Time scale separation leads to position-dependent diffusion along a slow coordinate

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When there is a separation of time scales, an effective description of the dynamics of the slow variables can be obtained by adiabatic elimination of fast ones. For example, for anisotropic Langevin dynamics in two dimensions, the conventional procedure leads to a Langevin equation for the slow coordinate that involves the potential of the mean force. The friction constant along this coordinate remains unchanged. Here, we show that a more accurate, but still Markovian, description of the slow dynamics can be obtained by using position-dependent friction that is related to the time integral of the autocorrelation function of the difference between the actual force and the mean force by a Kirkwood-like formula. The result is generalized to many dimensions, where the slow or reaction coordinate is an arbitrary function of the Cartesian coordinates. When the fast variables are effectively one-dimensional, the additional friction along the slow coordinate can be expressed in closed form for an arbitrary potential. For a cylindrically symmetric channel of varying cross section with winding centerline, our analytical expression immediately yields the multidimensional version of the Zwanzig-Bradley formula for the position-dependent diffusion coefficient. [doi:10.1063/1.3626215]

I. INTRODUCTION

The dynamics along one Cartesian coordinate, say x, of a multidimensional diffusive system is in general highly non-Markovian. However, when the dynamics along x is much slower than along all the other coordinates, it is well known that the slow dynamics can be described as simple diffusion along x in the presence of the potential of mean force, $U_{MF}(x)$, with the intrinsic diffusion coefficient, D_x. This description has the attractive feature that, even when there is not a sufficient separation of time scales, it describes the equilibrium properties of the system exactly in the sense that the density at long times is proportional to $\exp(-\beta U_{MF}(x))$, where $\beta = 1/(k_B T)$, k_B is the Boltzmann constant, and T is the absolute temperature. This property holds even if the diffusion coefficient is position dependent, $D_x \to D(x)$, as can be seen from the resulting evolution equation for the probability density, $p(x, t)$,

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial x} D(x) e^{-\beta U_{MF}(x)} \frac{\partial}{\partial x} \left[e^{\beta U_{MF}(x)} p \right]. \tag{1.1}$$

When the time scale separation is not sufficient, it should be possible to find a $D(x)$ such that the above equation describes the actual dynamics along x, better than the analogous equation that involves simply D_x. A widely used approach is to approximate the actual non-Markovian dynamics along x using a position-dependent diffusion coefficient that is extracted from simulations of the multidimensional system in such a way that Eq. (1.1) provides the best possible description.[1–5]

In this paper, we derive a physically transparent expression for $D(x)$ by extending the familiar adiabatic elimination of fast variables to the next order. Our derivation is a generalization of the procedure used by Zwanzig[6] to analyze diffusion in a channel of variable cross section with hard walls. The traditional one-dimensional description of this problem is based on the Fick-Jacobs equation, which describes diffusion along the symmetry axis, x, of the channel in the presence of a potential of mean force that is proportional to the logarithm of the cross section area (the width in two dimensions). Zwanzig showed that a better description of the dynamics can be obtained by using a position-dependent diffusion coefficient, which in two dimensions is given by

$$D(x) = \frac{D}{1 + \frac{w'(x)^2}{12}}, \tag{1.2}$$

where $w(x)$ is the width of the channel and $w'(x) = dw(x)/dx$. He derived this by treating the derivative as a small parameter, calculating $D(x)$ to the first order, and finally constructing the simplest Pade approximation. Zwanzig's paper[6] stimulated a number of studies on the effect of position-dependent confinement on transport.[7–11]

Here, we generalize Zwanzig's work in a number of directions. We consider an arbitrary multidimensional system undergoing Langevin dynamics. Instead of working with the diffusion equation, we start with the more general Klein-Kramers equation that describes diffusion in phase space and involves friction coefficients. This approach has the advantage that it is the friction coefficient rather than the diffusion coefficient that is renormalized. Specifically, we find that the friction along the slow x-coordinate is the sum of

