Brownian particles in stationary and moving traps: The mean and variance of the heat distribution function

Debarati Chatterjee and Binny J. Cherayil
Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore 560012, India
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A recent theoretical model developed by Imparato *et al.* [Phys. Rev. E **76**, 050101(R) (2007)] of the experimentally measured heat and work effects produced by the thermal fluctuations of single micron-sized polystyrene beads in stationary and moving optical traps has proved to be quite successful in rationalizing the observed experimental data. The model, based on the overdamped Brownian dynamics of a particle in a harmonic potential that moves at a constant speed under a time-dependent force, is used to obtain an approximate expression for the distribution of the heat dissipated by the particle at long times. In this paper, we generalize the above model to consider particle dynamics in the presence of *colored* noise, without passing to the overdamped limit, as a way of modeling experimental situations in which the fluctuations of the medium exhibit long-lived temporal correlations, of the kind characteristic of polymeric solutions, for instance, or of similar viscoelastic fluids. Although we have not been able to find an expression for the heat distribution itself, we do obtain *exact* expressions for its mean and variance, both for the static and for the moving trap cases. These moments are valid for arbitrary times and they also hold in the inertial regime, but they reduce exactly to the results of Imparato *et al.* in appropriate limits.

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I. INTRODUCTION

The growing sophistication of measurements of the thermodynamic changes accompanying the random thermal motions of small molecules in viscous and viscoelastic media has brought ever greater refinement to tests of the various fluctuation theorems that are believed to govern the behavior of matter away from equilibrium [1]. Such measurements have so far tended to focus on the determination of the *work* [2] produced during changes of state, W, rather than the heat [3], Q, a generally less accessible quantity. Experiments by Imparato *et al.* [4] have now generated data on single-molecule *heat* effects, providing fresh opportunities for further tests of statistical mechanical models of nonequilibrium systems.

The experiments of Imparato *et al.* tracked the fluctuating trajectories of single, water dissolved, optically trapped polystyrene beads of micrometer diameter over a long period of time. The trajectories were used to construct histograms, $P_{\mathrm{expt}}(Q,t\rightarrow\infty)$, of the heat produced or consumed by the bead when the trap was (a) stationary and (b) when it was moving with a constant speed u. Independently, Imparato *et al.* derived analytical expressions, $P_{\mathrm{theor}}(Q,t\rightarrow\infty)$, for these heat distribution functions from a model based on the overdamped Langevin dynamics of a harmonic oscillator acted on by a time-dependent force. The agreement between the calculated and measured curves is for the most part extremely close (although in the static trap case the theoretical heat distribution exhibits a logarithmic divergence that is not seen in the experimental data.)

However, the model has so far only considered particle dynamics in simple liquids, such as water, where the white noise approximation it uses to model the effects of thermal fluctuations, is generally thought to be quite satisfactory. But the kinds of solvent environments—such as those inside cells—in which it might be particularly interesting and potentially useful to carry out similar trapped-particle experiments, typically do not conform to the delta-correlated relaxation dynamics of aqueous media. [5] In such solvents, the effects of the thermal fluctuations are far better described by colored noise processes, which have finite correlation times, and which, in the special case of fractional Gaussian noise, for instance, span multiple time scales [6]. There is, therefore, a clear need to extend existing theoretical models of single-molecule dynamics to these other fluctuation regimes.

The present paper is a generalization of the model of Imparato *et al.* [4] that has this objective in mind. In this generalized model, the optically trapped particle is described as a forced harmonic oscillator that evolves under the action of *colored* Gaussian noise [7]; its dynamics are therefore described by a one-dimensional generalized Langevin equation (GLE) in both position (x) *and* velocity (v) variables [8]. The model reduces exactly to the model of Imparato *et al.* when the inertial contribution is neglected and the Gaussian noise is taken to be delta correlated. The GLE itself—such as the overdamped Langevin equation used by Imparato *et al.*—can be *exactly* transformed [9,10] to an equivalent Fokker-Planck equation (FPE) for the probability density distribution of x, v, and Q at time t, but at present it does not appear to be possible to solve this equation exactly. Rather than attempt to solve it approximately, therefore, (as Imparato *et al.* do in treating the corresponding equation they derive from their model), we determine instead expressions for the *moments* of the distribution, which we *can* calculate exactly (from the solution of the GLE [11]). These moments (in the overdamped white noise limit and in the limit of long times) are in complete agreement with those derived from the model of Imparato *et al.* Our results are also valid for arbitrary times, and also hold when the inertial term in the GLE is retained. They also suggest interesting parallels with the *work* theorems satisfied by similar non-Markovian systems [11].

