Stochastic thermodynamics of a harmonically trapped colloid in linear mixed flow

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(Received 24 June 2019; revised manuscript received 19 September 2019; published 19 November 2019)

In this paper, motivated by a general interest in the stochastic thermodynamics of small systems, we derive an exact expression—via path integrals—for the conditional probability density of a two-dimensional harmonically confined Brownian particle acted on by linear mixed flow. This expression is a generalization of the expression derived earlier by Foister and Van De Ven [J. Fluid Mech. **96**, 105 (1980)] for the case of the corresponding *free* Brownian particle, and reduces to it in the appropriate unconfined limit. By considering the long-time limit of our calculated probability density function, we show that the flow-driven Brownian oscillator attains a well-defined steady state. We also show that, during the course of a transition from an initial flow-free thermal equilibrium state to the flow-driven steady state, the integral fluctuation theorem, the Jarzynski equality, and the Bochkov-Kuzovlev relation are all rigorously satisfied. Additionally, for the special cases of pure rotational flow we derive an exact expression for the distribution of the heat dissipated by the particle into the medium, and for the special case of pure elongational flow we derive an exact expression for the distribution of the total entropy change. Finally, by examining the system's stochastic thermodynamics along a reverse trajectory, we also demonstrate that in elongational flow the total entropy change satisfies a detailed fluctuation theorem.

DOI: 10.1103/PhysRevE.100.052124

I. INTRODUCTION

The field of single colloid dynamics has emerged as a fertile area for the interplay between experiment and theory, spurred by advances in laser trapping and optical microscopy on the one hand [1] and by the development of simple analytically solvable models of stochastic particle motion on the other. It has now become possible, for instance, both to accurately measure various properties of single colloid systems (including thermodynamic properties like heat and work) and to analyze them in statistical mechanical terms. This has taken place against the backdrop of discoveries made some decades ago of several exact relations broadly referred to as fluctuation theorems [2] that are characteristic of the distributions that govern fluctuating thermodynamic variables away from equilibrium. Ongoing efforts to understand complex dynamics at the nanoscale level now often include comparisons of experimental results with the predictions of these fluctuation theorems. Such comparisons can be useful in cross-checking experimental data, validating technical protocols, and troubleshooting laboratory procedures.

While fluctuation theorems are mathematical statements of considerable generality, their significance and utility often become apparent only in the context of specific model systems, especially if the models can be treated exactly. There has been widespread interest in such models as a result, many of which have found applications in the analysis of data from different experimental systems, including optically trapped colloids dragged at a constant speed [3], electric circuits at constant mean current [4], and torsion pendulums under periodic torque [5], to cite a few representative examples. In these and related systems, the forces acting on the system are typically conservative, but in many other cases, they are nonconservative, originating, for instance, in temperature gradients or flow fields, and often producing nonequilibrium steady states at long times. Hydrodynamic forces represent an especially important source of time-dependent driving, being the basis for microfluidic approaches to the study of single molecules [6]. But there appear to have been no exact treatments of the stochastic thermodynamics of systems driven to nonequilibrium steady states by the action of flows with *general* velocity profiles. In this paper we show that, for a model defined by the overdamped dynamics of a Brownian particle in a harmonic potential acted on by a two-dimensional linear mixed flow (which contains different proportions α of rotational and elongational components, and which can generate nonequilibrium steady states), several *exact* thermodynamic results can, in fact, be derived, including the integral fluctuation theorem (IFT).

The IFT is a generalized version of the second law of thermodynamics that constrains the total amount of entropy, S_{tot}, that a system and its surroundings may produce in an interval of time t during a change of state [7]. It is given explicitly by the relation $\langle e^{-\Delta S_{\text{tot}}/k_B}\rangle = 1$, where the angular brackets denote an average over different realizations of the path that the system can take in going from its initial to final state. Using a path integral formalism, we show how the IFT and related theorems (such as the Bochkov-Kuzovlev relation) emerge from the equations of motion that define our flow-driven nonequilibrium system. For the special case of pure rotational flow (for which $\alpha = -1$), we also derive an exact expression for the particle's heat distribution function, which we find has exactly the same structure as the heat distribution function of a charged particle in a magnetic field. For another

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special case, that of pure elongational flow ($\alpha = +1$), we are able to verify that $\Delta S_{\rm tot}$ satisfies a detailed fluctuation theorem, which is a relation between the probabilities of occurrence of forward and reverse trajectories. Furthermore, from the steady-state solution of the Fokker-Planck equation that is equivalent to the particle's Langevin dynamics, we also derive expressions for the steady-state probability currents, allowing us to categorize the steady states as either equilibrium or nonequilibrium steady states, and simultaneously to compare our results in certain limits with known results [8].

The paper is organized as follows: Sec. II A sets down the Langevin equations that define the dynamics of our model particle system, and then uses these equations to derive an exact expression for the conditional probability density of the particle's position. Section II B considers the long-time limit of this density function, and demonstrates that it satisfies the steady-state limit of the Fokker-Planck equation that is equivalent to the given Langevin equations. In considering this $t \to \infty$ limit, we also derive expressions for the corresponding probability currents, which we find to be nonzero in all cases except pure elongational flow. Section II C discusses the stochastic thermodynamics of our model system, which we show is consistent with the integral fluctuation theorem, the Jarzynski equality, and the Bochkov-Kuzovlev relation. In Sec. III A we calculate the steady-state position distributions for the special cases of pure rotation, simple shear, and pure elongation, and in Sec. III B we treat these special cases in the limit of vanishing strength of the confining harmonic potential. For the case of rotational flow we also derive, in Sec. III C, an exact expression for the heat distribution function of the model system. We continue our study of the elongational flow case in Sec. III D, where we derive exact expressions for the distributions of the total entropy change along forward and reverse particle trajectories, and then use these expressions to prove yet another fluctuation theorem, the detailed fluctuation theorem for the total entropy change. Section IV is a summary of our principal findings.

II. MODEL AND THEORETICAL BACKGROUND

A. Particle dynamics in linear mixed flow

The model we use to describe the dynamics of a harmonically trapped colloid in a viscous fluid at temperature T in the presence of linear mixed flow is a generalization of a model we had introduced earlier to describe the time evolution of a Brownian oscillator in pure *elongational* flow [8,9]. The colloid is viewed as a point particle with coordinates $\mathbf{r}^T = (x, y)$ (T denoting transpose) that moves in a velocity field $\boldsymbol{v}(\boldsymbol{r}) = \boldsymbol{v}_0 + \dot{\gamma}\boldsymbol{\kappa}_\alpha \cdot \boldsymbol{r}$, and that is acted on by forces from thermal fluctuations and the static potential $U = k(x^2 + y^2)/2$. Here, $\boldsymbol{v}_0$ is the background solvent velocity (which we immediately set to 0), $\dot{\gamma}$ is a flow rate, k is the stiffness of the potential, and $\boldsymbol{\kappa}_\alpha = \begin{pmatrix} 0 & 1 \\ \alpha & 0 \end{pmatrix}$, with α a parameter that specifies the relative proportions of vorticity (rotation) and strain rate (elongation) in the flow, which can range from -1 (pure rotation) through 0 (simple shear) to $+1$ (pure elongation) [10]. So in overdamped conditions, the equation of motion of the particle is

$$\zeta(\dot{\boldsymbol{r}}(t) - \boldsymbol{v}(\boldsymbol{r})) + \frac{\partial U(\boldsymbol{r})}{\partial \boldsymbol{r}} = \boldsymbol{\theta}(t), \tag{1}$$

where ζ is the friction coefficient of the particle and $\boldsymbol{\theta}^T = (\theta_x, \theta_y)$ is a white noise variable representing the effects of thermal fluctuations; it is defined by the correlations $\langle\theta_i(t)\rangle = 0$ and $\langle\theta_i(t)\theta_j(t')\rangle = 2\zeta k_B T \delta_{ij}\delta(t - t')$, $i, j \in (x, y)$.

Since the statistics of $\boldsymbol{\theta}(t)$ are Gaussian, the probability $P[\boldsymbol{\theta}]$ that $\boldsymbol{\theta}(t)$ follows a particular trajectory in the interval of time t is given by the functional

$$P[\boldsymbol{\theta}] \propto \exp\left\{-\frac{\beta}{4\zeta}\int_0^t dt' \boldsymbol{\theta}^T(t') \cdot \boldsymbol{\theta}(t')\right\} \tag{2}$$

where $\beta \equiv 1/k_B T$. It follows from Eqs. (1) and (2) that the probability $P[\boldsymbol{r}]$ of realizing a particular trajectory of the particle in the same interval of time is

$$P[\boldsymbol{r}] \propto J \exp\left\{-\frac{\beta}{4\zeta}\int_0^t dt'[\zeta\dot{\boldsymbol{r}}(t') - \mathbf{D}\boldsymbol{r}(t')]^T \cdot [\zeta\dot{\boldsymbol{r}}(t') - \mathbf{D}\boldsymbol{r}(t')]\right\}, \tag{3}$$

where $\mathbf{D} = (\zeta\dot{\gamma}\boldsymbol{\kappa}_\alpha - k\mathbb{I})$, with $\mathbb{I}$ the unit matrix, and J is the Jacobian of the transformation from $\boldsymbol{\theta}$ to $\boldsymbol{r}$ variables, which can be shown to be given by $J \propto e^{kt/\zeta}$ [8,9]. After the dot product in Eq. (3) is expanded out, the equation becomes