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the intrinsic friction and the friction due to fluctuations of the force along x resulting from motion along the fast coordinates:

$$\zeta_e(x) = \zeta_x + \beta \int_0^\infty \langle \delta F_x(t)\delta F_x(0)\rangle_x \, dt, \tag{1.3}$$

where ζ_x and $\zeta_e(x)$ are intrinsic and position-dependent effective friction coefficients, δF_x is the difference between the actual force and the mean force, $-dU_{MF}(x)/dx$, and $\langle \delta F_x(t)\delta F_x(0)\rangle_x$ is the force-force autocorrelation function at fixed value of x. Because of the Einstein relation, this result can be expressed in terms of diffusion coefficients as

$$\frac{1}{D_e(x)} = \frac{1}{D_x} + \beta^2 \int_0^\infty \langle \delta F_x(t)\delta F_x(0)\rangle_x \, dt. \tag{1.4}$$

Equations (1.3) and (1.4) are key results of this paper. They are so natural that they may seem obvious at the first sight (see the heuristic arguments in Sec. II). The simplest rigorous derivation of these equations that we found is given in Sec. III.

II. HEURISTIC ARGUMENTS

Consider two-dimensional Langevin dynamics in a potential $U(x, y)$. The equation of motion along x is

$$m_x \dot{v} + \zeta_x v + \partial U(x, y)/\partial x = f_x(t), \tag{2.1}$$

where $v = \dot{x} = dx/dt$ and m_x, ζ_x, and $f_x(t)$ are the mass, friction constant, and random force associated with the x-coordinate motion. The random force is Gaussian, δ-correlated, with zero mean. It is related to the friction constant by the fluctuation-dissipation theorem $\langle f_x(t) f_x(t')\rangle = 2\zeta_x \delta(t - t')/\beta$. As a consequence, the friction constant is the time integral of the autocorrelation function of the random force,

$$\zeta_x = \beta \int_0^\infty \langle f_x(t) f_x(0)\rangle \, dt. \tag{2.2}$$

Dynamics along y is described by an equation of motion analogous to Eq. (2.1).

If the dynamics along y is much faster than along x, the motions along x and y become uncoupled. In this case, the distribution along y is close to the equilibrium one for a given value of x. The dynamics along x occurs in the presence of the potential of mean force, which is related to the local equilibrium average of $\partial U(x, y)/\partial x$ with respect to y by

$$\frac{\int \frac{\partial U(x,y)}{\partial x} e^{-\beta U(x,y)} dy}{\int e^{-\beta U(x,y)} dy} = \frac{dU_{MF}(x)}{dx}. \tag{2.3}$$

One can write Eq. (2.1) in terms of $U_{MF}(x)$ as

$$m_x \dot{v} + \zeta_x v + \frac{dU_{MF}(x)}{dx} - \delta F_x(y) = f_x(t), \tag{2.4}$$

where $\delta F_x(y)$ is the difference between the actual force along x at given value of y and the mean force,

$$\delta F_x(y) = -\frac{\partial U(x, y)}{\partial x} + \frac{dU_{MF}(x)}{dx}. \tag{2.5}$$

It follows from Eq. (2.3) that the average of $\delta F_x(y)$ over the equilibrium distribution along y is zero.

In the fast y dynamics limit, the simplest approximation is to ignore $\delta F_x(y)$ in Eq. (2.4). Here, we seek a better approximation. Dynamics along y influences the dynamics along x (through $\delta F_x(y)$) in two ways. It leads to an additional friction force as well as an additional random force, the two being related by the fluctuation-dissipation theorem. In general, these are non-Markovian leading to the generalized Langevin equation for dynamics along x. Here, we will consider the effect of $\delta F_x(y)$ only in the Markovian limit. In this limit, we can describe the influence of $\delta F_x(y)$ by an additional friction force $-\Delta\zeta(x)v$ and a corresponding additional random force $\Delta f_x(t)$ with zero mean, which is δ-autocorrelated, $\langle \Delta f_x(t)\Delta f_x(t')\rangle = 2\Delta\zeta(x)\delta(t - t')/\beta$. The relationship between $\Delta\zeta(x)$ and the autocorrelation function of the additional random force is analogous to that in Eq. (2.2),

$$\Delta\zeta(x) = \beta \int_0^\infty \langle \Delta f_x(t)\Delta f_x(0)\rangle \, dt. \tag{2.6}$$

To obtain the desired result, we now make the assumption that the above time integral, for each value of x, is equal to the time integral of the autocorrelation function of $\delta F_x(y(t))$, which fluctuates solely due to dynamics along y:

$$\Delta\zeta(x) = \beta \int_0^\infty \langle \delta F_x(y(t))\, \delta F_x(y(0))\rangle_x \, dt, \tag{2.7}$$

where it is understood that the correlation function describes fluctuations due to dynamics along y for the fixed value of x.