In the following section, we introduce the generalized Langevin equations that model the dynamics of an optically trapped particle in a thermal reservoir and show how their solutions (which yield the time-dependent position and velocity of the particle) are used to obtain an expression for the heat exchanged between the particle and reservoir during an interval of time t. By averaging this quantity over the noise and the initial phase space density distribution, we then derive expressions for its mean and variance. In Sec. III, we discuss how these averages compare with the experimental and theoretical results presented in Ref. [4].

II. MODEL AND CALCULATIONS

As in the calculations of Imparato *et al.* [4], we shall assume that the dynamics of a thermally fluctuating, dragged colloidal bead is adequately modeled by the one-dimensional dynamics of a Brownian particle of mass m that at the point x and at the time t experiences both a random force $\theta(t)$ and a systematic time-dependent force $F(x,t)$ derived from a potential $U(x,t)$. The potential $U(x,t)$ is taken to be $k(x-ut)^2/2$, where k is the force constant of the harmonic well, and u is the speed of the moving trap. (A static trap is modeled simply by setting u to 0). The random force is taken to be a Gaussian random variable of zero mean; it is eventually specialized to the case of white noise. The equations that govern the time evolution of this particle are therefore given, in their most general form, by [8,10,11]

$$\dot{x}(t) = v(t) \tag{1a}$$

$$m\dot{v}(t) = -kx(t) + f(t) - \zeta\int_0^t dt' K(t-t')v(t') + \theta(t) \tag{1b}$$

Here, $f(t) \equiv kut$, ζ is the friction coefficient of the particle, $K(t)$ is a memory function, which is related to the random force $\theta(t)$ by a fluctuation-dissipation relation: $\langle\theta(t)\theta(t')\rangle = \zeta k_B T K(|t-t'|)$, T being the temperature of the reservoir and k_B Boltzmann's constant, and the dots on $x(t)$ and $v(t)$ denote differentiation with respect to t. Equations (1a) and (1b) reduce to the equations used in Ref. [4] when the inertial term $m\dot{v}(t)$ is discarded and $\theta(t)$ is chosen to correspond to white noise (and the memory function thereby becomes proportional to the delta function $\delta(t-t')$). In the present calculations, the inertial term is retained, and $\theta(t)$, as noted earlier, is treated initially as a general Gaussian random variable (with the indicated time correlation function), and later, for purposes of comparison with Imparato *et al.*'s results as white noise. (It should be noted that the above model had been used earlier to resolve a puzzle about work theorems for forced oscillators in non-Markovian heat baths [12]. There it had been necessary to explicitly consider fluctuations that did, in fact, have long-lived temporal correlations).

The quantity measured experimentally is the heat exchanged by the bead with its surroundings during an interval of time t along a given stochastic trajectory; this quantity can be calculated from the relation [4,13]

$$Q(t) = k\int_0^t v(t')x(t')dt'. \tag{2}$$

Ideally, one would like to be able to obtain a theoretical expression for the probability density of $Q(t)$, viz., $P(Q,t)$, for which experimental data have been reported in Ref. [4]. A calculation of $P(Q,t)$ would require first setting up and solving the equation for the evolution of $P(x,v,Q,t)$, the probability density that at time t the particle is at x with velocity v, having exchanged an amount of heat Q with the surroundings, and then integrating out x and v. It proves to be fairly straightforward to derive the equation that governs the time dependence of $P(x,v,Q,t)$; it is found by averaging $\delta[x-x(t)]\delta[v-v(t)]\delta[Q-Q(t)]$—a *functional* of the noise $\theta(t)$—over all possible realizations of $\theta(t)$. The actual steps in this averaging procedure are somewhat involved, but they pose no special difficulties, and they have been discussed at some length in the context of the calculation of the evolution equation for the work distribution function [10,12]. So without going into further details, we shall simply set down the equation that governs the evolution of $P(x,v,Q,t)$; it is given by

