Energy dissipation and fluctuation response for particles in fluids

J. M. Deutsch and Onuttom Narayan
Department of Physics, University of California, Santa Cruz, California 95064, USA
(Received 18 January 2006; published 15 August 2006)

An equality was recently proved relating energy dissipation to the difference of the response and velocity correlation functions for a class of Langevin equations. We generalize this for the physically important case of particles in a fluid, where bath fluctuations are nonlocal in time due to hydrodynamic modes. We also show that the inclusion of a mass term does not alter the result and provide a simple physical interpretation of the original equality.

DOI: 10.1103/PhysRevE.74.026112 PACS number(s): 05.70.Ln, 82.20.Wt

Fluctuations in an equilibrium state are essential to the description of the state in statistical mechanics. However, these fluctuations also raise questions about how to understand the second law of thermodynamics, as the change in entropy in any process can sometimes be negative as a result of fluctuations. A quantitative measure of such anomalous entropy changes, the fluctuation theorem, was proved [1] for a nonequilibrium steady state, motivated by earlier numerical results for a shear stress model [2]. This theorem was subsequently extended to transient processes in an equilibrium state [3], and to transitions between nonequilibrium steady states [4]. A related identity for the work done in going from one equilibrium configuration to another was proved [5]; the connection between the transient fluctuation theorem and the Jarzynski equality [5] has been demonstrated [6] and clarified [7]. Although originally proved for Hamiltonian systems, the fluctuation theorem was later shown [8] to include Langevin dynamics; a simple proof of this result can be obtained [7]. Experimental measurements have been made on colloidal particles and macromolecules [9,10] and on driven granular gases [11], which have large fluctuations.

Related to the understanding of nonequilibrium entropy fluctuations is recent work by Harada and Sasa [12], who have obtained an identity for nonequilibrium steady states that relates the rate of energy dissipation to deviations from the fluctuation dissipation theorem [13]. In equilibrium, both of these quantities are zero. This result was derived for a massless particle described by a Langevin equation,

$$\gamma\dot{x}(t) = F(x(t),t) + \xi(t) + \varepsilon f^p(t). \tag{1}$$

Here $F(x(t),t)$ is the force from an underlying potential. It is required to be of a form that gives a well-defined steady state velocity distribution, with an average v_s. $\xi(t)$ represents thermal noise, has zero mean, and is Gaussian, satisfying

$$\langle\xi(t)\xi(t')\rangle = 2\gamma T\delta(t-t'). \tag{2}$$

The last term on the right-hand side of Eq. (1) is included in order to compute response functions even though it is zero for the unforced dynamics.

Now define the autocorrelation function for velocity fluctuations when $\varepsilon=0$,

$$C(t) = \langle[\dot{x}(t)-v_s][\dot{x}(0)-v_s]\rangle. \tag{3}$$

Let us now consider the response to an arbitrary forcing represented by the last term in Eq. (1). For sufficiently small ε we expect that the response to it will be linear, so that

$$\langle\dot{x}(t)\rangle_\varepsilon - v_s = \varepsilon\int_{-\infty}^{t} R(t-s)f^p(s)ds + O(\varepsilon^2), \tag{4}$$

where the left-hand average denotes an ensemble average over thermal noise realizations.

The rate of energy dissipation $J(t)$ is a straightforward extension of the one used previously [12,14].

$$J(t)dt \equiv \{F[x(t),t] + \varepsilon f^p(t)\}\circ dx(t). \tag{5}$$

Because the system is in steady state, the kinetic energy averaged over different realizations of the noise ξ is time independent. $\langle J_n\rangle$ is the average power dissipated into heat.

With these definitions, Ref. [12] derives a theorem for systems with dynamics satisfying Eq. (1)

$$\langle J\rangle = \gamma\left\{v_s^2 + \int_{-\infty}^{\infty}\frac{d\omega}{2\pi}[C(\omega) - 2TR'(\omega)]\right\}, \tag{6}$$

where the left-hand side is the average power dissipated, $C(\omega)$ is the Fourier transform of $C(t)$, and $R'(\omega)$ is the real part of the Fourier transform of $R(t)$.

