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Energy spectrum of a Langevin oscillator

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We derive analytical solutions for the autocorrelation and cross-correlation functions of the kinetic, potential, and total energy of a Langevin oscillator. These functions are presented in both the time and frequency domains and validated by independent numerical simulations. The results are applied to address the long-standing issue of temperature fluctuations in canonical systems.

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I. INTRODUCTION

The Langevin equation is widely used for the modeling of stochastic processes in many fields of physics and various branches of science and engineering [1]. In particular, the equation can describe Brownian motion of a particle in a harmonic potential well, often referred to as the Langevin oscillator. While many properties of the Langevin oscillator have been exhaustively studied over the past century, to our knowledge the correlation functions and other statistical characteristics of the oscillator energy have not been reported so far.

The goal of this paper is to investigate the fluctuations of the kinetic, potential, and total energy of a one-dimensional Langevin oscillator. The results are presented in the form of analytical expressions for the respective autocorrelation functions (ACFs) and cross-correlation functions (CCFs) and their frequency spectra. The paper heavily relies on the formalism of spectral representation of stochastic processes. Some of the basic formalism is reviewed in Appendix A. The calculations are enabled by a product rule of pair correlation functions presented in Appendix B. The correlation functions reported in this work permit a clear separation of two different time scales inherent in the Langevin model. This time scale separation is a key to addressing the delicate, and still controversial, issue of temperature fluctuations in systems connected to a thermostat.

The Langevin equation for a one-dimensional harmonic oscillator with a natural (resonant) frequency ω_0 and a friction coefficient (damping constant) γ has the form [2–4]

$$m\ddot{x} = -m\gamma v - m\omega_0^2 x + R, \tag{1}$$

where m is the particle mass, x is its deviation from equilibrium, $v = \dot{x}$ is the velocity, and the random force (noise) R satisfies the condition $\bar{R} = 0$. Here and everywhere below, the bar denotes the canonical ensemble average. The variance of R is adjusted to balance the friction force and achieve equilibrium with the thermostat at a chosen temperature T_0. The random force pumps mechanical energy into the oscillator by incessant tiny kicks and causes thermal fluctuations, whereas the friction force dissipates this energy into heat.

Equation (1) is solved by spectral methods [2–4]. Taking its Fourier transform we obtain

$$\hat{x}(\omega) = \frac{\hat{R}(\omega)/m}{\omega_0^2 - \omega^2 + i\gamma\omega}, \tag{2}$$

where the hat marks a Fourier transform with the angular frequency ω (see Appendix A). For the particle velocity we have

$$\hat{v}(\omega) = i\omega\hat{x}(\omega) = \frac{i\omega\hat{R}(\omega)/m}{\omega_0^2 - \omega^2 + i\gamma\omega}. \tag{3}$$

The random force R is considered to be a white noise, for which

$$\overline{\hat{R}(\omega)\hat{R}(\omega')} = \delta(\omega + \omega')I_R, \tag{4}$$

where I_R is a constant. Practically, this condition is satisfied when the correlation time of R is much shorter than both the vibration period $2\pi/\omega_0$ and the damping time $1/\gamma$. The standard calculation of $\overline{v^2}$ and application of the equipartition theorem leads to the fluctuation-dissipation relation [2–4]

$$I_R = \frac{\gamma m k T_0}{\pi} \tag{5}$$

linking the noise power I_R to the damping constant γ.

The Fourier transform $\hat{C}_{xx}(\omega)$ of the position ACF $C_{xx}(t) = \overline{x(0)x(t)}$ is obtained by inserting $\hat{x}(\omega)$ from Eq. (2) into Eq. (A11) (Wiener-Khinchin theorem, Appendix A):

$$\begin{aligned}\overline{\hat{x}(\omega)\hat{x}(\omega')} &= \frac{\overline{\hat{R}(\omega)\hat{R}(\omega')}/m^2}{(\omega_0^2 - \omega^2 + i\gamma\omega)(\omega_0^2 - \omega'^2 + i\gamma\omega')}\\ &= \frac{(I_R/m^2)\delta(\omega+\omega')}{(\omega_0^2 - \omega^2 + i\gamma\omega)(\omega_0^2 - \omega'^2 + i\gamma\omega')}\\ &= \hat{C}_{xx}(\omega)\delta(\omega+\omega'),\end{aligned} \tag{6}$$

where

$$\hat{C}_{xx}(\omega) = \frac{\gamma k T_0/\pi m}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}. \tag{7}$$

A similar calculation gives the spectral form of the velocity ACF:

$$\hat{C}_{vv}(\omega) = \frac{(\gamma k T_0/\pi m)\omega^2}{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}, \tag{8}$$

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where we used Eq. (3) for $\hat{v}(\omega)$. The position-velocity CCF $\hat{C}_{xv}(\omega)$ is obtained in a similar manner using Eq. (A7) from Appendix A:

$$\hat{C}_{xv}(\omega) = -\frac{i(\gamma k T_0/\pi m)\omega}{\left(\omega_0^2 - \omega^2\right)^2 + \gamma^2\omega^2}. \tag{9}$$

The correlation functions (7)–(9) are well known and are only reproduced here as ingredients for the subsequent calculations.