$$\frac{\partial P}{\partial t} = -v\frac{\partial P}{\partial x} + \Xi(t)\frac{\partial}{\partial v}vP - \Omega^2(t)x\frac{\partial P}{\partial v} - \frac{k_BT}{k}\left(\Omega^2(t) + \frac{k}{m}\right) \times\frac{\partial^2 P}{\partial v\,\partial x} + \frac{k_BT}{m}\Xi(t)\frac{\partial^2 P}{\partial v^2} - \Lambda(t)\frac{\partial P}{\partial v} - kvx\frac{\partial P}{\partial Q}, \tag{3}$$

where the coefficients $\Xi(t)$, $\Omega^2(t)$, and $\Lambda(t)$, which are complicated functions of the time (but which can be expressed in closed form) have been defined in Refs. [10,12], and are not reproduced here in the interests of brevity.

Unfortunately, we have not been able to solve Eq. (3) in closed form. Unlike the mechanical or thermodynamic work, which are linear functionals of the Gaussian random force $\theta(t)$, and are therefore themselves governed by Gaussian density distributions, as was shown in Ref. [12], the heat is not linearly related to the noise [see Eq. (2)], and as a result, its density distribution is not known a priori. It is, of course, still possible to get some information about $P(Q,t)$ by evaluating its moments. This can be done, without recourse to Eq. (3), by solving Eqs. (1a) and (1b) *directly* for $x(t)$ and $v(t)$ (using Laplace transform methods), substituting the expressions into Eq. (2) and the corresponding expression for $Q^2(t)$, and then averaging the resulting equations over the noise and the initial equilibrium distributions of the position and velocity [11]. This yields the desired first and second moments of $P(Q,t)-\langle Q(t)\rangle$ and $\langle Q^2(t)\rangle$, respectively—as a function of the trap speed u, and these can be compared with estimates obtained from the experimental histograms. Calculations of still higher moments can be carried out as well (though at the cost of greater algebra), so a great deal of the structure of the distribution function can be determined, in principle, without solving Eq. (3) itself. For the present purposes, we shall be content with the calculation of just the first and second moments of the heat distribution.

Turning, then, to the calculation of $x(t)$ and $v(t)$, we can show, following the approach discussed at length in Refs. [10,12], that the solutions of Eqs. (2) are

$$x(t) = x_0\chi(t) - \frac{mv_0}{k}G(t) + \frac{1}{m}H(t) + \frac{1}{m}I(t) \tag{4a}$$

$$v(t) = x_0\dot{\chi}(t) - \frac{mv_0}{k}\dot{G}(t) + \frac{1}{m}\dot{H}(t) + \frac{1}{m}\dot{I}(t), \tag{4b}$$

where x_0 and v_0 are the initial position and velocity of the particle, respectively. The functions $\chi(t)$, $G(t)$, $H(t)$, and $I(t)$ are the inverse Laplace transforms of the functions $\hat{\chi}(s)$, $\hat{G}(s)$, $\hat{H}(s)$, and $\hat{I}(s)$, the Laplace transform $\hat{y}(s)$ of a function $y(t)$ being defined by $\hat{y}(s) = \int_0^\infty dt y(t) e^{-st}$. Referring again to Refs. [10,12], we find that these functions are given by

$$\hat{\chi}(s) = \frac{1}{s + k\hat{\xi}(s)/m}, \tag{5a}$$

$$\hat{G}(s) = -\frac{k}{m}\hat{\chi}(s)\hat{\xi}(s), \tag{5b}$$

$$\hat{H}(s) = -\frac{m}{k}\hat{G}(s)\hat{f}(s), \tag{5c}$$

and

$$\hat{I}(s) = -\frac{m}{k}\hat{G}(s)\hat{\theta}(s), \tag{5d}$$

where $\hat{\xi}(s) = 1/[s + \zeta\hat{K}(s)/m]$, $\hat{K}(s)$ being the Laplace transform of the memory function. From these results, expressions can be derived for the mean and variance of the heat for different values of the trap speed u (after fairly lengthy algebra, some details of which are sketched in the Appendix). These expressions are [see Eqs. (A.4) and (A.22)]