$$\begin{aligned} P[\boldsymbol{r}] \propto e^{kt/\zeta} \exp\bigg\{-\frac{\beta}{4\zeta}\int_0^t dt'[\zeta^2(\dot{x}^2 + \dot{y}^2) + 2k\zeta(\dot{x}x + \dot{y}y) \\ + (k^2 + \alpha^2\zeta^2\dot{\gamma}^2)x^2 + (k^2 + \zeta^2\dot{\gamma}^2)y^2 \\ - 2\zeta^2\dot{\gamma}(\alpha x\dot{y} + \dot{x}y) - 2k\zeta\dot{\gamma}(1 + \alpha)xy]\bigg\}, \end{aligned} \tag{4}$$

the proportionality constant in this relation being fixed by a normalization condition. The conditional probability density $P(x_f, y_f, t|x_0, y_0)$ of finding the particle at x_f, y_f at time t given that it was at x_0, y_0 initially can now be written as

$$\begin{aligned} P(x_f, y_f, t|x_0, y_0) \propto e^{kt/\zeta - \beta k(x_f^2 + y_f^2 - x_0^2 - y_0^2)/4} \\ \times \int_{x(0)=x_0}^{x(t)=x_f} \mathcal{D}[x] \int_{y(0)=y_0}^{y(t)=y_f} \mathcal{D}[y] e^{-S_\alpha[\boldsymbol{r}]}, \end{aligned} \tag{5}$$

where $\mathcal{D}[x]$ and $\mathcal{D}[y]$ denote the measures on the space of x and y trajectories, and $S_\alpha[\boldsymbol{r}]$ is the action, defined as $S_\alpha[\boldsymbol{r}] = \int_0^t dt' \mathcal{L}_\alpha(\dot{x}, \dot{y}, x, y)$, with $\mathcal{L}_\alpha$ the Lagrangian, given by

$$\begin{aligned} \mathcal{L}_\alpha(\dot{x}, \dot{y}, x, y) = a_0(\dot{x}^2 + \dot{y}^2) + a_1 x^2 + a_2 y^2 - a_3 x\dot{y} \\ - a_4 \dot{x}y - a_5 xy. \end{aligned} \tag{6}$$

Here $a_0 = \frac{\beta\zeta}{4}$, $a_1 = \frac{\beta k^2}{4\zeta}(1 + \frac{(\alpha\zeta\dot{\gamma})^2}{k^2})$, $a_2 = \frac{\beta k^2}{4\zeta}(1 + \frac{(\zeta\dot{\gamma})^2}{k^2})$, $a_3 = \frac{\alpha\beta\zeta\dot{\gamma}}{2}$, $a_4 = \frac{\beta\zeta\dot{\gamma}}{2}$, and $a_5 = \frac{\beta k\dot{\gamma}}{2}(1 + \alpha)$.

Because the path integral

$$\int_{x(0)=x_0}^{x(t)=x_f} \mathcal{D}[x] \int_{y(0)=y_0}^{y(t)=y_f} \mathcal{D}[y]\, e^{-S_\alpha[\boldsymbol{r}]}$$

is a quadratic functional of particle positions, it can be determined using Feynman's variational procedure [11,12], which leads to the exact result $\phi_\alpha(t)\exp -\bar{S}_\alpha[\boldsymbol{r}]$. Here $\phi_\alpha(t)$ is the so-called fluctuation integral, which is found from the de

Witt–Morette formula [11,13]

$$\phi_\alpha(t)^2 \propto \det\begin{pmatrix} \frac{\partial^2 \bar{S}_\alpha}{\partial x_f \partial x_0} & \frac{\partial^2 \bar{S}_\alpha}{\partial x_f \partial y_0} \\ \frac{\partial^2 \bar{S}_\alpha}{\partial y_f \partial x_0} & \frac{\partial^2 \bar{S}_\alpha}{\partial y_f \partial y_0} \end{pmatrix},$$

$\bar{S}_\alpha[\boldsymbol{r}]$ being the action evaluated along the trajectories $\bar{x}(t)$ and $\bar{y}(t)$. These trajectories are the solutions to the Euler-Lagrange equations $\frac{\partial \mathcal{L}_\alpha}{\partial x} - \frac{d}{dt}\frac{\partial \mathcal{L}_\alpha}{\partial \dot{x}} = 0$ and $\frac{\partial \mathcal{L}_\alpha}{\partial y} - \frac{d}{dt}\frac{\partial \mathcal{L}_\alpha}{\partial \dot{y}} = 0$; that is, they are the solutions to

$$\ddot{\bar{\boldsymbol{r}}}(t) + \dot{\gamma}(1-\alpha)\mathbf{J}\dot{\bar{\boldsymbol{r}}}(t) + \mathbf{M}\bar{\boldsymbol{r}}(t) = 0, \tag{7}$$

where $\bar{\boldsymbol{r}}^T = (\bar{x}, \bar{y})$, $\mathbf{J} = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}$, and $\mathbf{M} = \frac{1}{2a_0}\begin{pmatrix} -2a_1 & a_5 \\ a_5 & -2a_2 \end{pmatrix}$. The solution of Eq. (7) (which we express in terms of a time variable s to distinguish it from the final time t) can be verified to have the form [14]

$$\bar{x}(s) = e^{-\kappa s}\left\{A\cosh as + \frac{B}{\sqrt{\alpha}}\sinh as\right\} + e^{\kappa s}\left\{C\left(\cosh as - \frac{2(1-\alpha^2)\omega}{\sqrt{\alpha}\mu_\alpha}\sinh as\right) + \frac{D[\mu_\alpha - 4(1+\alpha)]}{\sqrt{\alpha}\mu_\alpha}\sinh as\right\}, \tag{8a}$$

$$\bar{y}(s) = e^{-\kappa s}\left\{A\sqrt{\alpha}\sinh as + B\cosh as\right\} + e^{\kappa s}\left\{\frac{C[\alpha\mu_\alpha - 4(1+\alpha)]}{\sqrt{\alpha}\mu_\alpha}\sinh as + D\left(\cosh as + \frac{2(1-\alpha^2)\omega}{\sqrt{\alpha}\mu_\alpha}\sinh as\right)\right\}, \tag{8b}$$

where $\kappa = k/\zeta$, $\omega = \dot{\gamma}\zeta/k$, $a = \sqrt{\alpha}\dot{\gamma}$, $\mu_\alpha = 4 + (1-\alpha)^2\omega^2$, and A, B, C, D are unknown integration constants that are determined by applying the boundary conditions $\bar{x}(0) = x_0$, $\bar{y}(0) = y_0$, $\bar{x}(t) = x_f$, and $\bar{y}(t) = y_f$ to Eqs. (8a) and (8b). The expressions for these integration constants are given in Appendix A.

From its definition as the integral of the Lagrangian, the minimized action $\bar{S}_\alpha$ can be shown, using partial integration and the Euler-Lagrange equations, to be given by

$$\bar{S}_\alpha[x, y] = a_0[\dot{\bar{x}}(t)x_f + \dot{\bar{y}}(t)y_f - \dot{\bar{x}}(0)x_0 - \dot{\bar{y}}(0)y_0] - \frac{a_3 + a_4}{2}(x_f y_f - x_0 y_0). \tag{9}$$

After substituting the expressions for A, B, C, and D into this equation, collecting terms, and simplifying the result (using MATHEMATICA [15] to carry out the extremely lengthy calculations), we find that

$$\begin{aligned}\bar{S}_\alpha[x, y] = \frac{\beta k}{8\Delta_\alpha}\{&A_1(x_f^2 + x_0^2 + y_f^2 + y_0^2) + A_2(x_f^2 - x_0^2 - y_f^2 + y_0^2) - A_3[\alpha(x_f^2 + x_0^2) + y_f^2 + y_0^2] \\ &+ e^{-2\kappa t}[A_4 x_0 y_0 + A_5(x_0^2 - y_0^2)] - e^{2\kappa t}[A_4 x_f y_f + A_5(x_f^2 - y_f^2)] + A_6(x_0 y_0 + x_f y_f) - A_7(x_0 y_0 - x_f y_f) \\ &- A_8(x_0 x_f + y_0 y_f) + A_9(x_0 x_f - y_0 y_f) + A_{10}(\alpha x_0 x_f + y_0 y_f) + A_{11}(x_0 y_f + x_f y_0) + A_{12}(x_0 y_f - x_f y_0)\},\end{aligned} \tag{10}$$

where $\Delta_\alpha = \alpha\mu_\alpha(\cosh 2\kappa t - 1) - (1+\alpha)^2(\cosh 2at - 1)$, and the expressions for $A_1, A_2, \ldots, A_{12}$ are given in Appendix B.

Using the de Witt–Morette formula in combination with the normalization condition $\int_{-\infty}^{+\infty} dx_f \int_{-\infty}^{+\infty} dy_f\, P(x_f, y_f, t|x_0, y_0) = 1$, the fluctuation integral $\phi_\alpha(t)$ is now calculated as

$$\phi_\alpha(t) = \frac{\beta k}{\pi}\sqrt{\frac{\alpha(1-\alpha\omega^2)}{2\Delta_\alpha}}. \tag{11}$$

Thus the complete expression for the conditional probability density of the trapped colloid's time-dependent positions in the presence of linear mixed flow is given by

$$P(x_f, y_f, t|x_0, y_0) = \phi_\alpha(t) e^{\frac{kt}{\zeta} - \frac{\beta k}{4}(x_f^2 + y_f^2 - x_0^2 - y_0^2)} \exp -\bar{S}_\alpha \tag{12}$$

with $\phi_\alpha(t)$ given by Eq. (11) and $\bar{S}_\alpha$ by Eq. (10).