II. KINETIC ENERGY OF THE LANGEVIN OSCILLATOR

Our goal is to compute the ACF $C_{\Delta K\Delta K}(t) = \overline{\Delta K(0)\Delta K(t)}$ of the kinetic energy $K = mv^2/2$ relative to its average value $\overline{K} = kT_0/2$, where we denote $\Delta K = K - \overline{K}$. We first find the spectral ACF $\hat{C}_{\Delta K\Delta K}(\omega)$ by applying the equations derived in Appendix B. Taking $a(t) = v(t)$, Eq. (B12) gives

$$\hat{C}_{\Delta K\Delta K}(\omega) = \frac{m^2}{2}\int_{-\infty}^{\infty} \hat{C}_{vv}(\omega')\hat{C}_{vv}(\omega - \omega')d\omega'. \tag{10}$$

Inserting $\hat{C}_{vv}(\omega)$ from Eq. (8) we have

$$\hat{C}_{\Delta K\Delta K}(\omega) = \frac{(\gamma k T_0)^2}{2\pi^2}\int_{-\infty}^{\infty} \frac{\omega'^2(\omega - \omega')^2 d\omega'}{\left[\left(\omega_0^2 - \omega'^2\right)^2 + \gamma^2\omega'^2\right]\left[\left(\omega_0^2 - (\omega - \omega')^2\right)^2 + \gamma^2(\omega - \omega')^2\right]}. \tag{11}$$

The integral in Eq. (11) is evaluated by replacing ω' by a complex variable z and integrating the function

$$f(z) = \frac{z^2(\omega - z)^2}{\left[\left(\omega_0^2 - z^2\right)^2 + \gamma^2 z^2\right]\left[\left(\omega_0^2 - (\omega - z)^2\right)^2 + \gamma^2(\omega - z)^2\right]} \tag{12}$$

along a semicircular closed loop C in the complex plane [Fig. 1(a)]. This function has eight singularities, the following four of which lie inside the loop:

$$a_1 = -\omega_1 + i\gamma/2, \quad a_2 = \omega_1 + i\gamma/2,$$
$$a_3 = \omega - \omega_1 + i\gamma/2, \quad a_4 = \omega + \omega_1 + i\gamma/2, \tag{13}$$

where

$$\omega_1 = \sqrt{\omega_0^2 - \gamma^2/4} \tag{14}$$

and we assumed that $\omega_0 > \gamma/2$. Finding the residues at these singularities and inserting them in the residue theorem we have

$$\oint_C f(z)dz = 2\pi i \sum_{i=1}^{4} \mathrm{Res}(f, a_i)$$
$$= 2\pi \frac{\omega^4 + \omega^2\left(\gamma^2 - 3\omega_0^2\right) + 4\omega_0^4}{\gamma(\gamma^2 + \omega^2)\left[4\gamma^2\omega^2 + \left(\omega^2 - 4\omega_0^2\right)^2\right]}. \tag{15}$$

If $\omega_0 < \gamma/2$, then the four singularities enclosed by the loop are [Fig. 1(b)]:

$$a_1 = -i\omega_2 + i\gamma/2, \quad a_2 = i\omega_2 + i\gamma/2,$$
$$a_3 = \omega - i\omega_2 + i\gamma/2, \quad a_4 = \omega + i\omega_2 + i\gamma/2, \tag{16}$$

where

$$\omega_2 = \sqrt{\gamma^2/4 - \omega_0^2}, \tag{17}$$

and the calculations give the same result as in Eq. (15). When $|z| \to \infty$, $|f(z)|$ tends to zero as $1/|z|^4$ and the integral along the arc vanishes, leaving only the integral from $-\infty$ to ∞ along the real axis appearing in Eq. (11). We finally obtain the spectral ACF of the kinetic energy:

$$\hat{C}_{\Delta K\Delta K}(\omega) = \frac{\gamma(kT_0)^2}{\pi}\frac{\omega^4 + \omega^2\left(\gamma^2 - 3\omega_0^2\right) + 4\omega_0^4}{(\gamma^2 + \omega^2)\left[4\gamma^2\omega^2 + \left(\omega^2 - 4\omega_0^2\right)^2\right]}. \tag{18}$$

This function has three maxima: one at $\omega = 0$ and two more near $\omega = \pm 2\omega_0$ [Fig. 2(a)].

If $\gamma \ll \omega_0$ (underdamped regime), then the maxima of $\hat{C}_{\Delta K\Delta K}(\omega)$ are very sharp and separated by frequency gaps. Near the central maximum we have $|\omega| \ll \omega_0$ and Eq. (18)

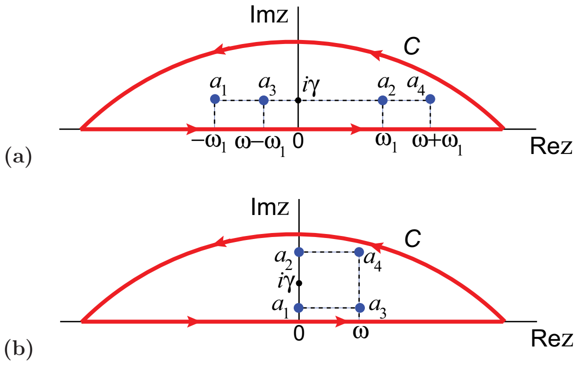

FIG. 1. Integration loop for computing $\hat{C}_{\Delta K\Delta K}(\omega)$ using Eq. (11). The four singularity points enclosed by the loop are indicated. (a) $\omega_0 > \gamma/2$ and (b) $\omega_0 < \gamma/2$.

