle$$
$$-\int_{-\infty}^{\xi}\mathrm{d}s\,\langle\delta(r(t)-r)r(\xi)g(\xi,s)\mathsf{g}(r(s))\rangle. \qquad (5.22)$$

By neglecting terms $O(T^2)\langle\delta(r(t)-r)\rangle$ and applying the usual transformations there results

$$\langle\delta(r(t)-r)\mathscr{D}^{(1)}(t,t_0)\rangle = \frac{-Tp'''(0)}{m^2\left(\frac{1}{m}p'(0)+\beta\right)}$$
$$\times\int_{t_0}^{t}\mathrm{d}\tau\int_{-\infty}^{\tau}\mathrm{d}\xi\,\exp\left\{-\left(\frac{1}{m}p'(0)+\beta\right)(t+\tau-2\xi)+\frac{1}{m}p'(0)(t-\tau)\right\}$$
$$\times\left[\int_{-\infty}^{\xi}\mathrm{d}\sigma\left\langle\delta'(r(t)-r)\frac{\delta r(t)}{\delta k(\sigma)}r(\xi)g(\xi,\sigma)\right\rangle 2m\beta T\right.$$
$$\left.+\left\langle\delta(r(t)-r)\left(\mathscr{D}^{(0)}(\xi,t_0)-\hat{D}_r^{\mathrm{tr}}\right)\right\rangle\right] + \text{h.o.t.}$$

$$\cong \frac{-2\beta T^2 p'''(0)}{m\left(\frac{1}{m}p'(0)+\beta\right)} \int_{t_0}^{t} \mathrm{d}\tau \int_{-\infty}^{\tau} \mathrm{d}\xi \exp\left\{-\left(\frac{1}{m}p'(0)+\beta\right)(t+\tau-2\xi) + \frac{1}{m}p'(0)(t-\tau)\right\} \langle \delta'(r(t)-r)r(\xi)\rangle \int_{-\infty}^{\xi} \left\langle \frac{\delta r(t)}{\delta k(\sigma)} g(\xi,\sigma)\right\rangle \mathrm{d}\sigma + \text{h.o.t.} \quad (5.23)$$

The first averaged product is easily evaluated by the Novikov decoupling procedure and yields

$$\langle \delta'(r(t)-r)r(\xi)\rangle = \langle \delta''(r(t)-r)\rangle \langle r(t)r(\xi)\rangle_c + \text{h.o.t.} \quad (5.24)$$

Again equation (5.7) proves to behave correctly when substituted into the rhs of (5.24). Evaluation of both sides of equation (5.24) for $\xi = t$, and assuming canonical equilibrium gives

$$-\frac{\partial}{\partial r}\langle \delta(r(t)-r)\rangle r = \left[\left(-\frac{U''(0)r}{T}\right)^2 - \frac{U''(0)}{T}\right] \frac{T}{U''(0)} \langle \delta(r(t)-r)\rangle \quad (5.25)$$

which is exact if $\langle \delta(r(t)-r)\rangle$ is the canonical equilibrium distribution [13, 19]. Then the calculation can proceed straight forwardly and yields

$$\langle \delta(r(t)-r)\mathscr{D}^{(1)}(t,t_0)\rangle = \frac{T^3 p'''(0)}{m^4\left(\frac{1}{m}p'(0)+\beta\right)\left(\frac{2}{m}p'(0)+\beta\right)^2} \langle \delta''(r(t)-r)\rangle \times \left[\frac{1}{\beta\left(\beta-\frac{2}{m}p'(0)\right)\frac{1}{m}p'(0)} - \frac{\beta}{4\left(\frac{1}{m}p'(0)+\beta\right)^3\left(\frac{2}{m}p'(0)+3\beta\right)} - \frac{\beta-\frac{2}{m}p'(0)}{2\beta\left(\frac{1}{m}p'(0)+\beta\right)\left(\frac{2}{m}p'(0)+3\beta\right)\frac{1}{m}p'(0)}\right]. \quad (5.26)$$

5.5. The diffusion equation in the proximity of the saddle point

By putting together all the results obtained, that is equations (5.3), (5.4), (5.4′), (5.20) and (5.26), there follows the evolution equation for the two-time transition probability density valid in the proximity of the saddle point for large $t - t_0$, small temperature and high or moderate values of frictional coefficient