The effective position-dependent friction coefficient is then given by

$$\begin{aligned}\zeta_e(x) &= \zeta_x + \Delta\zeta(x) \\ &= \zeta_x + \beta \int_0^\infty \langle \delta F_x(y(t))\, \delta F_x(y(0))\rangle_x \, dt.\end{aligned} \tag{2.8}$$

A more accurate, but, of course, still approximate, Langevin equation for dynamics along x is

$$m_x \dot{v} + \zeta_e(x) v + \frac{dU_{MF}(x)}{dx} = f_e(t), \tag{2.9}$$

where the effective Gaussian δ-correlated random force $f_e(t)$ has zero mean and its autocorrelation function is given by $\langle f_e(t) f_e(t')\rangle = 2\zeta_e(x)\delta(t - t')/\beta$. Using Eqs. (2.2) and (2.7) and the fact that forces $f_x(t)$ and $\delta F_x(y)$ are uncorrelated, we can express the effective friction coefficient as

$$\begin{aligned}\zeta_e(x) = \beta \int_0^\infty &\langle (f_x(t) + \delta F_x(y(t))) \\ &\times (f_x(0) + \delta F_x(y(0)))\rangle_x dt.\end{aligned} \tag{2.10}$$

However, this does not mean that $f_e(t) = f_x(t) + \delta F_x(y)$, because then Eqs. (2.4) and (2.9) would be inconsistent. Similarly, although $\delta F_x(y)$ results in both a frictional and a random force, as argued above, one cannot write $\delta F_x(y) = \Delta\zeta(x)v + \Delta f_x(t)$ because then Eqs. (2.6) and (2.7) would be inconsistent. This is why, we consider the above arguments to be heuristic, even though the final result seems so plausible.

The stochastic dynamics governed by Eq. (2.9) can also be described in terms of the evolution of the probability density in the phase space of the system. In the high friction limit, the corresponding Klein-Kramers equation reduces to the Smoluchowski equation for the probability density along x, $p(x,t)$,

$$\frac{\partial p}{\partial t} = \frac{\partial}{\partial x} D_e(x) e^{-\beta U_{MF}(x)} \frac{\partial}{\partial x}\left[e^{\beta U_{MF}(x)} p\right]. \tag{2.11}$$

Here, $e^{-\beta U_{MF}(x)} \propto \int e^{-\beta U(x,y)} dy$ and $D_e(x)$ is the position-dependent diffusion coefficient related to the friction coefficient by the Einstein relation

$$\begin{aligned}\frac{1}{D_e(x)} &= \beta\zeta_e(x) = \frac{1}{D_x} + \beta\Delta\zeta(x)\\ &= \frac{1}{D_x} + \beta^2 \int_0^\infty \langle \delta F_x(y(t))\delta F_x(y(0))\rangle_x \, dt,\end{aligned} \tag{2.12}$$

where $D_x = 1/(\beta\zeta_x)$. As we will see, in two dimensions, $\Delta\zeta(x)$ can be expressed analytically as

$$\Delta\zeta(x) = \zeta_y \int_{-\infty}^{\infty} \frac{dy}{p_{eq}(y|x)}\left[\frac{\partial}{\partial x}\int_y^\infty p_{eq}\left(y'|x\right) dy'\right]^2, \tag{2.13}$$

where

$$p_{eq}(y|x) = \frac{e^{-\beta U(x,y)}}{\int e^{-\beta U(x,y')} dy'}, \tag{2.14}$$

is the normalized Boltzmann distribution of y at a fixed value of x.

The above arguments are heuristic. The final result is, however, rigorous in the sense that in the high friction (diffusion) regime it is exact to linear order in $\zeta_y/\zeta_x = D_x/D_y$ in the limit that $\zeta_y/\zeta_x = D_x/D_y \to 0$. We will show this in Sec. III using a procedure that is a generalization of the one used by Zwanzig[6] to derive the generalized Fick-Jacobs equation which describes diffusion in a channel of varying cross section using a position-dependent diffusion coefficient.