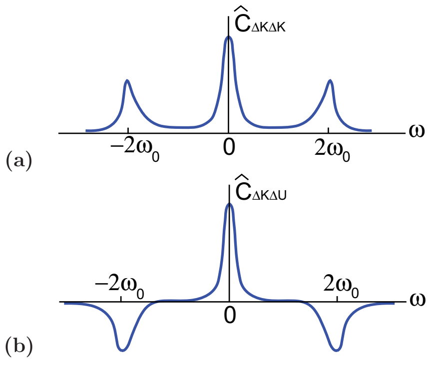

FIG. 2. Schematic plots of the kinetic energy autocorrelation function (a) and kinetic-potential energy cross-correlation function (b) of a Langevin oscillator in the frequency domain.

gives a Lorentz peak of width γ:

$$\hat{C}_{\Delta K\Delta K}(\omega) = \frac{\gamma (kT_0)^2}{4\pi}\frac{1}{\gamma^2+\omega^2}. \tag{19}$$

The ACF corresponding to this peak is

$$\begin{aligned} C_{\Delta K\Delta K}(t) &= \int_{-\infty}^{\infty} \hat{C}_{\Delta K\Delta K}(\omega) e^{i\omega t} d\omega \\ &= \frac{\gamma (kT_0)^2}{4\pi}\int_{-\infty}^{\infty}\frac{e^{i\omega t}}{\gamma^2+\omega^2} d\omega. \end{aligned} \tag{20}$$

The integral is readily computed using the residue theorem with the same semicircular loop as before. The loop encloses one singularity at $a = i\gamma$. The integral along the arc vanishes and we obtain (assuming $t > 0$)

$$C_{\Delta K\Delta K}(t) = \frac{(kT_0)^2}{4} e^{-\gamma t}. \tag{21}$$

This function describes long-range fluctuations of K due to energy exchanges with the thermostat.

Around the remaining maxima we have $|\omega \pm 2\omega_0| \ll \omega_0$, and $\hat{C}_{\Delta K\Delta K}(\omega)$ can be approximated by

$$\hat{C}_{\Delta K\Delta K}(\omega) = \frac{\gamma (kT_0)^2}{8\pi}\frac{1}{\gamma^2+(\omega\pm 2\omega_0)^2}. \tag{22}$$

This is again a Lorentz function of width γ, except that the height of these peaks is half of that at $\omega = 0$. The ACF corresponding to these peaks is found by inverse Fourier transformation:

$$C_{\Delta K\Delta K}(t) = \frac{\gamma (kT_0)^2}{8\pi}\int_{-\infty}^{\infty}\frac{e^{i\omega t}}{\gamma^2+(\omega\pm 2\omega_0)^2} d\omega. \tag{23}$$

We again apply the residue theorem using the same integration loop. There are two singularities lying inside the loop, $a_\pm = \pm 2\omega_0 + i\gamma$, and we obtain (assuming $t > 0$)

$$C_{\Delta K\Delta K}(t) = \frac{(kT_0)^2}{4} e^{-\gamma t}\cos(2\omega_0 t). \tag{24}$$

The peak at $\omega = 2\omega_0$ describes the kinetic energy variations during quasiharmonic oscillations. Since the kinetic and potential energies transform to each other twice per each period, the frequency is $2\omega_0$. The peak at $\omega = -2\omega_0$ describes physically the same process and only appears in the spectrum to formally satisfy the definition of the Fourier transformation.

The general form of $C_{\Delta K\Delta K}(t)$ is obtained by inverse Fourier transformation of Eq. (18):

$$C_{\Delta K\Delta K}(t) = \frac{\gamma (kT_0)^2}{\pi}\int_{-\infty}^{\infty}\frac{\left[\omega^4+\omega^2\left(\gamma^2-3\omega_0^2\right)+4\omega_0^4\right]e^{i\omega t}}{(\gamma^2+\omega^2)\left[4\gamma^2\omega^2+\left(\omega^2-4\omega_0^2\right)^2\right]} d\omega. \tag{25}$$

As usual, we apply the residue theorem. Suppose $\omega_0 > \gamma/2$. Then the function

$$f(z) = \frac{\left[z^4+z^2\left(\gamma^2-3\omega_0^2\right)+4\omega_0^4\right]e^{izt}}{(\gamma^2+z^2)\left[4\gamma^2 z^2+\left(z^2-4\omega_0^2\right)^2\right]}$$

has three singularities in the upper half-plane ($\mathrm{Im} z > 0$):

$$a_1 = i\gamma,\ a_2 = i\gamma - 2\omega_1,\ a_3 = i\gamma + 2\omega_1, \tag{26}$$

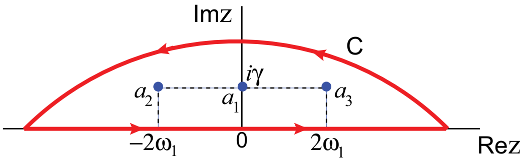

FIG. 3. Integration loop for computing $\hat{C}_{KK}(t)$ using Eq. (25). The singularity points lying inside the loop when $\omega_0 > \gamma/2$ are indicated.

with ω_1 given by Eq. (14). Choosing the same semicircular integration path as before (Fig. 3), we have

$$\begin{aligned} \oint_C f(z)dz &= 2\pi i\sum_{i=1}^{3}\mathrm{Res}(f,a_i) \\ &= \frac{\pi e^{-\gamma t}}{8\gamma\omega_1^2}\left[2\omega_0^2+\left(2\omega_0^2-\gamma^2\right)\cos(2\omega_1 t)\right. \\ &\quad \left. -\,2\gamma\omega_1\sin(2\omega_1 t)\right]. \end{aligned} \tag{27}$$

The integral along the arc vanishes and we finally obtain

$$\begin{aligned} C_{\Delta K\Delta K}(t) = \frac{(kT_0)^2 e^{-\gamma t}}{8\omega_1^2}&\left[2\omega_0^2+\left(2\omega_0^2-\gamma^2\right)\cos(2\omega_1 t)\right. \\ &\left. -\,2\gamma\omega_1\sin(2\omega_1 t)\right]. \end{aligned} \tag{28}$$

If $\omega_0 < \gamma/2$, then similar calculations give

$$\begin{aligned} C_{\Delta K\Delta K}(t) = -\frac{(kT_0)^2 e^{-\gamma t}}{8\omega_2^2}&\left[2\omega_0^2+\left(2\omega_0^2-\gamma^2\right)\cosh(2\omega_2 t)\right. \\ &\left. -\,2\gamma\omega_2\sinh(2\omega_2 t)\right], \end{aligned} \tag{29}$$

where ω_2 is given by Eq. (17). In the latter case, all three singularities lie on the imaginary axis.