B. Particle dynamics at long times

Having set up the equations that define the time evolution of a harmonically trapped Brownian particle in linear mixed flow, we turn now to a consideration of the particle's long-time dynamics, as a preliminary to examining the energetic and entropic changes that take place when the particle, initially assumed to be in thermal equilibrium in the absence of flow, is exposed to the effects of the flow at time $t = 0$ and then allowed to evolve for a long time. In its initial state, the particle's positions are governed by the Boltzmann distribution:

$$P_0 = \frac{\beta k}{2\pi} e^{-\frac{\beta k}{2}(x_0^2 + y_0^2)} \equiv Z_0^{-1} e^{-\beta U}, \tag{13}$$

where $Z_0 = \int_{-\infty}^{+\infty} dx_0 \int_{-\infty}^{+\infty} dy_0 e^{-\beta U(x_0, y_0)}$ is the configurational partition function of the system. Following the imposition of the flow field, the particle eventually reaches a state in which its positions are governed by the $t \to \infty$ limit of Eq. (12), which we find is given by

$$\begin{aligned}P_\alpha^\infty = \frac{\beta k}{\pi}\sqrt{\frac{1-\alpha\omega^2}{\mu_\alpha}} \exp\bigg\{-\frac{\beta k}{\mu_\alpha}\big([2 - (1-\alpha)\alpha\omega^2]x_f^2 \\ + [2 + (1-\alpha)\omega^2]y_f^2 - 2(1+\alpha)\omega x_f y_f\big)\bigg\}.\end{aligned} \tag{14}$$

In arriving at this expression, we have assumed that $k/\zeta > \alpha\dot{\gamma}$, which ensures that the particle is not permanently carried away from the trap in the presence of flow.

The structure of P_α^∞ suggests that at long times the particle experiences an effective flow-dependent potential V_α^∞ that is given by

$$\begin{aligned}V_\alpha^\infty(x, y) = \frac{k}{\mu_\alpha}\{&[2 - (1-\alpha)\alpha\omega^2]x^2 + [2 + (1-\alpha)\omega^2]y^2 \\ &- 2(1+\alpha)\omega xy\}.\end{aligned} \tag{15}$$

This in turn suggests that the coefficient $(\beta k/\pi)\sqrt{(1-\alpha\omega^2)/\mu_\alpha}$ in Eq. (14) can be thought of as the reciprocal of a partition function Z_α^∞, where $Z_\alpha^\infty = \int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy e^{-\beta V_\alpha^\infty(x,y)}$.

That the distribution P_α^∞ does correspond to a steady state of the system can be verified by showing that it satisfies the steady-state limit of the Fokker-Planck equation equivalent to Eq. (1). This Fokker-Planck equation is found to be

$$\frac{\partial P}{\partial t} = -\left\{\frac{\partial}{\partial x}\left(-\frac{k}{\zeta}x + \dot{\gamma}y - \frac{k_BT}{\zeta}\frac{\partial}{\partial x}\right) + \frac{\partial}{\partial y}\left(-\frac{k}{\zeta}y + \alpha\dot{\gamma}x - \frac{k_BT}{\zeta}\frac{\partial}{\partial y}\right)\right\}P, \tag{16}$$

where $P \equiv P(x, y, t) = \langle\delta(x - x(t))\delta(y - y(t))\rangle$, the angular brackets denoting an average over all realizations of the thermal noise. Equation (16) can be written equivalently as

$$\frac{\partial P}{\partial t} = -\frac{\partial}{\partial x}J_{\alpha,x} - \frac{\partial}{\partial y}J_{\alpha,y}, \tag{17}$$

where $J_{\alpha,x}$ and $J_{\alpha,y}$ are probability currents, and are given by

$$J_{\alpha,x} = \left(-\frac{k}{\zeta}x + \dot{\gamma}y - \frac{k_BT}{\zeta}\frac{\partial}{\partial x}\right)P \tag{18a}$$

and

$$J_{\alpha,y} = \left(-\frac{k}{\zeta}y + \alpha\dot{\gamma}x - \frac{k_BT}{\zeta}\frac{\partial}{\partial y}\right)P. \tag{18b}$$

If the system reaches a steady state, the distribution P no longer changes with time, and $\partial P/\partial t = 0$. Denoting the solution of Eq. (16) in this limit as P_α^{ss}, we see by direct substitution of Eq. (14) into the right-hand side of Eq. (16) that $P_\alpha^{ss} = P_\alpha^\infty$. So at long times the particle does in fact reach a steady state. The nature of this steady state can be determined from the structure of the steady-state currents, which can be obtained from Eqs. (18a) and (18b) by replacing P by P_α^{ss}. When this is done, the result is

$$J_{\alpha,x}^{ss} = \frac{\dot{\gamma}(1-\alpha)}{\mu_\alpha}[-(1+\alpha)\omega x + \{2 + (1-\alpha)\omega^2\}y]P_\alpha^{ss} \tag{19a}$$

and

$$J_{\alpha,y}^{ss} = -\frac{\dot{\gamma}(1-\alpha)}{\mu_\alpha}[\{2 - (1-\alpha)\alpha\omega^2\}x - (1+\alpha)\omega y]P_\alpha^{ss}. \tag{19b}$$

If these currents are identically 0 for any given α, the steady state is said to be an *equilibrium* steady state, while if they are nonzero, the steady state is said to be a *nonequilibrium* steady state. It is clear that for $\alpha = 1$, corresponding to pure elongational flow, the steady state is an equilibrium steady state, while for all other values of α it is a nonequilibrium steady state.

C. Stochastic thermodynamics and fluctuation relations

As shown by Hatano and Sasa [16], a system that is driven stochastically between different steady states by the action of external forces satisfies the following relation:

$$\left\langle \exp - \int_0^t dt'\,\dot{\eta}\frac{\partial\phi(\boldsymbol{r};\eta)}{\partial\eta}\right\rangle = 1, \tag{20}$$

where η is a set of control parameters and $\phi(\boldsymbol{r};\eta)$ is the function $-\ln P^{ss}$. Now in a steady state the probability density function has the general form $P^{ss} = Z^{-1}e^{-\beta V}$, where Z is the partition function and V the effective potential, so it follows that

$$\phi(\boldsymbol{r};\eta) = -\beta\mathcal{F} + \beta V \tag{21}$$

with $\mathcal{F} \equiv -k_BT\ln Z$ being the steady-state free energy. ($\mathcal{F}$ in our calculations is a free energy in the sense that it is defined in terms of the logarithm of a partition function, which may correspond either to equilibrium or to nonequilibrium steady-state conditions; depending on the nature of the flow, therefore, the associated $\mathcal{F}$ may be interpreted as an equilibrium free energy or a nonequilibrium free energy.) Since the free energy is a state function, the term $\beta\int_0^t dt'\,\dot{\eta}\frac{\partial\mathcal{F}(\eta)}{\partial\eta}$ that is obtained on substituting Eq. (21) into Eq. (20) is just the free energy change $\Delta\mathcal{F} = \mathcal{F}(t) - \mathcal{F}(0)$. Thus the Hatano-Sasa relation reduces to

$$\left\langle \exp -\beta\int_0^t dt'\,\dot{\eta}\frac{\partial V(\boldsymbol{r};\eta)}{\partial\eta}\right\rangle = e^{-\beta\Delta\mathcal{F}}, \tag{22}$$

which takes different forms depending on how the change in the potential V is assumed to be affected during the transition from one steady state to another. If it is assumed that V changes in time solely by virtue of a time-dependent protocol represented by $\lambda(t)$, then $\int_0^t dt'\dot{\eta}\,\partial V/\partial\eta$ becomes $\int_0^t dt'(\partial V/\partial\lambda)\dot{\lambda}$; this quantity is conventionally interpreted as the thermodynamic work done during the change of state [17], which we denote w. If on the other hand, it is assumed that V is not explicitly time dependent but changes in time by virtue of its dependence on the dynamical variable $\mathbf{r}$, then $\int_0^t dt'\dot{\eta}\,\partial V/\partial\eta$ becomes $\int_0^t dt'\mathbf{v}(\mathbf{r})\cdot\nabla_{\mathbf{r}}V$; this quantity is conventionally interpreted as the mechanical work done during the change of state [17], which we denote w_r. It is equivalent to the frame-invariant definition of work introduced by Speck *et al.* [18] in their study of flow-driven systems. The foregoing approaches to the treatment of V in Eq. (22) are discussed in the two subsections below.

1. Thermodynamic driving

When the change in V originates in the time dependence of the control parameter $\lambda(t)$, Eq. (22) reduces to

$$\langle e^{-\beta w}\rangle = e^{-\beta\Delta\mathcal{F}}, \tag{23}$$

which will be recognized as the Jarzynski equality [19]. This relation was initially assumed to hold only for systems that made transitions between equilibrium states, but it is now clear that it also holds when the transitions occur between steady states.