$$\langle Q(t)\rangle = -ku^2\left[\bar{\bar{\chi}}(t) - \frac{1}{2}\bar{\chi}(t)^2\right] \tag{6a}$$

and

$$\sigma_Q^2(t) \equiv \langle Q(t)^2\rangle - \langle Q(t)\rangle^2$$
$$= (k_BT)^2[1 - \chi(t)^2] + 2ku^2k_BT\left[\bar{\bar{\chi}}(t) - \frac{1}{2}\bar{\chi}(t)^2\right] \tag{6b}$$

where $\bar{\chi}(t) = \int_0^t dt_1 \chi(t_1)$ and $\bar{\bar{\chi}}(t) = \int_0^t dt_1 \bar{\chi}(t_1)$. These expressions (which are the principal results of this paper) are very general, in the sense that they hold for arbitrary times and for any Gaussian noise process $\theta(t)$. They hold, in particular, for the process known as fractional Gaussian noise, or fGn, which is of special relevance to biology [14]. First, however, we shall consider the special case $\langle\theta(t)\theta(t')\rangle \propto \delta(t-t')$, to confirm that our results in this limit recover results found in Ref. [4], where the experimental conditions can be taken to correspond to white noise thermal fluctuations. In considering this limit, we set m to 0 and t to ∞ (thereby simultaneously passing to the long-time regime of overdamped dynamics).

III. COMPARISON WITH EXPERIMENT [4]

Under the conditions specified above, $\chi(t)$ becomes a simple exponential, $e^{-kt/\zeta}$. For the static trap, we then find that Eqs. (6a) and (6b) reduce to [see also Eq. (A.15)]

$$\langle Q(t \to \infty)\rangle_0 = 0 \tag{6c}$$

and

$$\sigma_{Q,0}^2(t \to \infty)/(k_BT)^2 = 1 \tag{6d}$$

where the subscript 0 refers to the static trap condition.

Furthermore, for this case, the theoretical heat distribution function that the authors of Ref. [4] derive to fit their data is given by the very simple (approximate) expression

$$P_{\text{theor}}(Q, t \to \infty) = \frac{K_0(|Q|/k_BT)}{\pi k_BT}. \tag{7a}$$

Here K_0 is the 0th order modified Bessel function of the second kind. Although it is undefined at $Q=0$, where it diverges logarithmically (and does not therefore reproduce the experimental data there quantitatively), its first moment is identically zero (by symmetry), while the second moment is given by [15]

$$\langle Q^2\rangle = \int_{-\infty}^{\infty} dQ Q^2 P(Q, t \to \infty) = \frac{2}{\pi k_BT}\int_0^\infty dQ Q^2 K_0(Q/k_BT)$$
$$= \frac{2}{\pi k_BT}2(k_BT)^3\Gamma(3/2)^2 = (k_BT)^2. \tag{7b}$$

These results are therefore seen to coincide with the results derived from our model [see Eqs. (6c) and (6d)]. The actual values of the mean and variance of the heat have not been reported in Ref. [4], but an inspection of the experimental histogram in Fig. 2 of that reference suggests that $\langle Q(t \to \infty\rangle_{\text{expt}}/k_BT$ is 0, or very nearly 0. As for the variance of the heat, if one identifies this quantity with the experimental full width at half maximum, a similar inspection of the same figure suggests that $\sigma_{Q,\text{expt}}^2(t\to\infty)/(k_BT)^2$ is about 0.6–0.7. Both these estimates are consistent with the corresponding theoretical values.