Knowing $C_{\Delta K\Delta K}(t)$, we can find the mean-square fluctuation $\overline{(\Delta K)^2} = C_{\Delta K\Delta K}(0)$. Equations (28) and (29) both give the same result: $\overline{(\Delta K)^2} = (kT_0)^2/2$, which matches the independent calculation from the canonical distribution. On the other hand, using Eqs. (21) and (24), we find that the peaks at $\omega = 0$ and $\omega = 2\omega_0$ make equal contributions $\overline{(\Delta K)^2} = (kT_0)^2/4$. Thus, one half of the kinetic energy fluctuation $\overline{(\Delta K)^2}$ is caused by quasiharmonic vibrations, whereas the other half is due to energy fluctuations between the oscillator and the thermostat.

III. POTENTIAL ENERGY OF THE LANGEVIN OSCILLATOR

We next calculate the ACF $C_{\Delta U\Delta U}(t)$ of the potential energy $U = m\omega_0^2 x^2/2$ relative to its average value $\overline{U} = kT_0/2$, where $\Delta U = U - \overline{U}$. As with kinetic energy, we first find the spectral ACF $\hat{C}_{\Delta U\Delta U}(\omega)$ using the approximation discussed in Appendix B with $a(t) = x(t)$. Applying Eq. (B12), we have

$$\hat{C}_{\Delta U\Delta U}(\omega) = \frac{m^2\omega_0^4}{2}\int_{-\infty}^{\infty}\hat{C}_{xx}(\omega')\hat{C}_{xx}(\omega-\omega')d\omega'. \tag{30}$$

Inserting $\hat{C}_{xx}(\omega)$ from Eq. (7),

$$\hat{C}_{\Delta U\Delta U}(\omega)=\frac{(\gamma kT_0)^2\omega_0^4}{2\pi^2}\int_{-\infty}^{\infty}\frac{d\omega'}{\left[\left(\omega_0^2-\omega'^2\right)^2+\gamma^2\omega'^2\right]\left\{\left[\omega_0^2-(\omega-\omega')^2\right]^2+\gamma^2(\omega-\omega')^2\right\}}. \tag{31}$$

The right-hand side is evaluated by integrating the complex function

$$f(z)=\frac{1}{\left[\left(\omega_0^2-z^2\right)^2+\gamma^2z^2\right]\left\{\left[\omega_0^2-(\omega-z)^2\right]^2+\gamma^2(\omega-z)^2\right\}} \tag{32}$$

along a semicircular loop C in the complex plane (Fig. 1). The loop encloses the same four singularities as for the kinetic energy. The residue theorem gives

$$\oint_C f(z)dz=2\pi i\sum_{i=1}^{4}\mathrm{Res}(f,a_i)$$
$$=2\pi\frac{4\gamma^2+\omega^2+4\omega_0^2}{\gamma\omega_0^2(\gamma^2+\omega^2)\left[4\gamma^2\omega^2+\left(\omega^2-4\omega_0^2\right)^2\right]}, \tag{33}$$

from which

$$\hat{C}_{\Delta U\Delta U}(\omega)=\frac{\gamma(kT_0)^2\omega_0^2}{\pi}\frac{4\gamma^2+\omega^2+4\omega_0^2}{(\gamma^2+\omega^2)\left[4\gamma^2\omega^2+\left(\omega^2-4\omega_0^2\right)^2\right]}. \tag{34}$$

Similarly to the kinetic energy case, this function has maxima at $\omega=0$ and near $\omega=\pm2\omega_0$, which have the same physical meaning: The maximum at $\omega=0$ describes long-range fluctuations due to energy exchanges with the thermostat, whereas the maximum near $\omega=2\omega_0$ is due to quasiharmonic vibrations. Again, the maximum near $-2\omega_0$ represents physically the same process; the formal negative frequencies are only shown on the plots to better visualize the central peak.

The real-time ACF $C_{\Delta U\Delta U}(t)$ is calculated by inverse Fourier transformation of Eq. (34):

$$C_{\Delta U\Delta U}(t)=\int_{-\infty}^{\infty}\hat{C}_{\Delta U\Delta U}(\omega)e^{i\omega t}d\omega=\frac{\gamma(kT_0)^2\omega_0^2}{\pi}$$
$$\times\int_{-\infty}^{\infty}\frac{\left(4\gamma^2+\omega^2+4\omega_0^2\right)e^{i\omega t}}{(\gamma^2+\omega^2)\left[4\gamma^2\omega^2+\left(\omega^2-4\omega_0^2\right)^2\right]}d\omega. \tag{35}$$

The function

$$f(z)=\frac{\left[4\gamma^2+z^2+4\omega_0^2\right]e^{izt}}{(\gamma^2+z^2)\left[4\gamma^2z^2+\left(z^2-4\omega_0^2\right)^2\right]} \tag{36}$$

has the same three singularities in the upper half-plane ($\mathrm{Im}z>0$) as its kinetic energy counterpart (Fig. 3). Choosing the same semicircular integration path and assuming that $\omega_0>\gamma/2$, the residue theorem gives

$$\oint_C f(z)dz=2\pi i\sum_{i=1}^{3}\mathrm{Res}(f,a_i)=\frac{\pi e^{-\gamma t}}{8\omega_0^2\omega_1^2}\left[2\omega_0^2+\left(2\omega_0^2-\gamma^2\right)\right.$$
$$\left.\times\cos(2\omega_1t)+2\gamma\omega_1\sin(2\omega_1t)\right]. \tag{37}$$