For the present system, the control parameter $\lambda(t)$ can be thought of as the flow strength, which varies between 0 at $t = 0$ (where the potential is U) and $\dot{\gamma}$ at $t \gg 1$ (where the potential can be taken to be V_α^∞). The work done in this interval is calculated indirectly, by appeal to the first law in the form $w = \Delta V + q$, where $\Delta V = V(\dot{\gamma}) - V(\dot{\gamma} = 0) =$

$V_\alpha^\infty - U$ and q is the associated heat change, which, following Sekimoto's definition [20] is obtained from the relation

$$\dot{q} = -\frac{\partial V}{\partial x}\dot{x} - \frac{\partial V}{\partial y}\dot{y}. \tag{24}$$

When V in this relation is identified with V_α^∞, we find that

$$q = -\frac{k}{\mu_\alpha}\{(2-(1-\alpha)\alpha\omega^2)(x_f^2 - x_0^2) + (2+(1-\alpha)\omega^2) \times (y_f^2 - y_0^2) - 2\omega(1+\alpha)(x_f y_f - x_0 y_0)\}. \tag{25}$$

The work is therefore given by

$$w = \frac{k}{\mu_\alpha}\{[2-(1-\alpha)\alpha\omega^2]x_0^2 + [2+(1-\alpha)\omega^2]y_0^2 - 2\omega(1+\alpha)x_0y_0\} - \frac{k}{2}(x_0^2 + y_0^2), \tag{26}$$

and the exponential average of this quantity, $\langle e^{-\beta w}\rangle$, is calculated from the formula

$$\langle e^{-\beta w}\rangle = \int_{-\infty}^{+\infty} dx_f \int_{-\infty}^{+\infty} dy_f \int_{-\infty}^{+\infty} dx_0 \times \int_{-\infty}^{+\infty} dy_0 e^{-\beta w} P(x_f, y_f, t|x_0, y_0) P_0(x_0, y_0), \tag{27}$$

where $P(x_f, y_f, t|x_0, y_0)$ and $P_0(x_0, y_0)$ are given by Eqs. (12) and (13), respectively. The evaluation of this expression using Eq. (26) for w is straightforward, since the integrals are all Gaussian, but it helps to use MATHEMATICA [15] to complete the intermediate steps, which are extremely lengthy. The calculations eventually produce this simple expression

$$\langle e^{-\beta w}\rangle = \sqrt{\frac{\mu_\alpha}{4(1-\alpha\omega^2)}}. \tag{28}$$

The same result is obtained much more simply by replacing $P(x_f, y_f, t|x_0, y_0)$ in Eq. (27) by its $t \to \infty$ limit, which is given by Eq. (14). If the relation in Eq. (23) does indeed hold, then from Eq. (28) the free energy change between the system's initial and final states must be given by

$$\Delta\mathcal{F}_\alpha = \frac{k_BT}{2}\ln\frac{4(1-\alpha\omega^2)}{\mu_\alpha}. \tag{29}$$

This expression can be verified to be the free energy change between these states by using the partition functions Z_0 [Eq. (13)] and Z_α^∞ [the prefactor of the exponential in Eq. (14)] to independently calculate the free energy change from the formula $\Delta\mathcal{F}_\alpha = -k_BT\ln Z_\alpha^\infty/Z_0$. This calculation leads to exactly the same expression for $\Delta\mathcal{F}_\alpha$ as is shown in Eq. (29).

Given the above expressions for q, P_α^{ss}, and P_0, one can also calculate the total change in entropy of the system and its surroundings when the system evolves from its initial equilibrium state to its final steady state. If ΔS denotes the entropy change of the system, ΔS_m that of the medium, and $\Delta S_{\rm tot}$ their sum, then by making the following identifications [7] $\Delta S = -k_B\ln P_\alpha^{ss}/P_0$ and $\Delta S_m \equiv q/T$ it follows that

$$\Delta S_{\rm tot} = \frac{q}{T} + k_B\ln\frac{Z_\alpha^\infty}{Z_0} + \frac{\Delta V}{T}, \tag{30}$$

which becomes

$$\frac{\Delta S_{\rm tot}(x_0, y_0)}{k_B} = \frac{1}{2}\ln\left(\frac{\mu_\alpha}{4(1-\alpha\omega^2)}\right) + \frac{\beta k}{\mu_\alpha}\{(2-(1-\alpha)\alpha\omega^2)x_0^2 + (2+(1-\alpha)\omega^2)y_0^2 - 2\omega(1+\alpha)x_0y_0\} - \frac{\beta k}{2}(x_0^2 + y_0^2). \tag{31}$$

The exponential average of this quantity, $\langle e^{-\Delta S_{\rm tot}/k_B}\rangle$, therefore simplifies to

$$\langle e^{-\Delta S_{\rm tot}/k_B}\rangle = \sqrt{\frac{4(1-\alpha\omega^2)}{\mu_\alpha}}\langle e^{-\beta w}\rangle, \tag{32}$$

which from the Jarzynski relation, Eq. (28), further reduces to

$$\langle e^{-\Delta S_{\rm tot}/k_B}\rangle = 1. \tag{33}$$

Equation (33) is the statement of another fluctuation relation, the integral fluctuation theorem [7].

2. *Mechanical driving*

As shown earlier, when the change in V originates in the dynamics of $\mathbf{r}$, the work done during the process is $w_r = \int_0^t dt'\mathbf{v}(\mathbf{r})\cdot\nabla_{\mathbf{r}}V$, and the Hatano-Sasa relation reduces to

$$\langle e^{-\beta w_r}\rangle = e^{-\beta\Delta\mathcal{F}_r}, \tag{34}$$

where $\Delta\mathcal{F}_r$ is the free energy change for the process. For the present system, if V is identified with the time-independent equilibrium potential U, the work w_r is given by

$$w_r(t) = \dot{\gamma}k(1+\alpha)\int_0^t dt' x(t')y(t'). \tag{35}$$

This is a path-dependent quantity, and its exponential average, $\langle e^{-\beta w_r}\rangle$, is defined as

$$\langle e^{-\beta w_r}\rangle = \int_{-\infty}^{+\infty} dx_f \int_{-\infty}^{+\infty} dy_f \int_{-\infty}^{+\infty} dx_0 \times \int_{-\infty}^{+\infty} dy_0\, e^{\kappa t - \frac{\beta k}{4}(x_f^2 + y_f^2 - x_0^2 - y_0^2)} \times G_{w_r}(x_f, y_f, t|x_0, y_0) P_0(x_0, y_0), \tag{36}$$

where $G_{w_r}(x_f, y_f, t|x_0, y_0)$ is the path integral

$$G_{w_r}(x_f, y_f, t|x_0, y_0) = \int_{x(0)=x_0}^{x(t)=x_f}\mathcal{D}[x]\int_{y(0)=y_0}^{y(t)=y_f}\mathcal{D}[y]e^{-\int_0^t dt'\mathcal{L}'(\dot{x},\dot{y},x,y)}. \tag{37}$$

The function $\mathcal{L}'$ in this expression is a new Lagrangian for the system, and is given by

$$\mathcal{L}'(\dot{x},\dot{y},x,y) = \mathcal{L}_\alpha(\dot{x},\dot{y},x,y) + \beta\dot{\gamma}k(1+\alpha)xy = a_0(\dot{x}^2 + \dot{y}^2) + a_1x^2 + a_2y^2 - a_3x\dot{y} - a_4\dot{x}y + a_5xy, \tag{38}$$

where $\mathcal{L}_\alpha(\dot{x},\dot{y},x,y)$ is the function defined in Eq. (6) and $a_0, \ldots, a_5$ are the parameters defined in the paragraph following Eq. (6). The evaluation of the path integral in Eq. (37)

proceeds as before via Feynman's variational approach, which is discussed at greater length in Appendix C, where it is shown that

$$G_{w_r}(x_f, y_f, t|x_0, y_0) = \phi_\alpha(t) \exp -\bar{S}'_{w_r}. \tag{39}$$

In this expression, $\bar{S}'_{w_r}$ is the classical action (cf. Appendix C) and $\phi_\alpha(t)$ is the fluctuation integral of Eq. (11). On substituting Eq. (39) into Eq. (36) and carrying out the Gaussian integrals (using MATHEMATICA again to work out the very complicated intermediate steps), Eq. (36) collapses to the simple result

$$\langle e^{-\beta w_r} \rangle = 1, \tag{40}$$

which is an instance of what is now generally referred to as the Bochkov-Kuzovlev relation [21]. It can be thought of as a special case of the Jarzynski equality in which the free energy change $\Delta\mathcal{F}_r$ is zero.

The work defined in Eq. (35) can be substituted into the first law to derive an expression for the heat transferred to the medium, q_r, along a stochastic trajectory. Using U for the energy, one then obtains

$$q_r = \dot{\gamma} k(1+\alpha) \int_0^t dt' x(t')y(t') - \frac{k}{2}\big(x_f^2 + y_f^2 - x_0^2 - y_0^2\big). \tag{41}$$

If this expression is in turn used to determine the total entropy change of system and surroundings, the result is the following path-dependent expression:

$$\Delta S_{\mathrm{tot},r} = -k_B \ln \frac{P_\alpha^{ss}}{P_0} + \frac{\dot{\gamma} k}{T}(1+\alpha) \int_0^t dt' x(t')y(t') - \frac{k}{2T}\big(x_f^2 + y_f^2 - x_0^2 - y_0^2\big), \tag{42}$$

which when divided by the Boltzmann constant and exponentiated gives

$$e^{-\Delta S_{\mathrm{tot},r}/k_B} = \frac{P_\alpha^{ss}}{P_0} \exp\left\{-\beta k\dot{\gamma}(1+\alpha)\int_0^t dt'\, x(t')y(t') + \frac{\beta k}{2}\big(x_f^2 - x_0^2 + y_f^2 - y_0^2\big)\right\}, \tag{43}$$

where P_0 and P_α^{ss} are given by Eqs. (13) and (14), respectively. The average of Eq. (43) now leads to

$$\langle e^{-\Delta S_{\mathrm{tot},r}/k_B} \rangle = \int_{-\infty}^{+\infty} dx_f \int_{-\infty}^{+\infty} dy_f \int_{-\infty}^{+\infty} dx_0 \times \int_{-\infty}^{+\infty} dy_0 P_\alpha^{ss} e^{\frac{\beta k}{2}(x_f^2 - x_0^2 + y_f^2 - y_0^2)} \times \exp\left\{-\beta\dot{\gamma}k(1+\alpha)\int_0^t dt' x(t')y(t')\right\} \times P(x_f, y_f, t|x_0, y_0), \tag{44}$$