III. RIGOROUS DERIVATION

For the sake of simplicity, we consider only one fast coordinate, although the derivation below can be readily extended to a d-dimensional subspace of fast variables. Let $p_2(x, v, y, u, t)$, $v = \dot{x}$, $u = \dot{y}$, be the phase space probability density of a two-dimensional system undergoing Langevin dynamics. This function satisfies the Klein-Kramers equation

$$\frac{\partial p_2}{\partial t} = L p_2; \qquad L = L_{xv}(y) + L_{yu}(x) \tag{3.1}$$

with

$$L_{xv}(y) = -v\frac{\partial}{\partial x} + \frac{1}{m_x}\frac{\partial U(x,y)}{\partial x}\frac{\partial}{\partial v} + \frac{\zeta_x}{\beta m_x^2}\frac{\partial}{\partial v} f(v)\frac{\partial}{\partial v}\frac{1}{f(v)}, \tag{3.2}$$

where $f(v) = \sqrt{2\pi/(\beta m_x)}\exp(-\beta m_x v^2/2)$ is the Maxwell velocity distribution. $L_{yu}(x)$ is obtained from $L_{xv}(y)$ by replacing x, v, m_x, and ζ_x by y, u, m_y, and ζ_y, respectively. We assume that x and v are slow variables compared to y and u, and that we are outside the low friction (energy diffusion) regime. This implies that both the friction and the velocity relaxation time in the x-direction are larger than those in the y-direction ($\zeta_x > \zeta_y$ and $m_x/\zeta_x > m_y/\zeta_y$). The normalized local equilibrium distribution of the fast variables at a fixed value of x is given by

$$\Phi(y,u|x) = p_{eq}(y|x) f(u) = \frac{e^{-\beta U(x,y)} f(u)}{\int e^{-\beta U(x,y)} dy}. \tag{3.3}$$

The phase space probability density of the slow variables, $p_1(x, v, t)$, is defined as

$$p_1(x,v,t) = \int\int p_2(x,v,y,u,t)\, dy\, du. \tag{3.4}$$

Without loss of generality, we use $p_1(x, v, t)$ and $\Phi(y, u|x)$ to write $p_2(x, v, y, u, t)$ as

$$p_2(x,v,y,u,t) = \Phi(y,u|x) p_1(x,v,t) + \Delta(x,v,y,u,t), \tag{3.5}$$

where $\Delta(x, v, y, u, t)$ describes the deviation from the local equilibrium. Since $\int\int \Phi(y,u|x) dy du = 1$, $\Delta(x, v, y, u, t)$ satisfies

$$\int\int \Delta(x,v,y,u,t)\, dy\, du = 0. \tag{3.6}$$

Substituting the expression for $p_2(x, v, y, u, t)$ in Eq. (3.5) into Eq. (3.1), integrating over y and u, and using the relations in Eqs (2.3) and (2.5), and (3.6) we find that

$$\frac{\partial p_1}{\partial t} = L_{xv}^{MF} p_1 - \frac{1}{m_x}\frac{\partial}{\partial v}\int\int \delta F_x \Delta\, dy\, du, \tag{3.7}$$

where L_{xv}^{MF} is obtained from $L_{xv}(y)$, Eq. (3.2), by replacing $\partial U(x,y)/\partial x$ by $dU_{MF}(x)/dx$. Substituting $p_2(x, v, y, u, t)$ in Eq. (3.5) into Eq. (3.1) and using Eq. (3.7), we obtain

$$\frac{\partial\Delta}{\partial t} = L\Delta + \frac{\Phi}{m_x}\frac{\partial}{\partial v}\int\int \delta F_x \Delta\, dy\, du - \frac{\Phi}{m_x}\delta F_x f(v)\frac{\partial}{\partial v}\frac{p_1}{f(v)}. \tag{3.8}$$

The last two equations are exact.

By omitting the last term in Eq. (3.7) (i.e., putting $\Delta(x, v, y, u, t) = 0$), one recovers the familiar result that the motion along x occurs in the presence of the potential of mean force with the intrinsic mass and friction (if the dynamics along x and v is much slower than that of y and u). We will now derive a more accurate approximate closed-form evolution equation for the phase space probability density of the slow variables, $p_1(x, v, t)$, in two steps. First, we find an approximate solution for $\Delta(x, v, y, u, t)$ from Eq. (3.8). Then, we substitute the resulting expression for $\Delta(x, v, y, u, t)$ into Eq. (3.7).