In the same way, for the moving trap case, we find from our calculations that

$$\langle Q(t \to \infty)\rangle/k_BT = -u^2\zeta t/k_BT \tag{8a}$$

and

$$\sigma_Q^2(t \to \infty)/(k_BT)^2 = 2u^2\zeta t/k_BT \tag{8b}$$

For this case, the calculations of Imparato *et al.* [4] find that at long times, the heat distribution is Gaussian to leading order in the time, and is given by

$$P_{\text{theor}}(Q, t \to \infty) = \frac{1}{\sqrt{4\pi k_BT\zeta u^2 t}}\exp\left[-\frac{1}{4k_BT\zeta u^2 t}(Q + \zeta u^2 t)^2\right], \tag{9}$$

from which it is easily shown that $\langle Q(t\to\infty\rangle_{\text{theor}}/k_BT = -u^2\zeta t/k_BT$ and that $\sigma_Q^2(t\to\infty)/(k_BT)^2 = 2u^2\zeta t/k_BT$. These predictions are also identical to those derived from our model [Eqs. (8a) and (8b)].

The actual numerical value of $u^2\zeta t/k_BT$ turns out to be 2.1 when the following experimental values are used in the expression: $u = 10^{-6}$ m s^{-1}, $\zeta = 1.74 \times 10^{-8}$ kg s^{-1}, $t = 0.5$ s, and $T=296.5$ K. As estimated from Fig. 3 of Ref. [4], the experimental value of the mean, $\langle Q(t\to\infty\,\rangle_{\mathrm{theor}}/k_BT$, (identified with the maximum in the curve), is about −2.0, which is very close to the theoretical value. The corresponding value of the variance, $\sigma_Q^2(t)/(k_BT)^2$, for the same values of u, ζ, t, and T is about 4.3. An estimate of the experimental variance from Fig. 3 of Ref. [4] (identified as before with the full width at half maximum) yields a value in the vicinity of 5, which is again close to the theoretical prediction.

IV. CONCLUSIONS

The significance of the findings presented here is that they provide testable predictions about heat effects in dragged particle experiments in viscoelastic (as opposed to simple) fluids. Evidence already exists [11,16] that *work* distributions in such fluids are largely consistent with the model defined by Eq. (1), so it would interesting to see if the same is true of the distributions that govern other thermodynamic quantities. Experimentally, it should be possible to extend the methodology of Imparato *et al.* to study these kinds of fluids as well.

Viscoelasticity is distinguished, among other things, by memory effects, which can be included in our model by, for instance, taking the random force in Eq. (1) to correspond to fGn. When this is done, the memory function in that equation is given by [14] $K(|t-t'|)=2H(2H-1)|t-t'|^{2H-2}$, where H, the Hurst index, is a real number lying between $\frac{1}{2}$ and 1 that is a measure of the degree of temporal correlation in the noise. With this choice of kernel, the function $\chi(t)$, in the overdamped limit, is easily shown to equal $E_{2-2H}[-(t/\tau)^{2-2H}]$, where $E_a(z)\equiv\sum_{k=0}^{\infty}z^k/\Gamma(ak+1)$ is the Mittag-Leffler function, $\tau\equiv[\zeta\Gamma(2H+1)/k]^{1/(2-2H)}$ and $\Gamma(\cdots)$ is the gamma function. Exact expressions for the first and second moments of the heat distribution can be obtained for this case in both the static and moving trap cases in terms of the Mittag-Leffler function and a related function known as the generalized Mittag-Leffler function, $E_{a,b}(z)\equiv\sum_{k=0}^{\infty}z^k/\Gamma(ak+b)$, which enters into the expressions via the general result [17] $\int_0^y dt t^{\gamma-1}E_{\beta,\gamma}(wt^{\beta})=y^{\gamma}E_{\beta,\gamma+1}(wy^{\beta})$. Without writing done these expressions explicitly, we shall instead consider their asymptotic long-time limits (using the result $E_{a,b}(-z^a)\sim z^{-a}/\Gamma(b-a)$.) In this way we find that (i) $\langle Q(t)\rangle_0=0$ and $\sigma_{Q,0}^2\sim(k_BT)^2[1-(t/\tau)^{-(4-4H)}/\Gamma^2(2H-1)]$ for the case of the stationary trap, and (ii) $\langle Q(t)\rangle\sim-ku^2t^{2H}\tau^{2-2H}/\Gamma(2H+1)$, and $\sigma_Q^2\sim 2ku^2k_BTt^{2H}\tau^{2-2H}/\Gamma(2H+1)$ for the case of the moving trap. Thus, we predict that for fluids in which the temporal correlations of random thermal forces are long lived and decay algebraically, the moments of the heat distribution exhibit characteristic power-law behavior at long times. The parameter H in these expressions cannot in general be determined a priori from the model itself, but one should be able to estimate it from experiment. Knowledge of H would in turn provide insights into the viscoelastic character of the medium.