One restriction on this result is that it assumes that the heat bath, or thermal noise, is white noise. In reality, for a particle in a fluid, thermal noise at different times will have nonzero correlations where hydrodynamic effects result in long-time tails to the autocorrelation function of the noise [15]. These long-range correlations have qualitative effects on macromolecular dynamics where they substantially alter dynamic scaling exponents, shortening correlation times and diffusion coefficients [16,17], for instance, in protein dynamics [18]. Because of their dynamical effects, they are important for chemical reactions in the liquid phase [19]. The dynamics of complex systems such as spin glasses, when reduced to simplified equations, have a noise term with nontrivial correlations [20]. A Langevin equation with a memory kernel is also found to be applicable for a sphere in an upward flow of gas, even though the system is a driven one and is far from equilibrium [21]. Thus it is important to consider whether the limitation of white noise in Eq. (1) can be overcome. However, for the examples cited, the thermal noise is still Gaussian, so we shall retain this assumption.

In this paper, we generalize the result of Eq. (6) to the case of correlated thermal noise. We do so using a simple and powerful theorem for stochastic processes. As a by-product, the result obtained in Ref. [12] for white noise is derived very easily. We also discuss the effect of including a mass term, $m\ddot{x}$, in Eq. (1).

With correlated thermal noise, Eq. (1) is generalized to

$$\int_{-\infty}^{\infty} dt' \, \gamma(t-t')\dot{x}(t') = F(x(t),t) + \xi(t) + \varepsilon f^p(t), \tag{7}$$

where the Fourier transform of the correlation function of $\xi(t)$ satisfies

$$C_\xi(\omega) = 2T\gamma'(\omega), \tag{8}$$

where $\gamma'(\omega)$ is the real part of $\gamma(\omega)$. The damping function $\gamma(t-t')$ is zero for $t<t'$. If we evolve the particle according to Eq. (7) in small time steps Δt, the change in x in any time interval is given by

$$\sum_i \gamma_{ni}\Delta x_i = \tilde{F}_n \Delta t + \Delta V_n + \varepsilon f_n^p \Delta t. \tag{9}$$

Here $\Delta x_n = x_{n+1} - x_n$, and $\tilde{F}_n$ is equal to $\frac{1}{2}[F(x_{n+1})+F(x_n)]$, using Stratanovich dynamics appropriate for the massless Langevin equation. ΔV_n is the noise force integrated over the time interval Δt_n and γ_{ni} is the corresponding integral of the damping function. The discretized form of Eq. (8) is

$$\left\langle \frac{\Delta V_n}{\Delta t}\frac{\Delta V_j}{\Delta t}\right\rangle = \frac{T}{\Delta t}[\gamma_{nj} + \gamma_{jn}]. \tag{10}$$

Since γ_{nj} is the integral of $\gamma(t-t')$ over a small time interval in t, it is $O(\Delta t)$ for a general smooth damping kernel. However, for white noise, $\gamma(t-t') = \gamma\delta(t-t')$, and $\gamma_{nj} = \gamma\delta_{nj}$. Both sides of the equation depend on n, j only through the combination $n-j$. If we Fourier transform both sides, the symmetrization of γ_{nj} with respect to its arguments results in $2T\gamma'(\omega)$ on the right-hand side, in agreement with Eq. (8).

The power expended in the nth time interval by the underlying potential which causes the force F is the same as in Ref. [12]

$$J_n = \tilde{F}_n \frac{\Delta x_n}{\Delta t}, \tag{11}$$

with corrections that vanish in the $\Delta t \to 0$ limit [22]. Following the procedure in Ref. [12],

$$\langle J_n\rangle = \sum_i \gamma_{ni}\left\langle \frac{\Delta x_n}{\Delta t}\frac{\Delta x_i}{\Delta t}\right\rangle - \frac{1}{\Delta t^2}\langle \Delta V_n \Delta x_n\rangle + O(\Delta t^{1/2}). \tag{12}$$

Our task is to simplify the second term on the right-hand side. We use a theorem due to Novikov [23] and also Furutsu [24] for Gaussian stochastic processes

$$\langle \Delta x_n \Delta V_n\rangle = \sum_j \langle \Delta V_n \Delta V_j\rangle \left\langle \frac{\partial \Delta x_n}{\partial \Delta V_j}\right\rangle. \tag{13}$$