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial r}\left[\frac{1}{m}p'(0)r - \frac{U''''(0)}{6\left(\frac{4}{m}p'(0)+\beta\right)}r^3\right]P(r) + \left[\frac{\partial^2}{\partial r^2}\left(-\frac{T}{U''(0)}\frac{1}{m}p'(0)\right) + \frac{\partial^4}{\partial r^4}\frac{T^3 U''''(0)}{2m^2 p'(0)^2\left(\frac{1}{m}p'(0)+\beta\right)^4\left(\frac{4}{m}p'(0)+\beta\right)}\right]P(r) \quad (5.27)$$

which admits as an equilibrium solution the canonical Gibbs distribution of probability density in coordinate space, up to $O\left(\frac{1}{R^2}\right)$. This is also true for positive $U''(0)$, which means that the point with coordinate $r = 0$ is a point of stable equilibrium. Consequently there results that

$$P_{\text{eq}} \propto \exp\left\{-\frac{\frac{1}{2}U''(0)r^2 + \frac{1}{24}U''''(0)r^4}{T}\right\} \quad (5.28)$$

is the stable equilibrium solution around the extrema of potential energy, if deviations from linearity of the force are taken into account, up to $O\left(\frac{1}{R^2}\right)$.

Note that the first singular solution can equally be considered as a solution of equation (2.10), which leads to the substitution

$$\frac{1}{m}p'(0) \to -\frac{1}{m}p'(0) - \beta. \tag{5.29}$$

Some convergence problems may, however, arise in the derivation of (5.27), in the case the extremum is a maximum point. Actually, the following statement can be proved: in the vicinity of a maximum point of the potential energy function with high or moderate frictional coefficient, the diffusion coefficient relative to the first singular solution diverges, while that which refers to the second singular solution is convergent.

Proof. Let us consider the expression for the diffusion coefficient which was obtained in [18], equation (6.14). This is exact in the limit of high frictional coefficient or a perfectly parabolic potential profile. In either case there results

$$\frac{1}{t-\sigma}\int_\sigma^t U''(r(\alpha))\,\mathrm{d}\alpha \cong U''(0). \tag{5.30}$$

Therefore, calling $\frac{1}{m}p'(0)_\pm$ the two roots of equation (2.10), from equation (6.14) of [18] follows

$$\begin{aligned} D(t,t_0) = \frac{2\beta T}{m}\int_{t_0}^t \mathrm{d}\sigma \exp\left\{\frac{1}{2m}(p'(0)_+ + p'(0)_-)(t-\sigma)\right\} \\ \times\left[\exp\left\{\frac{1}{2m}(p'(0)_+ - p'(0)_-)(t-\sigma)\right\}\right. \\ \left. - \exp\left\{-\frac{1}{2m}(p'(0)_+ - p'(0)_-)(t-\sigma)\right\}\right] \\ \times \exp\left\{\frac{1}{m}p'(0)_-(t-\sigma)\right\}\left(\frac{1}{m}p'(0)_+ - \frac{1}{m}p'(0)_-\right)^{-1} \\ = \frac{2\beta T}{m}\int_{t_0}^t \mathrm{d}\sigma\left[\exp\left\{\frac{1}{m}(p'(0)_+ + p'(0)_-)(t-\sigma)\right\}\right. \\ \left. -\exp\left\{\frac{2}{m}p'(0)_-(t-\sigma)\right\}\right]\left(\frac{1}{m}p'(0)_+ - \frac{1}{m}p'(0)_-\right)^{-1}. \end{aligned} \tag{5.31}$$

This is always convergent for $U''(0) \gtreqless 0$. Conversely, by interchanging $p'(0)_+$ with $p'(0)_-$, it can be ascertained that the result diverges for $t - t_0 \to +\infty$ and $U''(0) \leqslant 0$. □

This result is in consistent with the formula

$$D(q) = -T\frac{p(q)}{mU'(q)} + O(T^2) \tag{5.32}$$

which can be deduced from the requirement that the stationary equilibrium probability density should be canonical.