Other noise sources that lead to memory effects in the equations that govern particle dynamics include exponentially correlated noise, which Mai and Dhar [11] used to simulate the non-Markovian thermal environment of harmonic and anharmonic oscillators driven by forces originating in sinusoidal and sawtooth potentials. The simulations confirmed the general validity of the results derived analytically from their calculated work distribution functions for the harmonic oscillator system, and suggested the strong possibility of the validity of the Jarzynski equality for the anharmonic oscillator system (for which analytic expressions are not known). No comparable numerical studies have been carried to explore heat distributions in non-Markovian systems. For the specific case of exponentially correlated noise, exact closed form expressions for the moments of these distributions are easily derived from our formalism, which only requires knowing the precise form of the function $\chi(t)$. In the overdamped limit, however, it turns out that this function has exactly the same structure as the corresponding function that describes delta-correlated noise, so the results of these calculations are not reproduced here.

There is an interesting parallel between the moments of the heat distribution function calculated in the present study, and the corresponding moments of the work distribution calculated in Ref. [11]. The parallel is established by combining Eqs. (6a) and (6b) with Eq. (A.15) in the form

$$\sigma_Q^2(t)=\sigma_{Q,0}^2-2k_BT\langle Q(t)\rangle \tag{10}$$

This recalls the relation

$$\sigma_W^2=-\,2k_BT\Delta F+2k_BT\langle W\rangle \tag{11}$$

derived by Mai and Dhar [11] between the variance of the work, σ_W^2, its mean, $\langle W\rangle$, and the free-energy change between two states, ΔF, for a model of dragged particle dynamics defined by exactly the same GLE as Eq. (1). Equation (11) formed the basis for the demonstration of the validity of the Jarzynski equality in non-Markovian systems. Although it cannot be concluded from Eq. (10) that a similar equality applies to heat effects in such systems (since the heat distribution function is not Gaussian, in general, even though the noise is), Eq. (10) is itself quite general, and may therefore point to the existence of some more fundamental underlying relation for the heat.

APPENDIX: DERIVATION OF THE MEAN AND VARIANCE OF THE HEAT

To calculate $\langle Q(t)\rangle$, the expressions for $x(t)$ and $v(t)$ in Eqs. (4a) and (4b) are first substituted into Eq. (2), and the result averaged over both the distribution of the random force $\theta(t)$ [using the relation $\langle\theta(t)\rangle=0$] as well as over the distribution of initial positions and velocities [using the relations $\langle x_0\rangle=\langle v_0\rangle=0$, $\langle x_0^2\rangle=k_BT/k$, and $\langle v_0^2\rangle=k_BT/m$, the subscript 0 denoting the initial value]. This yields

$$\langle Q(t)\rangle=\frac{k}{m^2}\int_0^t dt_1 H(t_1)\dot{H}(t_1)-\frac{1}{m}\int_0^t dt_1\dot{H}(t_1)f(t_1), \tag{A.1}$$

the dots indicating differentiation with respect to time t. Partial integration reduces Eq. (A.1) to

$$\langle Q(t)\rangle = \frac{k}{2m^2}H^2(t) - \frac{1}{m}\left[H(t)f(t) - \int_0^t dt_1 H(t_1)\dot{f}(t_1)\right] \tag{A.2}$$

Replacing $f(t)$ in this expression by kut and using Eqs. (5a)–(5d) to rewrite the function $H(t)$ entirely in terms of the function $\chi(t)$ (which contains details of the correlation of the random forces), it is now easily shown that

$$\langle Q(t)\rangle = -ku^2\int_0^t dt_1\int_0^{t_1} dt_2\chi(t_2) + \frac{k}{2}u^2\left[\int_0^t dt_1\chi(t_1)\right]^2 \tag{A.3}$$

The abbreviations $\bar{\chi}(t)\equiv\int_0^t dt_1\chi(t_1)$ and $\bar{\bar{\chi}}(t)=\int_0^t dt_1\bar{\chi}(t_1)=\int_0^t dt_1\int_0^{t_1}dt_2\chi(t_2)$ allow Eq. (A.3) to be written in the compact form

$$\langle Q(t)\rangle = -ku^2\bar{\bar{\chi}}(t) + \frac{k}{2}u^2\bar{\chi}(t)^2, \tag{A.4}$$

which is the final expression for the mean.