The integral along the arc vanishes and we obtain

$$C_{\Delta U\Delta U}(t)=\frac{(kT_0)^2e^{-\gamma t}}{8\omega_1^2}\left[2\omega_0^2+\left(2\omega_0^2-\gamma^2\right)\cos(2\omega_1t)\right.$$
$$\left.+2\gamma\omega_1\sin(2\omega_1t)\right]. \tag{38}$$

When $\omega_0<\gamma/2$, similar calculations give

$$C_{\Delta U\Delta U}(t)=-\frac{(kT_0)^2e^{-\gamma t}}{8\omega_2^2}\left[2\omega_0^2+\left(2\omega_0^2-\gamma^2\right)\cosh(2\omega_2t)\right.$$
$$\left.+2\gamma\omega_2\sinh(2\omega_2t)\right]. \tag{39}$$

Note that $C_{\Delta U\Delta U}(t)$ looks similar but differs from the previously derived $C_{\Delta K\Delta K}(t)$.

Knowing $C_{\Delta U\Delta U}(t)$, we find $\overline{(\Delta U)^2}=C_{\Delta U\Delta U}(0)=(kT_0)^2/2$. In the strongly underdamped (quasiharmonic) regime, this fluctuation is split equally between quasiharmonic vibrations and energy exchanges with the thermostat.

IV. TOTAL ENERGY OF THE LANGEVIN OSCILLATOR

The total energy of the oscillator can be factorized as follows:

$$E=\frac{mv^2}{2}+\frac{m\omega_0^2x^2}{2}=\frac{m}{2}ab, \tag{40}$$

where

$$a\equiv v+i\omega_0x,\ b\equiv v-i\omega_0x. \tag{41}$$

To find the ACF $C_{\Delta E\Delta E}(t)$ (where $\Delta E=E-\overline{E}$), we first calculate the spectral form of this ACF. Using Eq. (B10) from Appendix B,

$$\hat{C}_{\Delta E\Delta E}(\omega)=\frac{m^2}{4}\int_{-\infty}^{\infty}\hat{C}_{aa}(\omega')\hat{C}_{bb}(\omega-\omega')d\omega'$$
$$+\frac{m^2}{4}\int_{-\infty}^{\infty}\hat{C}_{ba}(\omega')\hat{C}_{ab}(\omega-\omega')d\omega'. \tag{42}$$

The correlation functions appearing in Eq. (42) are computed as follows. We have

$$\overline{\hat{a}(\omega)\hat{a}(\omega')}=\overline{\hat{v}(\omega)\hat{v}(\omega')}-\omega_0^2\overline{\hat{x}(\omega)\hat{x}(\omega')}$$
$$+i\omega_0\overline{\hat{x}(\omega)\hat{v}(\omega')}+i\omega_0\overline{\hat{v}(\omega)\hat{x}(\omega')}$$
$$=\delta(\omega+\omega')\left[\hat{C}_{vv}(\omega)-\omega_0^2\hat{C}_{xx}(\omega)\right.$$
$$\left.+i\omega_0\hat{C}_{xv}(-\omega)+i\omega_0\hat{C}_{vx}(-\omega)\right], \tag{43}$$

where we used Eqs. (A7) and (A11) from Appendix A. The last two terms cancel each other and we obtain

$$\overline{\hat{a}(\omega)\hat{a}(\omega')}=\delta(\omega+\omega')\left[\hat{C}_{vv}(\omega)-\omega_0^2\hat{C}_{xx}(\omega)\right], \tag{44}$$

from which

$$\hat{C}_{aa}(\omega)=\hat{C}_{vv}(\omega)-\omega_0^2\hat{C}_{xx}(\omega). \tag{45}$$

Similar calculations give

$$\hat{C}_{bb}(\omega)=\hat{C}_{vv}(\omega)-\omega_0^2\hat{C}_{xx}(\omega). \tag{46}$$

For the cross-correlation $\hat{C}_{ab}$ we have

$$\begin{aligned}\overline{\hat{a}(\omega)\hat{b}(\omega')} &= \overline{\hat{v}(\omega)\hat{v}(\omega')} + \omega_0^2\overline{\hat{x}(\omega)\hat{x}(\omega')}\\ &\quad + i\omega_0\overline{\hat{x}(\omega)\hat{v}(\omega')} - i\omega_0\overline{\hat{v}(\omega)\hat{x}(\omega')}\\ &= \delta(\omega+\omega')\big[\hat{C}_{vv}(\omega)+\omega_0^2\hat{C}_{xx}(\omega)\\ &\quad + i\omega_0\hat{C}_{xv}(-\omega) - i\omega_0\hat{C}_{vx}(-\omega)\big], \end{aligned} \tag{47}$$

from which

$$\hat{C}_{ab}(\omega) = \omega_0^2\hat{C}_{xx}(\omega) + \hat{C}_{vv}(\omega) - 2i\omega_0\hat{C}_{vx}(\omega). \tag{48}$$