To find an approximate solution for $\Delta(x, v, y, u, t)$, when there is a separation of the time scales, we neglect the second term on the right-hand side of Eq. (3.8) and replace L in the first term by $L_{yu}(x)$. As a result, Eq. (3.8) takes the form

$$\frac{\partial\Delta}{\partial t} = L_{yu}(x)\Delta - \frac{\Phi}{m_x}\delta F_x f(v)\frac{\partial}{\partial v}\frac{p_1}{f(v)}. \tag{3.9}$$

Solving this equation with the initial condition $\Delta(x, v, y, u, 0) = 0$ that corresponds to the local equilibrium of fast variables, we obtain

$$\Delta = -\frac{1}{m_x}\int_0^t e^{L_{yu}(x)t'}\delta F_x \Phi f(v)\frac{\partial}{\partial v}\frac{p_1(t-t')}{f(v)}dt'. \tag{3.10}$$

We use the separation of the time scales: (i) to ignore the dependence of $p_1(x, v, t-t')$ on t' and move this function outside the integral and (ii) to replace the upper limit of integration with respect to t' to infinity. This results in a Markovian approximation for $\Delta(x, v, y, u, t)$

$$\Delta = -\frac{1}{m_x}\left[\int_0^\infty e^{L_{yu}(x)t'}\delta F_x \Phi dt'\right] f(v)\frac{\partial}{\partial v}\frac{p_1(t)}{f(v)}. \tag{3.11}$$

Substituting this into Eq. (3.7), we finally have

$$\frac{\partial p_1}{\partial t} = -v\frac{\partial p_1}{\partial x} + \frac{1}{m_x}\frac{dU_{MF}(x)}{dx}\frac{\partial p_1}{\partial v} + \frac{\zeta_e(x)}{\beta m_x^2}\frac{\partial}{\partial v}f(v)\frac{\partial}{\partial v}\frac{p_1}{f(v)}, \tag{3.12}$$

where $\zeta_e(x)$ is the effective friction coefficient given in Eq. (2.10).

Equation (3.12) is the improved Klein-Kramers evolution equation for the phase space probability density of the slow variables that corresponds to the underlying stochastic dynamics described by the Langevin equation in Eq. (2.9). It was derived by making two approximations in Eq. (3.8) that determines the deviation $\Delta(x, v, y, u, t)$: (1) neglecting the term proportional to $\delta F_x \Delta$ on the right-hand side and (2) neglecting variation of the slow variables in the evolution operator ($L \to L_{yu}(x)$). We expect these approximations to give the correct result for the deviation $\Delta(x, v, y, u, t)$ to the lowest non-trivial order in the time-scale separation. This implies that the Langevin equation obtained in Sec. II on the basis of the heuristic arguments is rigorous in the sense that it provides the Markovian description of the stochastic dynamics of the slow variables that is correct to linear order in ζ_y/ζ_x, as $\zeta_y/\zeta_x \to 0$, as long as $m_x/\zeta_x > m_y/\zeta_y$. If either of the above approximations were relaxed in order to find a better approximation for $\Delta(x, v, y, u, t)$, the Klein-Kramers structure of the resulting evolution equation would be destroyed.

IV. ILLUSTRATIVE EXAMPLES: DIFFUSION IN CONFINED ENVIRONMENTS

We begin by deriving the general formula for $\Delta\zeta(x)$ given in Eq. (2.13) for an arbitrary potential $U(x, y)$ assuming that $\int U(x, y)dy$ is finite, so that the local equilibrium distribution $p_{eq}(y|x)$, Eq. (2.14), does exist. According to Eq. (2.7), to determine $\Delta\zeta(x)$ one has to find the area under the correlation function $\langle\delta F_x(t)\delta F_x(0)\rangle_x$. For diffusion in one dimension, the calculation of the area under a correlation function can be reduced to quadrature using a generalization of the theory of first-passage times.[12] This formalism was first applied to reorientational correlation functions that determine the fluorescence anisotropy in liquid crystals.[13] In the present context, this formalism can be used to find $\Delta\zeta(x)$, Eq. (2.7), in closed form. Specifically, $\Delta\zeta(x)$ can be written as

$$\frac{\Delta\zeta(x)}{\zeta_y} = \beta^2\int_{-\infty}^{\infty}\frac{dy}{p_{eq}(y|x)}\left[\int_y^\infty \delta F_x(y')p_{eq}(y'|x)dy'\right]^2, \tag{4.1}$$

where we have used Eq. (65) from Ref. 14. By differentiating Eq. (2.14) with respect to x and using Eqs. (2.3) and (2.5) we have

$$\delta F_x(y) = \frac{1}{\beta p_{eq}(y|x)}\frac{\partial p_{eq}(y|x)}{\partial x}. \tag{4.2}$$

Using this in Eq. (4.1), we obtain the result for $\Delta\zeta(x)$ given in Eq. (2.13).