6. Expansion in inverse powers of β

Expanding the coefficients of the evolution equation which was obtained in equation (5.27) in powers of $\frac{1}{\beta}$ there results

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial r}\left[\left(\frac{U''(0)}{m\beta} + \frac{U''(0)^2}{m^2\beta^3} + 2\frac{U''(0)^3}{m^3\beta^5} + 5\frac{U''(0)^4}{m^4\beta^7}\right) r \right.$$
$$\left. + \frac{U''''(0)}{6m}\left(\frac{1}{\beta} + \frac{4U''(0)}{m\beta^3} + \frac{20U''(0)^2}{m^2\beta^5} + 104\frac{U''(0)^3}{m^3\beta^7}\right) r^3\right] P(r,t)$$
$$+ \frac{\partial^2}{\partial r^2}\frac{T}{U''(0)}\left(\frac{U''(0)}{m\beta} + \frac{U''(0)^2}{m^2\beta^3} + \frac{2U''(0)^3}{m^3\beta^5} + \frac{5U''(0)^4}{m^4\beta^7}\right) P(r,t)$$
$$+ \frac{\partial^4}{\partial r^4}\frac{T^3 U''''(0)}{2m^4}\left(\frac{m^2}{\beta^3 U''(0)} + \frac{6m}{\beta^5 U''(0)} + \frac{33}{\beta^7}\right) P(r,t) + \text{h.o.t.} \tag{6.1}$$

This equation is markedly different from that which was obtained in [17] (see also [18]) by an expansion in powers of $\frac{1}{\beta}$ of the same functional $\mathscr{D}(t, t_0)$, or in [34] where the same expansion (4.2) was used as in this work. We rewrite those previous results in the present notation, so as to make comparison easier:

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial r}\left[\left(\frac{U''(0)}{m\beta} + \frac{U''(0)^2}{m^2\beta^3} + 2\frac{U''(0)^3}{m^3\beta^5} + 5\frac{U''(0)^4}{m^4\beta^7}\right) r \right.$$
$$\left. + \frac{U''''(0)}{6m}\left(\frac{1}{\beta} + \frac{4U''(0)}{m\beta^3} + 20\frac{U''(0)^2}{m^2\beta^5} + 104\frac{U''(0)^3}{m^3\beta^7}\right) r^3\right] P(r,t)$$
$$+ \frac{\partial^2}{\partial r^2} T\left(\frac{1}{m\beta} + \frac{U''(0)}{m^2\beta^3} + 2\frac{U''(0)^2}{m^3\beta^5} + 5\frac{U''(0)^3}{m^4\beta^7}\right)$$
$$\left. + U''''(0)\left(\frac{1}{2m^2\beta^3} + \frac{9}{2}\frac{U''(0)}{m^3\beta^5} + 31\frac{U''(0)^2}{m^4\beta^7}\right) r^2\right] P(r,t)$$
$$+ \frac{\partial^3}{\partial r^3} T^2\left[\left(\frac{3}{2}\frac{1}{m^3\beta^5} + \frac{103}{6}\frac{U''(0)}{m^4\beta^7}\right)\right] U''''(0) r + \frac{59}{9}\frac{U''''(0)^2}{m^4\beta^7} r^3\right] P(r,t)$$
$$+ \frac{\partial^4}{\partial r^4} T^3 \frac{8}{3}\frac{U''''(0)}{m^4\beta^7} P(r,t) + \text{h.o.t.} \tag{6.2}$$

Equations (6.1) and (6.2) are asymptotic equations which are valid after a time interval $t - t_0 \gg \frac{1}{\beta}$ has elapsed from the original time t_0. It can be verified that they admit the same stationary distribution of probability density as a solution. Consequently, they have in common the stationary equilibrium solutions to some second-order differential equation, with the same drift velocity which appears in both equations above. The Green function of this second-order equation can be interpreted, under suitable conditions [19], as the two-time transitional probability density in the asymptotic regime.

7. Reduction to a second-order equation

The fourth-order equation (5.27) for the asymptotic two-time transition probability density can be transformed into a lower order integro-differential equation which incorporates suitable boundary conditions. To this end we rewrite it in the form of the following eigenvalue equation in a Kramers–Moyal expansion up to the fourth-order derivative:

$$\left(\frac{\partial^4}{\partial r^4} D_2 + \frac{\partial^2}{\partial r^2} D_0\right) P_\lambda(r) = \frac{\partial}{\partial r}\frac{1}{m} p(r) P_\lambda(r) - \lambda P_\lambda(r) \tag{7.1}$$

where D_2 and D_0 are defined according to equation (5.27) and $-\lambda$ is the eigenvalue. Let us note that

$$\left(\frac{\partial^2}{\partial\rho^2}D_2 + D_0\right)\sqrt{\frac{D_2}{D_0}}h(r-\rho)\sin\sqrt{\frac{D_0}{D_2}}(r-\rho) = D_2\,\delta(r-\rho) \tag{7.2}$$