where $P(x_f, y_f, t|x_0, y_0)$ is given by Eq. (5). The substitution of P_α^{ss} and $P(x_f, y_f, t|x_0, y_0)$ into the average then gives the integral

$$\langle e^{-\Delta S_{\mathrm{tot},r}/k_B} \rangle = \int_{-\infty}^{+\infty} dx_f \int_{-\infty}^{+\infty} dy_f \int_{-\infty}^{+\infty} dx_0 \int_{-\infty}^{+\infty} dy_0\, Z_\alpha^{\infty\,-1} e^{-\beta V_\alpha^\infty} \times e^{\kappa t + \frac{\beta k}{4}(x_f^2 + y_f^2 - x_0^2 - y_0^2)} G_{w_r}(x_f, y_f, t|x_0, y_0), \tag{45}$$

where V_α^∞ is the steady-state potential of Eq. (15) and G_{w_r} is the path integral defined by Eq. (39), the classical action in that expression being determined by the Lagrangian of Eq. (38). The evaluation of this path integral by the variational method (cf. Appendix C), followed by integration over x_f, y_f, x_0, y_0 (using MATHEMATICA [15]) eventually leads, after considerable algebra, to the result

$$\langle e^{-\Delta S_{\mathrm{tot},r}/k_B} \rangle = 1, \tag{46}$$

which is an independent validation of the integral fluctuation theorem.

III. SPECIAL CASES

A. Steady-state distributions

The steady-state distribution in Eq. (14) can be used to obtain the steady-state distributions for the special cases of rotational, shear, and elongational flow, which correspond to the limits $\alpha = -1$, $\alpha = 0$, and $\alpha = +1$, respectively. The shapes of these distributions as a function of the dimensionless variables $\bar{X} = x\sqrt{\beta k}$ and $\bar{Y} = y\sqrt{\beta k}$ at a fixed (arbitrary) value of 0.005 for the dimensionless probability density $P_\alpha^{ss}/\beta\kappa\zeta$, with $\kappa \equiv k/\zeta$, are shown in Fig. 1, as viewed along the z axis. As may be verified, the rotational flow distribution in the steady state happens to coincide with the flow-free equilibrium thermal distribution defined in Eq. (13), so the projection of the latter onto the same two-dimensional plane defined by $\bar{X}$ and $\bar{Y}$ has exactly the same circular profile as the rotational flow distribution, and is therefore not shown. For the case of shear flow and elongational flow the distributions can be interpreted as having the shapes of a distorted Gaussian surface.

B. The flow-driven free particle

In the limit $k = 0$ and $x_0 = y_0 = 0$, which describes an unconfined particle starting out from the origin, Eq. (12) reduces to

$$P(x, y, t|0, 0) = \frac{\alpha}{2\pi}\left(\frac{2\dot{\gamma}}{D\chi(t)}\right)^{1/2} \exp\left\{-\frac{\alpha^{1/2}}{2\chi(t)}[\alpha\psi(t)x^2 + \Lambda(t)y^2 - 2\alpha^{1/2}(1+\alpha)\varphi(t)xy]\right\}, \tag{47}$$

where $D = k_B T/\zeta$, $\psi(t) = (1+\alpha)\sinh 2at + 2\alpha^{1/2}(1-\alpha)\dot{\gamma}t$, $\Lambda(t) = (1+\alpha)\sinh 2at - 2\alpha^{1/2}(1-\alpha)\dot{\gamma}t$, $\varphi(t) = \cosh 2at - 1$, and $\chi(t) = D\dot{\gamma}^{-1}\{(1+\alpha)^2(\cosh at - 1) - 2\alpha(1-\alpha)^2\dot{\gamma}^2 t^2\}$. This expression agrees exactly with the expression derived by Foister and Van De Ven as the solution to a Fokker-Planck equation [22] (see Eq. (2.18) in Ref. [22]). Equation (47), in turn, reduces to the following expressions in

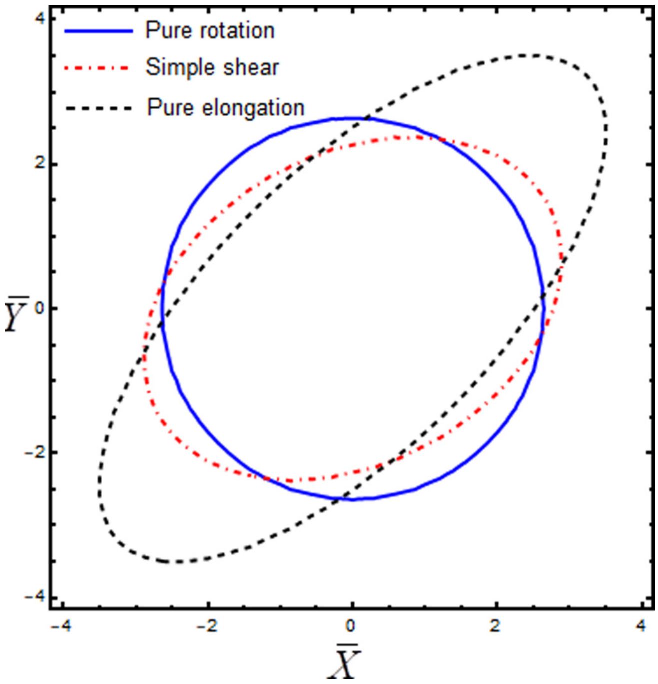

FIG. 1. The shapes of the steady-state distribution [Eq. (14)] as viewed along the z axis for a flow-driven particle trapped by a harmonic potential in two dimensions plotted for a fixed value (0.005) of $P_\alpha^{ss}/\beta\kappa\zeta$ against the dimensionless quantities $\bar{X} = x\sqrt{\beta k}$ and $\bar{Y} = y\sqrt{\beta k}$, at the parameter values $\kappa = 1\ \mathrm{s}^{-1}$ and $\dot{\gamma} = 0.7\ \mathrm{s}^{-1}$, and for different values of α: $\alpha = -1$ (solid blue curve), $\alpha = 0$ (dot-dashed red curve), and $\alpha = 1$ (dashed black curve), which correspond to pure rotational, simple shear and pure elongational flow, respectively.

the limits $\alpha = -1$ (pure rotation), $\alpha = 0$ (simple shear), and $\alpha = 1$ (pure elongation):

$$P_{\alpha=-1}(x, y, t|0, 0) = \frac{1}{4\pi Dt} \exp\left\{-\frac{x^2 + y^2}{4Dt}\right\}, \tag{48}$$

$$P_{\alpha=0}(x, y, t|0, 0) = \frac{1}{2\pi Dt}\sqrt{\frac{3}{\dot{\gamma}^2 t^2 + 12}} \times \exp\left\{-\frac{3\left[x - \frac{1}{2}y\dot{\gamma}t\right]^2}{Dt[\dot{\gamma}^2 t^2 + 12]} - \frac{y^2}{4Dt}\right\}, \tag{49}$$

and

$$P_{\alpha=1}(x, y, t|0, 0) = \frac{\dot{\gamma}}{2\sqrt{2}\pi D(\cosh 2\dot{\gamma}t - 1)^{1/2}} \times \exp\left[-\frac{\dot{\gamma}}{4D}\left\{\frac{\sinh 2\dot{\gamma}t}{\cosh 2\dot{\gamma}t - 1}(x^2 + y^2) + 2xy\right\}\right]. \tag{50}$$

In Eq. (48) we have selected the negative root of the $\sqrt{\chi(t)}$ term in Eq. (47) to ensure that $P_{\alpha=-1}$ is well defined, and in Eq. (49) our expression for the coefficient of the exponential factor corrects a typographical error in Eq. (2.20)

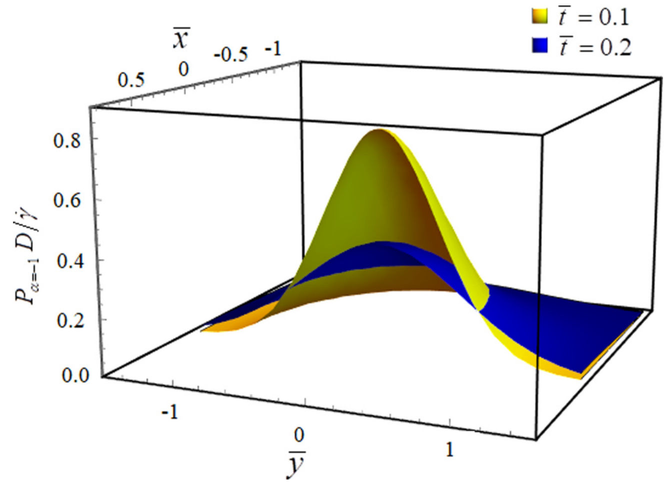

FIG. 2. The time-dependent probability $P_{\alpha=-1}D/\dot{\gamma}$ as calculated from Eq. (48) and plotted against the dimensionless variables $\bar{x} = x\sqrt{\dot{\gamma}/D}$ and $\bar{y} = y\sqrt{\dot{\gamma}/D}$ at two different dimensionless times: $\bar{t} = \dot{\gamma}t = 0.1$ (yellow surface) and $\bar{t} = 0.2$ (blue surface).

of Ref. [22]. The time-dependent probability distribution in Eq. (48), nondimensionalized by the factor $D/\dot{\gamma}$, is plotted in Fig. 2 as a function of the dimensionless variables $\bar{x} = x\sqrt{\dot{\gamma}/D}$ and $\bar{y} = y\sqrt{\dot{\gamma}/D}$ at two arbitrary values of the dimensionless time $\bar{t} = \dot{\gamma}t$. The distributions corresponding to Eq. (49) and (50) show similar trends, except that the Gaussian surfaces are distorted, much as they are in these cases for the flow-driven harmonically trapped particle (cf. Fig. 1).