The functions $\hat{C}_{vv}(\omega)$, $\hat{C}_{xx}(\omega)$, and $\hat{C}_{vx}(\omega)$ are given by Eqs. (8), (7), and (9), respectively. Inserting them into Eqs. (45), (46), and (48) we obtain

$$\hat{C}_{aa}(\omega) = \hat{C}_{bb}(\omega) = \frac{(\gamma kT_0/\pi m)\big(\omega^2-\omega_0^2\big)}{\big(\omega_0^2-\omega^2\big)^2+\gamma^2\omega^2}, \tag{49}$$

$$\hat{C}_{ab}(\omega) = \hat{C}_{ba}(-\omega) = \frac{(\gamma kT_0/\pi m)(\omega-\omega_0)^2}{\big(\omega_0^2-\omega^2\big)^2+\gamma^2\omega^2}. \tag{50}$$

These functions provide the input to Eq. (42), which then becomes

$$\begin{aligned}\hat{C}_{\Delta E\Delta E}(\omega) &= \frac{(\gamma kT_0)^2}{4\pi^2}\int_{-\infty}^{\infty}\frac{(\omega_0+\omega')^2(\omega-\omega'-\omega_0)^2d\omega'}{\big[\big(\omega_0^2-\omega'^2\big)^2+\gamma^2\omega'^2\big]\big[\big(\omega_0^2-(\omega-\omega')^2\big)^2+\gamma^2(\omega-\omega')^2\big]}d\omega'\\ &\quad+\frac{(\gamma kT_0)^2}{4\pi^2}\int_{-\infty}^{\infty}\frac{(\omega_0+\omega')^2(\omega-\omega'-\omega_0)^2d\omega'}{\big[\big(\omega_0^2-\omega'^2\big)^2+\gamma^2\omega'^2\big]\big[\big(\omega_0^2-(\omega-\omega')^2\big)^2+\gamma^2(\omega-\omega')^2\big]}d\omega'. \end{aligned} \tag{51}$$

The integrals are readily evaluated using the residue theorem with the same semicircular integration loop as for the kinetic and potential energies. The singularities of the integrands lying inside the loop are the same as in Eqs. (11) and (31). Somewhat lengthy calculations give

$$\hat{C}_{\Delta E\Delta E}(\omega) = \frac{\gamma(kT_0)^2}{\pi}\frac{\big(\omega^2-4\omega_0^2\big)^2+\gamma^2\big(\omega^2+4\omega_0^2\big)}{(\gamma^2+\omega^2)\big[4\gamma^2\omega^2+\big(\omega^2-4\omega_0^2\big)^2\big]}. \tag{52}$$

This function has a maximum at $\omega = 0$ and local minima near $\pm 2\omega_0$. When $\gamma \ll \omega_0$, these extrema are separated by frequency gaps. Near the maximum, $\hat{C}_{\Delta E\Delta E}(\omega)$ behaves as

$$\hat{C}_{\Delta E\Delta E}(\omega) = \frac{\gamma(kT_0)^2}{\pi}\frac{1}{\gamma^2+\omega^2}. \tag{53}$$

This is a Lorentz peak of width γ and height $(kT_0)^2/\pi\gamma$. This peak represents the energy fluctuations between the system and the thermostat and is 4 times as high as the similar peaks for the kinetic and potential energies. Near $\omega = 2\omega_0$, $\hat{C}_{\Delta E\Delta E}(\omega)$ behaves approximately as

$$\hat{C}_{\Delta E\Delta E}(\omega) = \frac{\gamma(kT_0)^2}{8\pi\omega_0^2}\frac{\gamma^2+2(\omega-2\omega_0)^2}{\gamma^2+(\omega-2\omega_0)^2}. \tag{54}$$

This equation describes a Lorentz-shape local minimum of width γ and depth $\gamma(kT_0)^2/8\pi\omega_0^2$. This depth is a factor of $\gamma^2/8\omega_0^2$ smaller than the height of the maximum $\omega = 0$. In the strongly underdamped regime ($\gamma \ll \omega_0$), this minimum is extremely shallow and can be neglected. It describes an "antiresonance" effect wherein the oscillator is less willing to exchange the total energy with the thermostat at the natural frequency of the kinetic-potential energy fluctuations (which is $2\omega_0$) than at nearly frequencies. In the underdamped regime this is a tiny second-order effect. Most of the energy exchanges between the oscillator and the thermostat occur at low frequencies.

The time-dependent ACF $C_{\Delta E\Delta E}(t)$ can now be obtained by inverse Fourier transformation of Eq. (52):

$$\begin{aligned}C_{\Delta E\Delta E}(t) &= \int_{-\infty}^{\infty}\hat{C}_{\Delta E\Delta E}(\omega)e^{i\omega t}d\omega = \frac{\gamma(kT_0)^2}{\pi}\\ &\quad\times\int_{-\infty}^{\infty}\frac{\big[\big(\omega^2-4\omega_0^2\big)^2+\gamma^2\big(\omega^2+4\omega_0^2\big)\big]e^{i\omega t}}{(\gamma^2+\omega^2)\big[4\gamma^2\omega^2+\big(\omega^2-4\omega_0^2\big)^2\big]}d\omega. \end{aligned} \tag{55}$$