For the potential $U(x, y) = V(x) + k(x)[y - y_0(x)]^2/2$ the formula in Eq. (2.13) leads to the following relation between $\Delta\zeta(x)$ and the parameters of the y-coordinate dynamics:

$$\frac{\Delta\zeta(x)}{\zeta_y} = \frac{k'(x)^2}{4\beta k(x)^3} + y_0'(x)^2. \tag{4.3}$$

Kalinay and Percus[9] recently obtained the first term on the right-hand side using a different approach.

When the y-coordinate motion occurs in a strip constrained by two rigid walls located at $y_-(x)$ and $y_+(x)$, i.e., $y_-(x) < y < y_+(x)$, the potential $U(x, y)$ is $U(x, y) = V(x)/[H(y - y_-(x))H(y_+(x) - y)]$, where $H(z)$ is the Heaviside step function. In this case, the formula in Eq. (2.13) leads to

$$\frac{\Delta\zeta(x)}{\zeta_y} = \int_{y_-(x)}^{y_+(x)}\frac{dy}{p_{eq}(y|x)}\left[\frac{\partial}{\partial x}\int_y^{y_+(x)} p_{eq}(y'|x)dy'\right]^2 = \frac{w'(x)^2}{12} + y_0'(x)^2. \tag{4.4}$$

Here, $w(x) = y_+(x) - y_-(x)$ and $y_0(x) = [y_+(x) + y_-(x)]/2$ are the width and the centerline of the strip. When $\zeta_x = \zeta_y$ and hence $D_x = D_y = D$, the result in Eq. (4.4) allows us to write the effective diffusion coefficient, Eq. (2.12), as

$$D_e(x) = \frac{D}{1 + y_0'(x)^2 + \frac{w'(x)^2}{12}}. \tag{4.5}$$

This is the Zwanzig-Bradley formula for the effective diffusion coefficient. Zwanzig[6] considered diffusion in a strip of varying width with a straight centerline parallel to the x-axis and obtained this result with $y_0'(x) = 0$. The slowdown of the effective diffusion along x due to the winding of the centerline was considered in a recent paper by Bradley,[11] who obtained the result in Eq. (4.5). It is interesting to note that both Eqs. (4.3) and (4.4) can be written as

$$\frac{\Delta\zeta(x)}{\zeta_y} = \left(\frac{d}{dx}\sqrt{\langle\delta y^2\rangle_x}\right)^2 + \left(\frac{d}{dx}\langle y\rangle_x\right)^2, \tag{4.6}$$

where $\delta y = y - \langle y\rangle_x$ and $\langle f(y)\rangle_x = \int f(y)p_{eq}(y|x)dy$.

When the fast dynamics occurs in d dimensions, the formula analogous to that in Eq. (2.13) can be obtained only when the dynamics perpendicular to x is effectively one-dimensional because of the axial symmetry of the potential. When the motion occurs in the potential $U(x, \mathbf{r}) = U(x, |\mathbf{r}$

$-\,\mathbf{r}_0(x)|)$, the formula analogous to that in Eq. (2.12) is given by

$$\frac{\Delta\zeta(x)}{\zeta_r} = \int_0^\infty \frac{d\rho}{p_{eq}(\rho|x)}\left[\frac{\partial}{\partial x}\int_\rho^\infty p_{eq}(\rho'|x)d\rho'\right]^2 + \left(\frac{d\mathbf{r}_0(x)}{dx}\right)^2. \tag{4.7}$$