according to the definition of equality in distribution theory [35]. Then from equation (7.1) we get

$$\int_{-\infty}^{+\infty}\mathrm{d}\rho\sqrt{\frac{D_2}{D_0}}h(r-\rho)\sin\sqrt{\frac{D_0}{D_2}}(r-\rho)\left(\frac{\partial^2}{\partial\rho^2}D_2 + D_0\right)\frac{\partial^2}{\partial\rho^2}P_\lambda(\rho)$$
$$= \int_{-\infty}^{+\infty}\mathrm{d}\rho\sqrt{\frac{D_2}{D_0}}h(r-\rho)\sin\sqrt{\frac{D_0}{D_2}}(r-\rho)\left(\frac{\partial}{\partial\rho}\frac{1}{m}p(\rho) - \lambda\right)P_\lambda(\rho). \tag{7.3}$$

We recall that in the formulae above $h(\alpha)$ and $\delta(\alpha)$ are the Heaviside and Dirac functions of argument α, respectively. Then equation (7.3) upon repeated integration by parts with the appropriate boundary conditions at minus infinity yields

$$\left[\frac{\partial^3}{\partial r^3}\frac{D_2}{mD_0}p(r) + \frac{\partial^2}{\partial r^2}D_0\right]P_\lambda(r) = \left[\frac{\partial}{\partial r}\frac{1}{m}p(r) - \lambda + \lambda\frac{D_2}{D_0}\frac{\partial^2}{\partial r^2}\right]P_\lambda(r) + O\left(\frac{D_2^2}{D_0^2}\right) \tag{7.4}$$

where terms which are higher order in r/R have been neglected. Now we substitute

$$\left[\frac{\partial^3}{\partial r^3}\frac{D_2}{mD_0}p(r) + \frac{\partial^2}{\partial r^2}D_0\right]P_\lambda(r) \cong \left[\frac{D_2}{mD_0}p(r)\frac{\partial^3}{\partial r^3} + \left(\frac{3D_2}{mD_0}p'(r) + D_0\right)\frac{\partial^2}{\partial r^2}\right]P_\lambda(r). \tag{7.5}$$

The terms which have been omitted are higher order as $T \to 0$. Then we multiply both members of equation (7.4) (with substitution (7.5)) by $\mathrm{e}^{+\tau(r)}$ where

$$\frac{\mathrm{d}\tau}{\mathrm{d}r} = +\left(\frac{2p'(r)}{p(r)} + \frac{mD_0^2}{D_2 p(r)}\right) \gtrless 0 \tag{7.6}$$

according to $r \gtrless 0$, as results from equations (5.4), (5.4′) and (5.27). We have

$$\tau(r) = 2\ln|p(r)| + \frac{mD_0^2}{D_2 p'(0)}\left[\ln|r| - \frac{1}{2}\ln\left(r^2 + \frac{6p'(0)}{p'''(0)}\right)\right]. \tag{7.7}$$

Upon integration from $\rho = 0$ to $\rho = r$ is obtained the integro-differential equation

$$\mathrm{e}^{\tau(r)}\frac{D_2}{D_0}\frac{1}{m}p(r)\frac{\partial^2}{\partial r^2}P_\lambda(r) = \int_0^r \mathrm{d}\rho\,\mathrm{e}^{\tau(\rho)}\left(\frac{\partial}{\partial\rho}\frac{1}{m}p(\rho) - \lambda + \frac{\lambda D_2}{D_0}\frac{\partial^2}{\partial\rho^2}\right)P_\lambda(\rho) \tag{7.8}$$

which yields, upon integration by parts and multiplication by $\frac{mD_0^2}{D_2}$ [36]:

$$D_0 p(r)\frac{\partial^2}{\partial r^2}P_\lambda(r) = \mathrm{e}^{\tau(\rho)-\tau(r)}\frac{mD_0^2}{D_2}\sum_{n=0}^{\infty}\left(-\frac{\mathrm{d}\rho}{\mathrm{d}\tau}\frac{\partial}{\partial\rho}\right)^n\frac{\mathrm{d}\rho}{\mathrm{d}\tau}$$
$$\times\left[\frac{\partial}{\partial\rho}\frac{1}{m}p(\rho) - \lambda + \lambda\frac{D_2}{D_0}\frac{\partial^2}{\partial\rho^2}\right]P_\lambda(\rho)\Big|_0^r. \tag{7.9}$$