This equation is analogous to Wick's theorem in field theory. Since ΔV and f^p appear together in Eq. (9) (for all n), it is clear that

$$\left\langle \frac{\partial \Delta x_n}{\partial \Delta V_j}\right\rangle = \frac{1}{\Delta t}\left\langle \frac{\partial \Delta x_n}{\partial \varepsilon f_j^p}\right\rangle = \frac{1}{\Delta t}\frac{\partial}{\partial \varepsilon f_j^p}\langle \Delta x_n\rangle. \tag{14}$$

To evaluate the right-hand side of Eq. (14), we use the definition of the response function

$$\frac{1}{\Delta t}\langle \Delta x_n\rangle_\varepsilon = v_s + \varepsilon \Delta t \sum_j R_{nj} f_j^p, \tag{15}$$

where an ensemble average has been performed on the left-hand side, and R_{nj} is the discretized form of $R((n-j)\Delta t)$ of Eq. (4). Using this result in Eq. (14), substituting in Eq. (13), and then in Eq. (12), we see that

$$\langle J_n\rangle = \sum_i \gamma_{ni}\left\langle \frac{\Delta x_n}{\Delta t}\frac{\Delta x_i}{\Delta t}\right\rangle - \sum_j \frac{\langle \Delta V_n \Delta V_j\rangle}{\Delta t} R((n-j)\Delta t). \tag{16}$$

In Fourier space, in the continuum limit this equation is equivalent to

$$\langle J\rangle = \int_{-\infty}^{\infty} \frac{d\omega}{2\pi}\gamma'(\omega)[C(\omega) + v_s^2] - 2T\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}\gamma'(\omega)R'(\omega), \tag{17}$$

where, since $C(\omega)$ is a symmetric function of ω, we can replace $\gamma(\omega)$ by its symmetric part $\gamma'(\omega)$, and similarly for $\gamma'(\omega)$ and $R(\omega)$. This is the main result of this paper.

With the general result in Eq. (17), it is easy to extend the analysis to the case when the particle has a finite mass. In Fourier space, this just corresponds to an extra $im\omega$ term in $\gamma(\omega)$. Since Eqs. (8) and (17) only depend on the real part of $\gamma(\omega)$, the result is unchanged by the mass term.

At the expense of slightly more complex notation, this method also easily generalizes to the case of many particles recently considered by Harada and Sasa [25]. We consider a generalization of their many-body Langevin equation, to allow for a nonlocal damping function

$$\int_{-\infty}^{\infty} dt' \, \gamma^i(t-t')\dot{x}^i(t') = F^i(\{x_j(t)\},t) + \xi^i(t) + \varepsilon f^{p,i}(t), \tag{18}$$

where there are now N particles labeled by the superscript i. As before, γ^j can also contain inertial effects. As usual, $\langle \xi^i(t)\xi^j(t')\rangle = 0$ for $i \neq j$. Here we have applied a separate perturbative force to each particle $\varepsilon[f^{p,1}(t), f^{p,2}(t), \ldots, f^{p,N-1}(t)]$. The force on the ith particle F_i can depend arbitrarily on all the coordinates.

The response ensemble averaged over ξ in the presence of these perturbative forces is now generalized to

$$\langle \dot{x}^i(t)\rangle_\varepsilon - \bar{v}^i = \varepsilon \sum_{j=0}^{N-1} \int_{-\infty}^{t} R_{ij}(t-s) f^{p,j}(s) ds + O(\varepsilon^2). \quad (19)$$

The autocorrelation function for velocity fluctuations when $\varepsilon=0$, generalizes to

$$C_{ij}(t) = \langle (\dot{x}^i(t) - \bar{v}^i)(\dot{x}^j(0) - \bar{v}^j)\rangle. \quad (20)$$

The power dissipated by the ith particle $J^i(t)$ is the generalization of Eq. (5) with particle labels added so that upon discretization, Eq. (11) becomes

$$J_n^i = \tilde{F}^i_n \frac{\Delta x_n^i}{\Delta t} + O(\Delta t^{1/2}). \quad (21)$$

The total power J, is the sum of these terms over all the particles.