The calculation of $\langle Q(t)^2\rangle$ is somewhat more involved. The first step, as before, is the substitution of Eqs. (4a) and (4b) into Eq. (2). The resulting expression, when squared, yields

$$\langle Q(t)^2\rangle = k^2\int_0^t dt_1\int_0^t dt_2\langle x(t_1)v(t_1)x(t_2)v(t_2)\rangle - 2k\int_0^t dt_1\int_0^t dt_2\langle x(t_1)v(t_1)v(t_2)f(t_2)\rangle + \int_0^t dt_1\int_0^t dt_2\langle v(t_1)f(t_1)v(t_2)f(t_2)\rangle \tag{A.5}$$

$$\equiv k^2A(t) - 2kB(t) + C(t) \tag{A.6}$$

The integral $A(t)$ in the above expression, after averaging over the initial positions and velocities, and again using the result $\langle\theta(t)\rangle=0$, becomes

$$A(t) = \frac{\langle Q(t)^2\rangle_0}{k^2} + \frac{k_BT}{m^2k}\chi(t)^2H(t)^2 + \frac{k_BT}{mk^2}G(t)^2H(t)^2 + \frac{1}{4m^4}H(t)^4 + \frac{1}{m^4}H(t)^2\langle I(t)^2\rangle \tag{A.7}$$

where

$$\langle Q(t)^2\rangle_0 \equiv \langle Q(t)^2(u=0)\rangle \tag{A.8}$$

and

$$\langle I(t)^2\rangle = \frac{m^2}{k^2}\int_0^t dt_1\int_0^t dt_2 G(t-t_1)G(t-t_2)\langle\theta(t_1)\theta(t_2)\rangle. \tag{A.9}$$

The calculation of $\langle Q(t)^2\rangle_0$ also starts by substituting Eqs. (4a) and (4b) into Eq. (2) (after first setting u to 0), squaring the result, and averaging over the noise and initial positions and velocities. Using the relations $\langle x_0^4\rangle=3(k_BT)^2/k^2$, $\langle v_0^4\rangle=3(k_BT)^2/m^2$, and $\langle x_0^2\rangle\langle v_0^2\rangle=(k_BT)^2/mk$, one can show that these steps lead after considerable algebra to

$$\frac{4\langle Q(t)^2\rangle_0}{k^2} = \frac{3(k_BT)^2}{k^2}[\chi(t)^2-1]^2 + \frac{3m^2(k_BT)^2}{k^4}\dot{\chi}(t)^4 + \frac{2k_BT}{m^2k}[3\chi(t)^2-1]\langle I(t)^2\rangle + \frac{6k_BT}{mk^2}\dot{\chi}(t)^2\langle I(t)^2\rangle + \frac{2m^2(k_BT)^2}{mk^3}[3\chi(t)^2-1]\dot{\chi}(t)^2 + \frac{1}{m^4}\langle I(t)^4\rangle. \tag{A.10}$$

Here

$$\langle I(t)^4\rangle = \frac{m^4}{k^4}\int_0^t dt_1\int_0^t dt_2\int_0^t dt_3\int_0^t dt_4 G(t-t_1)G(t-t_2) \times\langle\theta(t_1)\theta(t_2)\theta(t_3)\theta(t_4)\rangle. \tag{A.11}$$