After expansion of the coefficients of this equation up to $O\left(\frac{1}{R^2}\right)$ there results, with $p'(0) \neq 0$ (or, equivalently $U''(0) \neq 0$):

$$\left[D_0\frac{\partial^2}{\partial r^2} + \frac{D_2}{m^2D_0^2}\frac{\partial}{\partial r}p(r)\frac{\partial}{\partial r}p(r)\right]P_\lambda(r) + \left[-\frac{\partial}{\partial r}\frac{1}{m}p(r) + \frac{2D_2}{m^2D_0^2}p'(r)\frac{\partial}{\partial r}p(r)\right]P_\lambda(r)$$
$$= \lambda\left[\frac{D_2}{D_0}\frac{\partial^2}{\partial r^2} + \frac{D_2}{mD_0^2}\frac{\partial}{\partial r}p(r) - 1 + \frac{2D_2}{mD_0^2}p'(r)\right]P_\lambda(r). \tag{7.10}$$

This equation needs to be fulfilled to leading order in T at low temperature because the temperature dependence of the mean velocity has been neglected (equation (2.1)). Therefore, the steady equilibrium state ($\lambda = 0$ and zero current) $P_{\text{eq}}(r)$ must satisfy

$$\left[D_0 + \frac{D_2}{m^2 D_0^2} p(r)^2\right] \frac{\partial}{\partial r} P_{\text{eq}}(r) = \frac{1}{m} p(r) P_{\text{eq}}(r). \tag{7.11}$$

Equation (5.28) yields the solution to equation (7.11) up to $O\left(\frac{1}{R^2}\right)$, as expected. The diffusion coefficient has exactly the form required to fulfil this condition.

8. Conclusions

In this paper, we have analysed the solutions to the HJY equation (which is the low-temperature limit of the HJYR equation) which are obtained by equating to zero the time derivative of the action [18]. There result singular solutions [18] which are most suitable to represent the drift component of velocity in a diffusion process to which the system is submitted. These singular solutions have been compared with those pertaining to the frictionless system, which are obtained by equating to zero the derivatives of the complete integral (the action) over the two arbitrary parameters [18]. Moreover, it has been shown that these singular solutions, in the neighbourhood of an extremum of the potential energy, may exhibit two different types of characteristic behaviour, depending upon the values of the momentum. This behaviour has been made explicit for each type, through an expansion which is valid in the environment of the extremum. For high values of frictional coefficient β, the result is that the first singular solution (as defined in [13, 18]), may belong to either of the two classes specified above, while the second singular solution always belongs to the same class, in every stationary point of the potential. This has been proved for solutions which may be represented by power series expansion in $1/\beta$. For low values of β, every solution belongs in general to both classes.

In the remaining part of this paper (from section 4 onwards), a diffusion process in a quartic double-well unidimensional potential profile has been considered, by assuming that the drift is well represented by the second singular solution to the HJY equation, in the region of high or moderate frictional forces. Making use of the results proved in sections 2 and 3, the solutions to the HJY equation near the extremum of the potential energy have been calculated, and the diffusion coefficient has been evaluated including nonlinearity. The correlation functions of position which are needed have been evaluated for the linearized system, by assuming canonical equilibrium in configuration space, which results for the linearized system (see [13, 19]).

To first order in the parameter of nonlinearity, the result is a fourth-order equation for the two-time transition probability density, which admits the projected canonical distribution as an equilibrium probability density, consistent with the assumptions that have been made in order to evaluate the correlation functions.

The coefficients of this equation not being expanded in inverse powers of β, their validity has no limitations except for the assumptions made about the local validity of the solutions. This equation is expected to be valuable as a tool for investigating properties of diffusion and fluctuations in the proximity of a barrier. In fact, it has been shown in section 5 that only the second singular solution yields consistent results in this context, for strong frictional forces.

Actually, this diffusion operator is unexpectedly nonunique, as it results also from a similar calculation in [10], and we do not dispose at present of any criterion for selecting the best operator for some specific problem (see, however, the introduction for a possible approach to this problem). Now given that the equations that have been obtained are correct and that the memory of initial data has been eliminated by the asymptotic limiting procedure, the only way to preserve unequivocally a physical significance to the equations is by assuming that they have in common a subset of solutions which satisfy a second-order equation, as has been shown in [10]. The diffusion operator that we have obtained can therefore be reduced to second order by standard methods, and the second-order diffusion coefficient is in fact uniquely defined (see equation (5.32)), because of the uniqueness of the stationary equilibrium solution. We consider therefore the second-order equation (7.10) as the main result of this work, which can be applied to the calculation of transition times or first-passage times [6–10, 37] across the barrier.