C. Heat distribution function in rotational flow

The calculation of the exponential averages of quantities like heat or work can often be carried out exactly, but, because such quantities are generally path dependent, it is typically more difficult to calculate their distribution functions exactly. For a Brownian oscillator in pure rotational flow, however, the work done along a given trajectory is identically 0 [cf. Eqs. (26) and (35)]. This means that the heat produced during the process is just the negative of the change in internal energy. That is,

$$q(\alpha \to -1) = -\frac{k}{2}\left(x_f^2 + y_f^2 - x_0^2 - y_0^2\right), \tag{51}$$

which is independent of the path. This makes it possible to derive an analytical expression for the heat distribution function. This function is defined, in general, as

$$P(q, t) = \langle\delta(q - q(t))\rangle \tag{52}$$

with $q(t)$ given by Eq. (51). The average in this expression is taken over the distribution of x_f, y_f, x_0, and y_0. By representing the delta function in this expression as a Fourier integral, Eq. (52) can be written as

$$P(q, t) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} d\lambda e^{i\lambda q}\langle\exp -i\lambda q(t)\rangle, \tag{53}$$

where the average $\langle\exp -i\lambda q(t)\rangle$ is carried out using the expressions for the conditional probability density of Eq. (12) in the limit $\alpha \to -1$ and the equilibrium density distribution of Eq. (13); this leads to

$$\langle \exp - i\lambda q(t)\rangle = \frac{4\pi}{\beta^2(1+\coth\kappa t)+2\lambda^2}\frac{\beta}{k}\phi_{-1}(t)e^{\kappa t}. \quad (54)$$

The fluctuation integral $\phi_{-1}(t)$ in this expression can be calculated from Eq. (11) as

$$\phi_{-1}(t) = \lim_{\alpha\to -1}\phi_\alpha(t) = \frac{\beta k}{4\pi}\operatorname{csch}\kappa t. \quad (55)$$

The heat distribution function is then obtained by substituting Eqs. (55) and (54) back into Eq. (53) and carrying out the integral over λ using tabulated results [23]. In this way, one finds that

$$P(q,t) = \frac{\beta e^{\frac{\kappa t}{2}}}{2\sqrt{2\sinh\kappa t}}\exp -|q|\frac{\beta e^{\frac{\kappa t}{2}}}{\sqrt{2\sinh\kappa t}}. \quad (56)$$

The structure of this distribution is exactly the same as that of the heat distribution of a charged Brownian particle in a static magnetic field [24], and plots of its variation with q at two different times have exactly the same appearance as Fig. 1 in Ref. [24] when the parameters β and ζ are set to 1.

D. Detailed fluctuation theorem for total entropy in elongational flow

The total entropy change in Eq. (31) vanishes in the limit $\alpha \to -1$, implying that in rotational flow the trajectory the particle follows in going from thermal equilibrium to a nonequilibrium steady state is reversible. This is not the case for $\alpha \neq -1$, but when $\alpha = 1$ (i.e., when the flow is elongational), $\Delta S_{\rm tot}$ assumes the following simple form:

$$\frac{\Delta S_{\rm tot}^{\alpha=1}(x_0,y_0)}{k_B} \equiv \sigma_{\alpha=1}(\mathbf{r}_0) = \ln\sqrt{\frac{1}{1-\omega^2}} - \beta k\omega x_0 y_0, \quad (57)$$

for which the distribution of entropy values $\sigma_{\alpha=1}$ can be calculated from

$$P(\sigma_{\alpha=1}) = \langle\delta(\sigma_{\alpha=1} - \sigma_{\alpha=1}(\mathbf{r}_0))\rangle \quad (58)$$

Written out in full, Eq. (58) is given by

$$P(\sigma_{\alpha=1}) = \int_{-\infty}^{+\infty}dx_f\int_{-\infty}^{+\infty}dy_f\int_{-\infty}^{+\infty}dx_0 \times \int_{-\infty}^{+\infty}dy_0\, P_{\alpha=1}^{ss}(x_f,y_f)P_0(x_0,y_0) \times \delta(\sigma_{\alpha=1} - \sigma_{\alpha=1}(x_0,y_0)) \quad (59)$$

where we have used the steady-state limit of $P(x_f, y_f, t|x_0, y_0)$ in the calculation [as given by Eq. (14)] rather than the full time-dependent conditional probability density itself [as given by Eq. (12)] since our interest is limited to the regime $t \to \infty$. After the expression for $\sigma_{\alpha=1}(x_0, y_0)$ is substituted into Eq. (59), and the integrations over the final positions carried out using the normalization condition on $P^{ss}_{\alpha=1}$, Eq. (59) is reduced to an integral over just the initial positions x_0 and y_0; the integral over x_0 is then carried out using the scaling property $\delta(ax) = \delta(x)/|a|$, leading to an integral in y_0 of

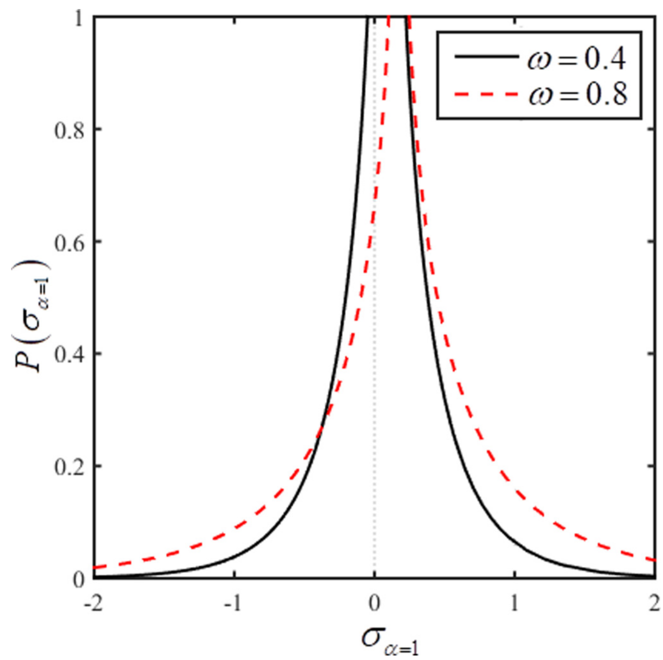

FIG. 3. The entropy distribution for the total entropy change as calculated from Eq. (60) and plotted against $\sigma_{\alpha=1}$ at two different values of ω: $\omega = 0.4$ (solid black curve) and $\omega = 0.8$ (dashed red curve).

known form, which then results in

$$P(\sigma_{\alpha=1}) = \frac{1}{\pi|\omega|}K_0\left(\sqrt{\left(\frac{\sigma_{\alpha=1}}{\omega} + \frac{\ln\sqrt{1-\omega^2}}{\omega}\right)^2}\right), \quad (60)$$

where $K_0(\cdots)$ is the modified Bessel function of order 0. The above distribution function may be verified to be normalized; it is plotted in Fig. 3 for two different values of ω. It is clear from the figure that the average $\langle\Delta\sigma_{\alpha=1}\rangle$ is positive, which is consistent with the requirements of the second law.

Similar calculations can be carried out for a process that proceeds in the reverse direction. In this process, the system is imagined to start out in the steady state P^{ss} that it reaches in the forward direction, and it is then assumed to end up in the thermal equilibrium state P_0 that it starts out from in the forward direction, with the flow being reversed simultaneously, so that $\omega \to -\omega$. If the coordinates of the particle along a trajectory in the reverse direction are labeled with tildes, the reverse process can thus be defined as $\tilde{x}_0 = x_f$, $\tilde{y}_0 = y_f$, $\tilde{x}_f = x_0$, and $\tilde{y}_f = y_0$. Recalling that the total entropy change $\Delta S_{\rm tot}$ is given, in general, by the relation $\Delta S_{\rm tot} = -k_B\ln P^{ss}/P_0 + q/T$, we can now determine $\Delta S_{\rm tot}$ for the reverse process (which we denote $\Delta S^R_{\rm tot}$ and for which we introduce the abbreviation $\sigma^R \equiv \Delta S^R_{\rm tot}/k_B$) from the formula

$$\sigma^R = \ln\frac{P^{ss}(\tilde{x}_0,\tilde{y}_0)}{P_0(\tilde{x}_f,\tilde{y}_f)} + \beta q^R, \quad (61)$$

where q^R, the heat dissipated in the reverse direction, is obtained from Eq. (24), except that V in that equation is replaced by U, since the thermal equilibrium state is now the

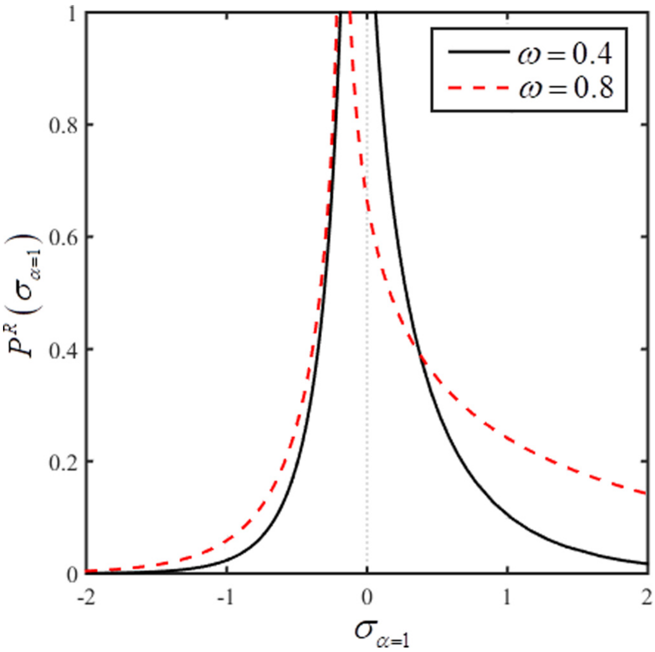

FIG. 4. The entropy distribution for the total entropy change in the reverse direction as calculated from Eq. (65) and plotted against $\sigma_{\alpha=1}$ at two different values of ω: $\omega = 0.4$ (solid black curve) and $\omega = 0.8$ (dashed red curve).