As before, we apply the residue theorem utilizing the semicircular integration loop shown in Fig. 3. We obtain

$$C_{\Delta E\Delta E}(t) = \frac{(kT_0)^2}{4\omega_1^2}e^{-\gamma t}\big[4\omega_0^2-\gamma^2\cos(2\omega_1 t)\big] \tag{56}$$

if $\omega_0 > \gamma/2$ and

$$C_{\Delta E\Delta E}(t) = -\frac{(kT_0)^2}{4\omega_2^2}e^{-\gamma t}\big[4\omega_0^2-\gamma^2\cosh(2\omega_2 t)\big] \tag{57}$$

if $\omega_0 < \gamma/2$. These equations correctly give the mean-square fluctuation of the total energy:

$$\overline{(\Delta E)^2} = (kT_0)^2. \tag{58}$$

V. THE CROSS-CORRELATION FUNCTIONS

In this section we calculate the CCFs among the kinetic, potential, and total energies. We start by computing the spectral form of the kinetic-potential energy CCF $\hat{C}_{\Delta K\Delta U}(\omega)$ using the equations from Appendix B with $a(t) = v(t)$ and $b(t) = x(t)$. In the notations of Appendix B, $G(t) = v^2(t)$ and $H(t) = x^2(t)$. Equation (B11) gives

$$\hat{C}_{\Delta K\Delta U}(\omega) = \frac{m^2\omega_0^2}{4}\int_{-\infty}^{\infty}\hat{C}_{xv}(\omega')\hat{C}_{xv}(\omega-\omega')d\omega' = -\int_{-\infty}^{\infty}\frac{(\gamma kT\omega_0/4\pi)^2\omega'(\omega-\omega')d\omega'}{\big[\big(\omega_0^2-\omega'^2\big)^2+\gamma^2\omega'^2\big]\big[\big(\omega_0^2-(\omega-\omega')^2\big)^2+\gamma^2(\omega-\omega')^2\big]}d\omega'. \tag{59}$$

At the second step we inserted $\hat{C}_{xv}(\omega)$ from Eq. (9). The integral is evaluated by integration along the usual path C in the complex plane (Fig. 1). The loop contains the same singularities as in the ACF calculations for the kinetic and potential energies. Calculations employing the residue theorem give

$$\hat{C}_{\Delta K \Delta U}(\omega) = \frac{\gamma (kT_0)^2}{\pi} \frac{\omega_0^2\left(4\omega_0^2 - 3\omega^2\right)}{(\gamma^2+\omega^2)\left[4\gamma^2\omega^2 + \left(\omega^2 - 4\omega_0^2\right)^2\right]}. \tag{60}$$

This function has a central maximum at $\omega = 0$ and two negative minima at $\omega = \pm 2\omega_0$ [Fig. 2(b)]. When $\gamma \ll \omega_0$, these extrema are separated by frequency gaps and have a Lorentz shape of width γ and the heights of $(kT_0)^2/4\pi\gamma$ and $-(kT_0)^2/8\pi\gamma$, respectively. As before, the central maximum represents the energy exchanges with the thermostat while the minima arise from quasiharmonic vibrations. The negative sign of the minima reflects the fact that the kinetic and potential energies oscillate in antiphase: When one increases, the other decreases.

Since $\hat{C}_{\Delta K \Delta U}(\omega)$ is an even function of frequency, $\hat{C}_{U \Delta K}(\omega)$ is given by the same equation (60). We can now calculate the CCFs of the total energy with the kinetic and potential energies. We have

$$\begin{aligned}\hat{C}_{\Delta E \Delta K}(\omega) &= \hat{C}_{\Delta K \Delta K}(\omega) + \hat{C}_{\Delta U \Delta K}(\omega)\\ &= \frac{\gamma (kT_0)^2}{\pi} \frac{\omega^4 + \left(\gamma^2 - 6\omega_0^2\right)\omega^2 + 8\omega_0^4}{(\gamma^2+\omega^2)\left[4\gamma^2\omega^2 + \left(\omega^2 - 4\omega_0^2\right)^2\right]},\end{aligned} \tag{61}$$

where we used Eq. (18) for $\hat{C}_{\Delta K \Delta K}(\omega)$. Similarly,

$$\begin{aligned}\hat{C}_{\Delta E \Delta U}(\omega) &= \hat{C}_{\Delta K \Delta U}(\omega) + \hat{C}_{\Delta U \Delta U}(\omega)\\ &= \frac{\gamma (kT_0)^2}{\pi} \frac{8\omega_0^4 + 4\gamma^2\omega_0^2 - 2\omega^2\omega_0^2}{(\gamma^2+\omega^2)\left[4\gamma^2\omega^2 + \left(\omega^2 - 4\omega_0^2\right)^2\right]},\end{aligned} \tag{62}$$

where we used Eq. (34) for $\hat{C}_{\Delta U \Delta U}(\omega)$. At $\gamma \ll \omega_0$, both $\hat{C}_{\Delta E \Delta K}(\omega)$ and $\hat{C}_{\Delta E \Delta U}(\omega)$ have a central peak at $\omega = 0$ and a tiny wiggle near $\omega = \pm 2\omega_0$, the latter being associated with the "antiresonance" effect mentioned above. Thus, at low frequencies, the kinetic and potential energies strongly correlate with the total energy, which is consistent with the picture of long-range fluctuations due to slow energy exchanges with the thermostat maintaining nearly equilibrium partitioning between the kinetic and potential energies.

The time domain forms of these CCFs are obtained by Fourier transformations using the residue theorem and the semicircular integration path shown in Fig. 3. In all cases, the three singularities enclosed by the path are given by Eq. (26). The calculations are similar to those for the ACFs and, assuming $\omega_0 > \gamma/2$, give

$$C_{\Delta K \Delta U}(t) = \frac{(kT_0)^2\omega_0^2}{4\omega_1^2} e^{-\gamma t}[1 - \cos(2\omega_1 t)], \tag{63}$$

$$\begin{aligned}C_{\Delta E \Delta K}(t) = \frac{(kT_0)^2 e^{-\gamma t}}{8\omega_1^2}\big[&4\omega_0^2 - \gamma^2\cos(2\omega_1 t)\\ &- 2\gamma\omega_1 \sin(2\omega_1 t)\big],\end{aligned} \tag{64}$$

$$\begin{aligned}C_{\Delta E \Delta U}(t) = \frac{(kT_0)^2 e^{-\gamma t}}{8\omega_1^2}\big[&4\omega_0^2 - \gamma^2\cos(2\omega_1 t)\\ &+ 2\gamma\omega_1 \sin(2\omega_1 t)\big].\end{aligned} \tag{65}$$