Here, ζ_r is the friction constant in the d-dimensional subspace of fast variables and $p_{eq}(\rho|x)$ is the local equilibrium distribution at a fixed value of the slow x-coordinate, $p_{eq}(\rho|x) = \rho^{d-1}e^{-\beta U(x,\rho)}/\int_0^\infty \rho^{d-1}e^{-\beta U(x,\rho)}d\rho$, with $\rho = |\mathbf{r} - \mathbf{r}_0(x)|$. In the special case of $U(x,\mathbf{r}) = V(\mathbf{r}_0(x)) + u(|\mathbf{r} - \mathbf{r}_0(x)|/l(x))$, using Eq. (4.7) one can obtain a formula that is a generalization of Eq. (4.6), namely,

$$\frac{\Delta\zeta(x)}{\zeta_r} = \left(\frac{d}{dx}\sqrt{\langle\delta\mathbf{r}^2\rangle_x}\right)^2 + \mathbf{r}'_0(x)^2, \tag{4.8}$$

where $\langle\delta\mathbf{r}^2\rangle_x = \int_0^\infty \rho^2 p_{eq}(\rho|x)d\rho$. If the fast coordinate motion occurs in a tube of variable radius $R(x)$ with rigid walls, so that $u(\mathbf{r}) = 0$ for $|\mathbf{r} - \mathbf{r}_0(x)| < R(x)$ and infinity otherwise, Eq. (4.8) leads to

$$\frac{\Delta\zeta(x)}{\zeta_r} = \frac{d}{d+2}R'(x)^2 + \mathbf{r}'_0(x)^2. \tag{4.9}$$

When $\zeta_x = \zeta_r$ and hence $D_x = D_r = D$, the effective diffusion coefficient along the slow x-coordinate is given by

$$D_e(x) = \frac{1}{\beta\zeta_e(x)} = \frac{D}{1 + \mathbf{r}'_0(x)^2 + [d/(d+2)]R'(x)^2}. \tag{4.10}$$

This is a multidimensional generalization of the Zwanzig-Bradley formula for $D_e(x)$.

V. CONCLUDING REMARKS

This paper focuses on the effective Markovian description of the dynamics of a slow x-coordinate when a separation of time scales exists. The conventional approach describes the slow dynamics by the Langevin equation that involves a potential of mean force $U_{MF}(x)$ and intrinsic friction constant ζ_x. Here, we show that this zeroth-order description can be extended to the next order in the ratio of the time scales by replacing the intrinsic friction constant by an effective position-dependent friction coefficient $\zeta_e(x) = \zeta_x + \Delta\zeta(x)$. The physical reason for this is that the fast degrees of freedom behave as an additional heat bath for the slow coordinate motion. This leads to additional x-dependent random and friction forces, which are related by the fluctuation-dissipation theorem.

When motion along the fast coordinates is diffusive and effectively one-dimensional, we found a closed-form expression for $\Delta\zeta(x)$ that only involves the local equilibrium distribution and the friction constant of the fast coordinates. Using these formulas, we show how one can obtain the d-dimensional generalization of the Zwanzig-Bradley formula for the effective diffusion coefficient of a particle diffusing in a cylindrically symmetric channel of varying diameter and winding centerline.

Finally, we mention how our results can be generalized to many dimensions when the slow reaction coordinate is a nonlinear function of the Cartesian coordinates. Consider a system diffusing with diffusion tensor $\mathbf{D}$ in N dimensions in the presence of a potential $U(x_1, x_2, ..., x_N) \equiv U(\mathbf{x})$. Let $q(\mathbf{x})$ be a "reaction coordinate." The corresponding potential of mean force is

$$\mathrm{e}^{-\beta U_{MF}(q)} \propto \int \delta\left(q - q(\mathbf{x})\right)\mathrm{e}^{-\beta U(\mathbf{x})}d\mathbf{x}. \tag{5.1}$$

If $q(\mathbf{x})$ is a nonlinear function of $\mathbf{x}$, then the intrinsic diffusion coefficient along q is already position-dependent:

$$D(q) = \frac{\sum_{i,j}\int \delta\left(q - q(\mathbf{x})\right)\frac{\partial q(\mathbf{x})}{\partial x_i}D_{ij}\frac{\partial q(\mathbf{x})}{\partial x_j}\mathrm{e}^{-\beta U(\mathbf{x})}d\mathbf{x}}{\int \delta\left(q - q(\mathbf{x})\right)\mathrm{e}^{-\beta U(\mathbf{x})}d\mathbf{x}}. \tag{5.2}$$

Dynamics along coordinates that are orthogonal to q lead to additional friction, so that the effective diffusion coefficient along q is

$$\frac{1}{D_e(q)} = \frac{1}{D(q)} + \beta^2\int_0^\infty \left\langle\delta F_q(t)\delta F_q(0)\right\rangle_q dt, \tag{5.3}$$

where δF_q is the difference between the actual force and the mean force along q, and it is understood that the correlation function is evaluated keeping q fixed.

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