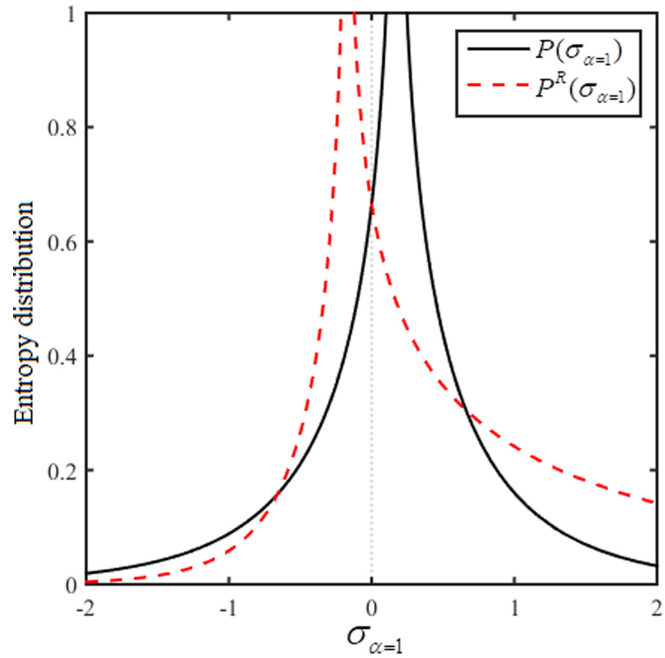

FIG. 5. The entropy distribution for total entropy change in the forward and the reverse directions as calculated, respectively, from Eqs. (60) (solid black curve) and (65) (dashed red curve) and plotted against $\sigma_{\alpha=1}$ at a fixed value of $\omega = 0.8$

final state. This leads to the result

$$q^R = -\frac{k}{2}\left(\tilde{x}_f^2 + \tilde{y}_f^2 - \tilde{x}_0^2 - \tilde{y}_0^2\right), \tag{62}$$

so from Eq. (61) and the equations for P_0 and P^{ss} [Eqs. (13) and (14), respectively], σ^R, for the special case $\alpha = 1$, is now found to be

$$\sigma^R_{\alpha=1}(\tilde{x}_0, \tilde{y}_0) = \ln\sqrt{1-\omega^2} - \beta k\omega\tilde{x}_0\tilde{y}_0. \tag{63}$$

(It may be verified that for $\alpha = -1$ the total entropy change is 0, again confirming the reversibility of the rotational flow case.) The distribution P^R of possible values of $\sigma^R_{\alpha=1}(\tilde{x}_0, \tilde{y}_0)$ can now be calculated from the integral

$$P^R(\sigma_{\alpha=1}) = \int_{-\infty}^{+\infty} d\tilde{x}_f \int_{-\infty}^{+\infty} d\tilde{y}_f \int_{-\infty}^{+\infty} d\tilde{x}_0 \times \int_{-\infty}^{+\infty} d\tilde{y}_0\, P^{ss}_{\alpha=1}(\tilde{x}_0, \tilde{y}_0) P_0(\tilde{x}_f, \tilde{y}_f) \times \delta\big(\sigma_{\alpha=1} - \sigma^R_{\alpha=1}(\tilde{x}_0, \tilde{y}_0)\big). \tag{64}$$

The evaluation of this integral proceeds along the same lines as the evaluation of Eq. (59), and it yields the result

$$P^R(\sigma_{\alpha=1}) = \frac{1}{\pi|\omega|}\exp\sigma_{\alpha=1} \times K_0\left(\sqrt{\left(\frac{-\sigma_{\alpha=1}}{\omega} + \frac{\ln\sqrt{1-\omega^2}}{\omega}\right)^2}\right). \tag{65}$$

The above distribution is also normalized, but this can only be established numerically. A plot of $P^R(\sigma_{\alpha=1})$ as a function of $\sigma_{\alpha=1}$ is shown in Fig. 4 for the same two values of ω as used in Fig. 3. A comparison of the entropy distributions for the forward and reverse processes [Eqs. (60) and (65), respectively] is shown in Fig. 5 for a single ω value.

Having found the analytic structure of these two distributions, we immediately see that

$$\frac{P(\sigma_{\alpha=1})}{P^R(-\sigma_{\alpha=1})} = e^{\sigma_{\alpha=1}}, \tag{66}$$

which is the statement of another fluctuation theorem, the detailed fluctuation theorem [25].

IV. SUMMARY

In this paper, starting from a set of coupled Langevin equations, we have developed a model of the stochastic thermodynamics of a single harmonically trapped colloid in two-dimensional linear mixed flow. By reformulating these equations in terms of path integrals, we have been able to derive exact expressions, valid for arbitrary time t, for the probability density distributions of the particle's positions as a function of the following parameters: the degree of admixture α of the rotational and elongational components of the flow, the strength k of the confining potential, and the strength $\dot{\gamma}$ of the externally imposed flow. Further, by constructing the equivalent Fokker-Planck representation of the Langevin equations, we have determined the structure of the probability currents that characterize the long-time steady-state dynamics of the system for any α. On the basis of these currents, we have been able to classify the steady state corresponding to pure elongational flow ($\alpha = 1$) as an equilibrium steady state, and the steady states corresponding to flows with $\alpha \neq 1$ as nonequilibrium steady states. We have also verified that our model system satisfies the integral fluctuation theorem, the Jarzynski equality, and the Bochkov-Kuzovlev relation.

At the single-molecule level, heat is often a nonlinear functional of particle trajectories; its distribution can therefore be particularly difficult to calculate analytically. For the special case of a Brownian oscillator driven by pure rotational flow, however, we have been able to show that the heat dissipated by the particle into the medium during a certain interval of time becomes trajectory independent, and that its distribution can then be found in closed form. These findings may have implications for the dynamics of charged particles in magnetic fields, as there are exact mathematical analogies between this system and the rotational flow-driven oscillator system.

In the special case of elongational flow, we have also calculated the distribution functions for the total entropy change along the particle's forward and reverse trajectories, and have used these functions to demonstrate the validity of the detailed fluctuation theorem for this case.

APPENDIX A: INTEGRATION CONSTANTS IN CALCULATING THE DISTRIBUTION OF THE POSITION

The unknown integration constants A, B, C, D involved in the calculation of the classical action $\bar{S}_\alpha$ in Eq. (5) are determined by applying the boundary conditions $\bar{x}(0) = x_0$, $\bar{y}(0) = y_0$, $\bar{x}(t) = x_f$, and $\bar{y}(t) = y_f$ to Eqs. (8a) and (8b). From the solution of the resulting simultaneous equations (obtained using MATHEMATICA [15]), it can be shown that

$$A = \frac{1}{2\Delta_\alpha}\{(1+\alpha)(1-\cosh 2at)(2x_0-(1-\alpha)\omega y_0\big) - \alpha\mu_\alpha[(1-e^{2\kappa t})x_0 + 2x_f \sinh\kappa t\cosh at] + 2\sqrt{\alpha}\sinh at \times [(1+\alpha)\{((1-\alpha)\omega x_0+2y_0)\cosh at - e^{\kappa t}((1-\alpha)\omega x_f + 2y_f)\} + y_f\mu_\alpha \sinh\kappa t]\} \tag{A1}$$

$$B = \frac{1}{2\Delta_\alpha}\{\alpha(1+\alpha)(1-\cosh 2at)((1-\alpha)\omega x_0+2y_0) - \alpha\mu_\alpha[(1-e^{2\kappa t})y_0 + 2y_f\sinh\kappa t\cosh at] + 2\sqrt{\alpha}\sinh at \times [(1+\alpha)\{(2x_0-(1-\alpha)\omega y_0)\cosh at - e^{\kappa t}(2x_f-(1-\alpha)\omega y_f)\} + x_f\alpha\mu_\alpha\sinh\kappa t]\}, \tag{A2}$$

$$C = \frac{1}{2\Delta_\alpha}\{(1+\alpha)(1-\cosh 2at)(2\alpha x_0+(1-\alpha)\omega y_0) - \alpha\mu_\alpha[(1-e^{-2\kappa t})x_0 - 2x_f\sinh\kappa t\cosh at] - 2\sqrt{\alpha}\sinh at \times [(1+\alpha)\{((1-\alpha)\omega x_0+2y_0)\cosh at - e^{\kappa t}((1-\alpha)\omega x_f+2y_f)\} + y_f\mu_\alpha\sinh\kappa t]\}, \tag{A3}$$

$$D = \frac{1}{2\Delta_\alpha}\{-(1+\alpha)(1-\cosh 2at)((1-\alpha)\alpha\omega x_0 - 2y_0) - \alpha\mu_\alpha[(1-e^{-2\kappa t})y_0 - 2y_f\sinh\kappa t\cosh at] - 2\sqrt{\alpha}\sinh at \times [(1+\alpha)\{(2x_0-(1-\alpha)\omega y_0)\cosh at - e^{\kappa t}(2x_f-(1-\alpha)\omega y_f)\} + x_f\alpha\mu_\alpha\sinh\kappa t]\}, \tag{A4}$$

where $\Delta_\alpha = \alpha\mu_\alpha(\cosh 2\kappa t - 1) - (1+\alpha)^2(\cosh 2at - 1)$.