Following the same procedure as in the one-particle case, we evaluate $\langle \Delta V_n^i \Delta x_n^i\rangle$ by using the theorem of Furutsu and Novikov to relate this to the autocorrelation of ξ, that is V_n^i and the averaged partial derivative

$$\left\langle \frac{\partial \Delta x_n^i}{\partial \Delta V_m^i} \right\rangle = \frac{1}{\Delta t}\left\langle \frac{\partial \Delta x_n^i}{\partial \varepsilon f_m^{pi}} \right\rangle = \frac{1}{\Delta t}\frac{\partial}{\partial \varepsilon f_j^{pm}} \langle \Delta x_n^i\rangle. \quad (22)$$

Using the discretized version of Eq. (19), we can then evaluate this derivative, yielding $\Delta t R_{ii}(n-m)$. Following the same steps as in the one-particle case, this leads to

$$\langle J\rangle = \sum_{i=0}^{N-1} \int_{-\infty}^{\infty} \frac{d\omega}{2\pi} \gamma'^i(\omega)\{C_{ii}(\omega) + \bar{v}^{i^2} - 2TR'_{ii}(\omega)\}, \quad (23)$$

which is a generalization of the equation derived in Ref. [25].

For the case of white noise, since $\gamma(\omega)$ is independent of ω, we recover Eq. (6). In this limit, both terms in Eq. (17) are divergent because the integrands tend to nonzero constants at large ω. However, the difference is finite. In fact, with white noise the whole derivation simplifies considerably, since most of the summations over indices are eliminated. Note that for white noise with finite mass, Eq. (6) is unaltered, but the dynamics is affected by the mass term and the two parts of the integral are both finite.

With white noise, it is also possible to easily understand Eq. (6) physically. Equation (12) simplifies to

$$\langle J_n\rangle = \gamma\left\langle \left(\frac{\Delta x_n}{\Delta t}\right)^2 \right\rangle - \frac{1}{\Delta t^2}\langle \Delta V_n \Delta x_n\rangle + O(\Delta t^{1/2}). \quad (24)$$

As before, the second part of the right-hand side needs simplification. From Eq. (1), we observe that for a single time step it is sufficient to linearize $F(x(t),t)$ as $F_0 - F_1(x-x_n)$, where $F_{0,1}$ depends on x_n and t. This is because in a time interval Δt, $\Delta x \sim O(\Delta t^{1/2})$, so that this linear approximation is sufficient to obtain x_{n+1} to $O(\Delta t^{3/2})$. With this linear approximation, it is straightforward to verify that

$$\left\langle \frac{\Delta x_n}{\Delta t}\frac{\Delta V_n}{\Delta t} \right\rangle = 2\gamma T\left[\frac{1}{\Delta t}\frac{1}{\gamma + \frac{1}{2}F_1 \Delta t}\right], \quad (25)$$

where the expectation value is an average over the thermal noise. Also, the instantaneous response function before performing an ensemble average is

$$R_{x_n}(0) = \frac{1}{\Delta t}\frac{1}{\gamma + \frac{1}{2}F_1\Delta t}. \quad (26)$$

Comparing the right-hand sides of Eqs. (25) and (26) and substituting this into Eq. (24) yields

$$\langle J_n\rangle = \gamma\left\langle \left(\frac{\Delta x_n}{\Delta t}\right)^2\right\rangle - 2T\gamma R(0), \quad (27)$$

and thence Eq. (6). A similar analysis is possible for the finite mass case.

A natural experimental system where this result should be directly applicable is that of a particle in a fluid moving in a thermal ratchet [26]. The applicability of the fluctuation dissipation theorem to such systems [27] and more generally to tilted periodic potentials [28] has already been the subject of experimental investigations. Therefore we believe that it should be interesting to attempt to verify this equality using similar experimental systems.

In conclusion, we have generalized the equality of Harada and Sasa [12] to include the case of a particle in a fluid. Their proof was only for the white noise case, that is, for a Langevin equation without a memory kernel, which therefore omits the long-time tails present in the autocorrelation function of a liquid. Our proof follows a different approach to the one originally presented and instead utilizes the identity Eq. (13) to relate fluctuations to response. Using this method we were also able to easily extend this to the case where the particle is given a finite mass. We also showed that it is possible to extend these results to the case of a many-body system with analogous Langevin dynamics in a straightforward manner, obtaining a generalization of a previous equality [25]. Finally, we observed that in the white noise case first considered in the original proof [12], the equality can be written in the time domain, in which case it is local in time as it only involves the instantaneous response to the perturbation f^p. This leads to simple and physically intuitive derivation of their important result.