Generally speaking, as the order of the equations increases, the higher derivatives can be eliminated among several independent equations describing the same process, thus reducing the number of initial data which are necessary to specify the physical process.

The fact that the character of the second singular solution necessarily changes at some of the extrema (see section 3), may bear nontrivial consequences in the turn-over problem [4, 10], as may be guessed from equation (5.32). It is hoped to examine this topic in greater detail in a forthcoming paper [38].

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References

[1] Kramers H A 1940 *Physica* **7** 284
[2] Chandrasekhar S 1943 *Rev. Mod. Phys.* **15** 1
[3] Benzi R, Sutera A and Vulpiani A 1981 *J. Phys. A: Math. Gen.* **14** L453
[4] Mel'nikov V I and Meshkov S V 1986 *J. Chem. Phys.* **85** 1018
[5] Hänggi P, Talkner P and Borkovec M 1990 *Rev. Mod. Phys.* **62** 251
[6] Perico A, Pratolongo R, Freed K F, Pastor R W and Szabo A 1993 *J. Chem. Phys.* **101** 564
[7] Ferrando R, Spadacini R and Tommei G E 1993 *Physica* A **196** 83
[8] Perico A, Pratolongo R, Freed K F and Szabo A 1994 *J. Chem. Phys.* **101** 2554
[9] Pankratov A L 1997 *Phys. Lett.* A **234** 329
[10] Battezzati M 1999 *J. Chem. Phys.* **111** 9932
[11] Battezzati M and Magnasco V 2001 *J. Chem. Phys.* **114** 3398
[12] Battezzati M 1979 *Nuovo Cimento* B **50** 7
[13] Battezzati M 1982 *Nuovo Cimento* B **70** 13
[14] Battezzati M 1989 *Chem. Phys. Lett.* **164** 363
[15] Battezzati M 1990 *Chem. Phys. Lett.* **167** 137
[16] Battezzati M 1992 *Phys. Lett.* A **172** 119
[17] Battezzati M 1995 *Nuovo Cimento* B **110** 1287
[18] Battezzati M 1996 *Trends Chem. Phys.* **4** 167
[19] Battezzati M 1996 *J. Chem. Phys.* **105** 6525
[20] Fisz M 1963 *Probability Theory and Mathematical Statistics* (New York: Wiley) ch 8
[21] San Miguel M and Sancho M 1980 *J. Stat. Phys.* **22** 605
[22] Dekker H 1982 *Phys. Lett.* A **90** 26
[23] Volkov V S and Pokrovski V N 1983 *J. Math. Phys.* **24** 267
[24] Hänggi P, Marchesoni F and Grigolini P 1984 *Z. Phys.* B **56** 333
[25] Fox R F 1986 *Phys. Rev.* A **33** 467
[26] Venkatesh T G and Patnaik L M 1993 *Phys. Rev.* E **38** 2402
[27] Meeron E 1957 *J. Chem. Phys.* **27** 1246
[28] Kubo R 1962 *Fluctuation, Relaxation and Resonance in Magnetic Systems* ed D F ter Haar (Edinburgh: Oliver and Boyd)
[29] Fox R F 1978 *Phys. Rep.* **48** 231
[30] Uhlenbeck G E and Ornstein L S 1930 *Phys. Rev.* **36** 823
[31] Callen H B and Greene R F 1952 *Phys. Rev.* **86** 702

[32] Osanger L and Machlup S *Phys. Rev.* **91** 1505
[33] Henery R J 1971 *J. Phys. A: Gen. Phys.* **4** 885
[34] Battezzati M 1993 *Chem. Phys. Lett.* **216** 585
[35] Schwartz L 1965 *Méthodes Mathématiques pour les Sciences Physiques* (Paris: Hermann) ch 2
[36] Laurentiev M and Chabat P 1972 *Méthodes de la théorie des fonctions d'une variable complexe* (Moscow: Mir) ch 5 p 482
[37] Battezzati M and Magnasco V 2002 *J. Phys. A: Math Gen.* **35** 5653
[38] Battezzati M 2003 to be published