Because the integrals in Eqs. (A.9) and (A.11) have a convolution structure, they can be evaluated using multiple Laplace transforms [two such transforms in the case of Eq. (A.9)and four in the case of Eq. (A.11)], along with the pair decomposability property of Gaussian random variables, which renders the average in Eq. (A.11) expressible solely in terms of the average $\langle\theta(t)\theta(t')\rangle=\zeta k_BTK(|t-t'|)$. In this way, one finds the general result

$$\langle I(t_1)I(t_2)\rangle = \frac{m^2k_BT}{k^2}\{k[\chi(|t_1-t_2|)-\chi(t_1)\chi(t_2)] - m\dot{\chi}(t_1)\dot{\chi}(t_2)\} \tag{A.12}$$

from which it may be shown that

$$\langle I(t)^2\rangle = \frac{m^2k_BT}{k^2}\{k[1-\chi(t)^2] - m\dot{\chi}(t)^2\} \tag{A.13}$$

and that

$$\langle I(t)^4\rangle = \frac{3m^4(k_BT)^2}{k^4}\{k[1-\chi(t)^2] - m\dot{\chi}(t)^2\}^2 \tag{A.14}$$

After substituting Eqs. (A.13) and (A.14) into Eq. (A.10), we get the very simple result

$$\langle Q(t)^2\rangle_0 = (k_BT)^2[1-\chi(t)^2] \tag{A.15}$$

Recognizing from Eqs. (5a)–(5d) that the function $G(t)$ in Eq. (A.7) actually reduces to $\dot{\chi}(t)$ (given that $\chi(0)=1$ and $\dot{\chi}(0)=0$) and that $H(t)$ can be written as $H(t)=mu[t-\bar{\chi}(t)]$, $A(t)$ can now be simplified to

$$A(t) = \frac{(k_BT)^2}{k^2}[1-\chi(t)^2] + \frac{u^2k_BT}{k}[t-\bar{\chi}(t)]^2 + \frac{u^4}{4}[t-\bar{\chi}(t)]^4 \tag{A.16}$$

In the same way, it can be shown that the integral $B(t)$ in Eq. (A.5) first reduces to

$$B(t) = \frac{uk_BT}{m}\chi(t)H(t)[t\chi(t) - \bar{\chi}(t)] + \frac{uk_BT}{k}G(t)H(t)[tG(t) - \chi(t) + 1] + \frac{ku}{2m^3}H(t)^2\left[tH(t) - \int_0^t dt_1 H(t_1)\right] + \frac{ku}{m^3}\left[tH(t)\langle I(t)^2\rangle - H(t)\int_0^t dt_1\langle I(t)I(t_1)\rangle\right]. \quad (A.17)$$

From Eq. (A.12), it is easily established that

$$\int_0^t dt_1\langle I(t)I(t_1)\rangle = \frac{m^2k_BT}{k^2}[1-\chi(t)][k\bar{\chi}(t) + m\dot{\chi}(t)] \quad (A.18)$$

This result, together with the expressions for $G(t)$ and $H(t)$ in terms of $\chi(t)$, further simplify $B(t)$ to

$$B(t) = [t - \bar{\chi}(t)]^2\left[u^2k_BT + \frac{ku^4}{2}\left(\frac{t^2}{2} - t\bar{\chi}(t) + \bar{\bar{\chi}}(t)\right)\right] \quad (A.19)$$

Similarly, it can be shown that

$$C(t) = u^2kk_BT[t^2 - 2t\bar{\chi}(t) + 2\bar{\bar{\chi}}(t)] + k^2u^4\left(\frac{t^2}{2} - t\bar{\chi}(t) + \bar{\bar{\chi}}(t)\right)^2, \quad (A.20)$$

which makes use of the result

$$\int_0^t dt_2\int_0^t dt_1\langle I(t_1)I(t_2)\rangle = \frac{m^2k_BT}{k^2}\{2k\bar{\bar{\chi}}(t) - k\bar{\chi}(t)^2 - m[\chi(t)-1]^2\} \quad (A.21)$$

Substituting Eqs. (A.16), (A.19), and (A.20) into Eq. (A.6), and combining with Eq. (A.4), we finally obtain

$$\langle Q(t)^2\rangle - \langle Q(t)\rangle^2 = (k_BT)^2[1-\chi(t)^2] + ku^2k_BT[2\bar{\bar{\chi}}(t) - \bar{\chi}(t)^2] \quad (A.22)$$

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