[1] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74**, 2694 (1995).
[2] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. **71**, 2401 (1993).
[3] D. J. Evans and D. J. Searles, Phys. Rev. E **50**, 1645 (1994).
[4] T. Hatano and S.-i. Sasa, Phys. Rev. Lett. **86**, 3463 (2001).
[5] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
[6] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).

[7] O. Narayan and A. Dhar, J. Phys. A **37**, 63 (2004).
[8] J. Kurchan, J. Phys. A **31**, 3719 (1998).
[9] G. M. Wang, E. M. Sevick, E. Mittag, D. J. Searles, and D. J. Evans, Phys. Rev. Lett. **89**, 050601 (2002); D. M. Carberry, J. C. Reid, G. M. Wang, E. M. Sevick, D. J. Searles, and D. J. Evans, *ibid.* **92**, 140601 (2004).
[10] J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco, and C. Bustamante, Science **296**, 1832 (2002); F. Ritort, C. Bustamante, and I. Tinoco, Proc. Natl. Acad. Sci. U.S.A. **99**, 13544 (2002); D. Collin, F. Ritort, C. Jarzynski, S. B. Smith, I. Tinoco, and C. Bustamante, Nature (London) **437**, 231 (2005).
[11] S. Ciliberto and C. Laroche, J. Phys. IV **8**, 215 (1998); K. Feitosa and N. Menon, Phys. Rev. Lett. **92**, 164301 (2004). For an alternative interpretation of the experiments on granular materials, see Ref. [29].
[12] T. Harada and S.-i. Sasa, Phys. Rev. Lett. **95**, 130602 (2005).
[13] R. Kubo, M. Toda, and N. Hashitsume, *Statistical Physics II: Nonequilibrium Statistical Mechanics* (Springer Verlag, Berlin, 1991).
[14] K. Sekimoto, J. Phys. Soc. Jpn. **66**, 1234 (1997).
[15] T. S. Chow and J. J. Hermans, Physica (Amsterdam) **65**, 156 (1973); D. Bedeaux and P. Mazur, Physica (Amsterdam) **78**, 505 (1974); D. H. Berman, J. Stat. Phys. **20**, 57 (1979); G. van der Zwan and P. Mazur, Physica A **98**, 169 (1979); P. P. J. M. Schram and I. P. Yakimenko, *ibid.* **73**, 260 (1998).
[16] B. H. Zimm, J. Chem. Phys. **24**, 269 (1956).
[17] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, NY, 1985).
[18] W. Min, G. Luo, B. J. Cherayil, S. C. Kou, and X. S. Xie, Phys. Rev. Lett. **94**, 198302 (2005).
[19] R. F. Grote and J. T. Hynes, J. Chem. Phys. **73**, 2715 (1980).
[20] H. Sompolinsky and A. Zippelius, Phys. Rev. Lett. **47**, 359 (1981); Phys. Rev. B **25**, 6860 (1982).
[21] R. P. Ojha, P.-A. Lemieux, P. K. Dixon, A. J. Liu, and D. J. Durian, Nature (London) **427**, 521 (2004).
[22] We assume here that the noise has positive correlations, i.e., $\langle \Delta V_n \Delta V_n \rangle / \Delta t$ does not diverge for $\Delta t \rightarrow 0$. (This condition is satisfied in most physical situations.); See also W. Dai and C. C. Heyde, J. Appl. Math. Stoch. Anal. **9**, 439 (1996).
[23] E. A. Novikov, Zh. Eksp. Teor. Fiz. **47**, 1919 (1964) [Sov. Phys. JETP **20**, 1290 (1965)].
[24] K. Furutsu, J. Res. Natl. Bur. Stand., Sect. D **67**, 303 (1963).
[25] T. Harada and S.-i. Sasa, e-print cond-mat/0510723.
[26] F. Jülicher, A. Ajdari, and J. Prost, Rev. Mod. Phys. **69**, 1269 (1997). P. Reimann, Phys. Rep. **361**, 57 (2002).
[27] T. Harada and K. Yoshikawa, Phys. Rev. E **69**, 031113 (2004).
[28] K. Hayashi and S-i. Sasa, Phys. Rev. E **69**, 066119 (2004).
[29] A. Puglisi, P. Visco, A. Barrat, E. Trizac, and F. van Wijland, Phys. Rev. Lett. **95**, 110202 (2005).