APPENDIX B: THE COEFFICIENTS $A_1, \ldots, A_{12}$ IN EQ. (10)

The expressions for the coefficients $A_1, \ldots, A_{12}$ in Eq. (10) are given below:

$$\begin{aligned}
A_1 &= 2\alpha\mu_\alpha \sinh 2\kappa t,\\
A_2 &= 2(1-\alpha^2)(\cosh 2at - 1 + \alpha\omega^2),\\
A_3 &= 4\sqrt{\alpha}(1+\alpha)\omega\sinh 2at,\\
A_4 &= 8\alpha(1+\alpha)\omega,\\
A_5 &= 2\alpha\omega^2(1-\alpha^2),\\
A_6 &= 8\sqrt{\alpha}(1+\alpha)\sinh 2at,\\
A_7 &= 8\alpha\omega(1+\alpha)\cosh 2at,\\
A_8 &= 8\alpha\mu_\alpha\sinh\kappa t\cosh at,\\
A_9 &= 8\alpha(1-\alpha^2)\omega^2\sinh\kappa t\cosh at,\\
A_{10} &= 16\sqrt{\alpha}(1+\alpha)\omega\cosh\kappa t\sinh at,\\
A_{11} &= 16(1+\alpha)(\alpha\omega\sinh\kappa t\cosh at - \sqrt{\alpha}\cosh\kappa t\sinh at),\\
A_{12} &= 16\sqrt{\alpha}(1-\alpha)(1-\alpha\omega^2)\sinh\kappa t\sinh at.
\end{aligned}$$

APPENDIX C: CALCULATION OF THE PROPAGATOR $G_{w_r}(x_f, y_f, t|x_0, y_0)$ IN EQ. (37)

The path integral of Eq. (37), with $\mathcal{L}'(\dot{x}, \dot{y}, x, y)$ given by Eq. (38), is evaluated by the variational method, which proceeds by first deriving the Euler-Lagrange equations corresponding to $\mathcal{L}'$; these equations are

$$\ddot{\bar{\boldsymbol{r}}}(t) + \dot{\gamma}(1-\alpha)\mathbf{J}\dot{\bar{\boldsymbol{r}}}(t) - \mathbf{M}'\bar{\boldsymbol{r}}(t) = 0, \tag{C1}$$

where $\mathbf{J}$ has the form given after Eq. (7) and $\mathbf{M}' = \frac{1}{2a_0}\begin{pmatrix} 2a_1 & a_5 \\ a_5 & 2a_2 \end{pmatrix}$. The solution of Eq. (C1) can be shown to be given by

$$\bar{x}'(s) = e^{\kappa s}\left\{A'\cosh as + \frac{B'}{\sqrt{\alpha}}\sinh as\right\} + e^{-\kappa s}\left\{C'\left(\cosh as + \frac{2(1-\alpha^2)\omega}{\sqrt{\alpha}\mu_\alpha}\sinh as\right) + \frac{D'[\mu_\alpha - 4(1+\alpha)]}{\sqrt{\alpha}\mu_\alpha}\sinh as\right\} \tag{C2}$$

$$\bar{y}'(s) = e^{\kappa s}\left\{A'\sqrt{\alpha}\sinh as + B'\cosh as\right\} + e^{-\kappa s}\left\{\frac{C'[\alpha\mu_\alpha - 4(1+\alpha)]}{\sqrt{\alpha}\mu_\alpha}\sinh as + D'\left(\cosh as - \frac{2(1-\alpha^2)\omega}{\sqrt{\alpha}\mu_\alpha}\sinh as\right)\right\}, \tag{C3}$$

where κ, ω, a, and μ_α are the parameters defined after Eq. (8b), and A', B', C', and D' are unknown integration constants. These constants are determined by imposing the boundary conditions $\bar{x}'(0) = x_0$, $\bar{y}'(0) = y_0$, $\bar{x}'(t) = x_f$, and $\bar{y}'(t) = y_f$ on Eqs. (C2) and (C3) and solving the resulting simultaneous equations. This leads to

$$\begin{aligned} A' = \frac{1}{2\Delta_\alpha}\{&(1+\alpha)(1-\cosh 2at)(2x_0 + (1-\alpha)\omega\, y_0) - \alpha\mu_\alpha[(1-e^{-2\kappa t})x_0 - 2x_f\sinh\kappa t\cosh at] - 2\sqrt{\alpha}\sinh at \\ &\times[(1+\alpha)\{((1-\alpha)\omega\, x_0 - 2y_0)\cosh at - e^{-\kappa t}((1-\alpha)\omega\, x_f - 2y_f)\} + y_f\mu_\alpha\sinh\kappa t]\}, \end{aligned} \tag{C4}$$

$$\begin{aligned} B' = \frac{1}{2\Delta_\alpha}\{&\alpha(1+\alpha)(1-\cosh 2at)(-(1-\alpha)\omega\, x_0 + 2y_0) - \alpha\mu_\alpha[(1-e^{-2\kappa t})y_0 - 2y_f\sinh\kappa t\cosh at] + 2\sqrt{\alpha}\sinh at \\ &\times[(1+\alpha)\{(2x_0 + (1-\alpha)\omega\, y_0)\cosh at - e^{-\kappa t}(2x_f + (1-\alpha)\omega\, y_f)\} - x_f\alpha\mu_\alpha\sinh\kappa t]\}, \end{aligned} \tag{C5}$$

$$\begin{aligned} C' = \frac{1}{2\Delta_\alpha}\{&(1+\alpha)(1-\cosh 2at)(2\alpha x_0 - (1-\alpha)\omega\, y_0) - \alpha\mu_\alpha[(1-e^{2\kappa t})x_0 + 2x_f\sinh\kappa t\cosh at] + 2\sqrt{\alpha}\sinh at \\ &\times[(1+\alpha)\{((1-\alpha)\omega\, x_0 - 2y_0)\cosh at - e^{-\kappa t}((1-\alpha)\omega\, x_f - 2y_f)\} + y_f\mu_\alpha\sinh\kappa t]\}, \end{aligned} \tag{C6}$$

$$\begin{aligned} D' = \frac{1}{2\Delta_\alpha}\{&(1+\alpha)(1-\cosh 2at)((1-\alpha)\alpha\omega\, x_0 + 2y_0) - \alpha\mu_\alpha[(1-e^{2\kappa t})y_0 + 2y_f\sinh\kappa t\cosh at] - 2\sqrt{\alpha}\sinh at \\ &\times[(1+\alpha)\{(2x_0 + (1-\alpha)\omega\, y_0)\cosh at - e^{-\kappa t}(2x_f + (1-\alpha)\omega\, y_f)\} - x_f\alpha\mu_\alpha\sinh\kappa t]\}, \end{aligned} \tag{C7}$$

where, as before $\Delta_\alpha = \alpha\mu_\alpha(\cosh 2\kappa t - 1) - (1+\alpha)^2(\cosh 2at - 1)$. By partially integrating the Lagrangian $\mathcal{L}'$ and applying the Euler-Lagrange equations to the result, the classical action is now found as

$$\bar{S}'_{w_r}[x, y] = a_0[\dot{\bar{x}}'(t)x_f + \dot{\bar{y}}'(t)y_f - \dot{\bar{x}}'(0)x_0 - \dot{\bar{y}}'(0)y_0] - \frac{a_3 + a_4}{2}(x_f y_f - x_0 y_0), \tag{C8}$$

which from Eqs. (C2) and (C3), using Eqs. (C4)–(C7) for A', B', C', and D', becomes

$$\begin{aligned} \bar{S}'_{w_r}[x, y] = \frac{\beta k}{8\Delta_\alpha}\{&A_1(x_f^2 + x_0^2 + y_f^2 + y_0^2) - A_2(x_f^2 - x_0^2 - y_f^2 + y_0^2) - A_3[\alpha(x_f^2 + x_0^2) + y_f^2 + y_0^2] \\ &- e^{-2\kappa t}[A_4 x_f y_f - A_5(x_f^2 - y_f^2)] + e^{2\kappa t}[A_4 x_0 y_0 - A_5(x_0^2 - y_0^2)] - A_6(x_0 y_0 + x_f y_f) - A_7(x_0 y_0 - x_f y_f) \\ &- A_8(x_0 x_f + y_0 y_f) + A_9(x_0 x_f - y_0 y_f) + A_{10}(\alpha x_0 x_f + y_0 y_f) - A_{11}(x_0 y_f + x_f y_0) + A_{12}(x_0 y_f - x_f y_0)\}, \end{aligned} \tag{C9}$$

where $A_1, A_2, \ldots, A_{12}$ are the same coefficients given in Appendix B. The fluctuation integral $\phi'_{w_r}(t)$ is obtained from the de Witt–Morrette formula, which leads to the same expression obtained earlier for $\phi_\alpha(t)$ [Eq. (11)]. The path integral in Eq. (37) therefore finally assumes the form

$$G_{w_r}(x_f, y_f, t|x_0, y_0) = \phi_\alpha(t)\exp -\bar{S}'_{w_r}. \tag{C10}$$

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