If $\omega_0 < \gamma/2$, these equations become, respectively,

$$C_{\Delta K \Delta U}(t) = -\frac{(kT_0)^2\omega_0^2}{4\omega_2^2} e^{-\gamma t}[1 - \cosh(2\omega_2 t)], \tag{66}$$

$$\begin{aligned}C_{\Delta E \Delta K}(t) = -\frac{(kT_0)^2 e^{-\gamma t}}{8\omega_2^2}\big[&4\omega_0^2 - \gamma^2\cosh(2\omega_2 t)\\ &- 2\gamma\omega_1 \sinh(2\omega_2 t)\big],\end{aligned} \tag{67}$$

$$\begin{aligned}C_{\Delta E \Delta U}(t) = -\frac{(kT_0)^2 e^{-\gamma t}}{8\omega_2^2}\big[&4\omega_0^2 - \gamma^2\cosh(2\omega_2 t)\\ &+ 2\gamma\omega_1 \sinh(2\omega_2 t)\big].\end{aligned} \tag{68}$$

At $t = 0$, these equations give $\overline{\Delta K \Delta U} = 0$ and $\overline{\Delta E \Delta K} = \overline{\Delta E \Delta U} = (kT_0)^2/2$.

VI. MOLECULAR DYNAMICS SIMULATIONS

The analytical calculations presented in the previous sections rely on the approximation discussed in Appendix B. In this approximation, the four-member correlation functions are replaced by sums of products of pair correlation functions. To demonstrate the accuracy of this approximation, the energy ACFs and CCFs were computed by molecular dynamics (MD) simulations and the results were compared with the analytical solutions.

The Langevin equation (1) was integrated numerically by implementing the velocity Verlet algorithm with $m = 1$, $\omega_0 = 1$, and $\gamma = 0.1\omega_0$. Because $\gamma/\omega_0 = 0.1$ is relatively small, the simulations realize the underdamped regime. The time step of integration was 0.001. Every 100 MD steps, the random force R was updated by drawing a new number from the normal distribution with the standard deviation of 0.5. Alternatively, a uniform distributions of R was used in a few test runs and the same results were obtained. (In fact, the popular LAMMPS molecular dynamics package [5] implements the Langevin thermostat with a uniform distribution for speed.) A total of 5000 statistically independent MD runs, each $80\gamma^{-1}$ long, were performed to reach convergence. For each run, the discrete Fourier transformations of the kinetic, potential, and total energies were computed and the Fourier amplitudes were averaged over all MD runs. The Fourier amplitudes obtained were used to calculate the respective correlation functions in the frequency domain, which were then mapped into the time domain by inverse Fourier transformation.

To facilitate comparison with the analytical solutions, all correlation functions were expressed in terms of the dimensionless frequency ω/ω_0, time $t\gamma$, and damping constant γ/ω_0, and normalized as follows:

$$\hat{\mathcal{C}}_{\Delta X \Delta Y}(\omega/\omega_0, \gamma/\omega_0) = \frac{\hat{C}_{\Delta X \Delta Y}(\omega)}{\left(\overline{(\Delta X)^2}\ \overline{(\Delta Y)^2}\right)^{1/2}}, \tag{69}$$

$$\mathcal{C}_{\Delta X \Delta Y}(t\gamma, \gamma/\omega_0) = \frac{C_{\Delta X \Delta Y}(t)}{\left(\overline{(\Delta X)^2}\ \overline{(\Delta Y)^2}\right)^{1/2}}, \tag{70}$$

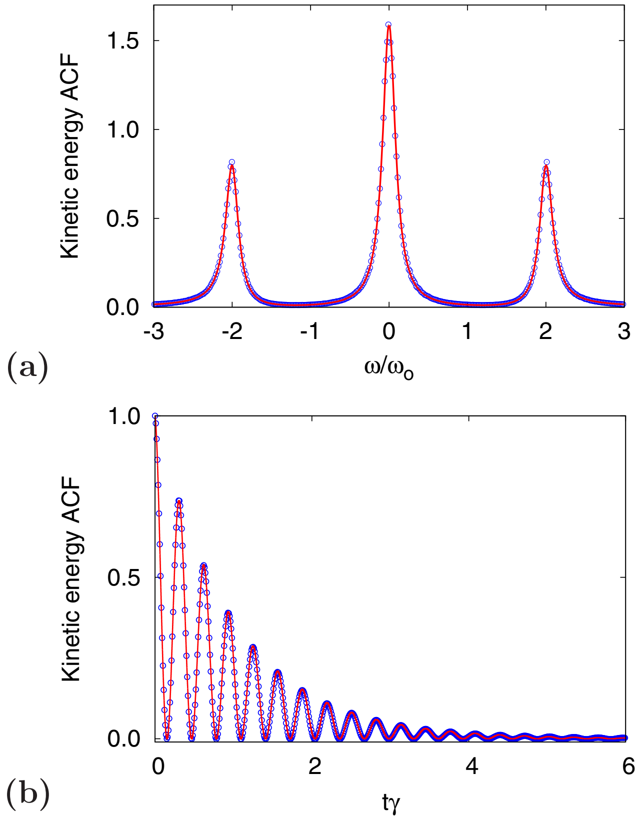

FIG. 4. The kinetic energy ACF in the frequency (a) and time (b) domains for underdamped vibrations with the damping constant $\gamma = 0.1\omega_0$. The points and lines represent MD results and analytical solutions, respectively. The functions are normalized according to Eqs. (69) and (70).

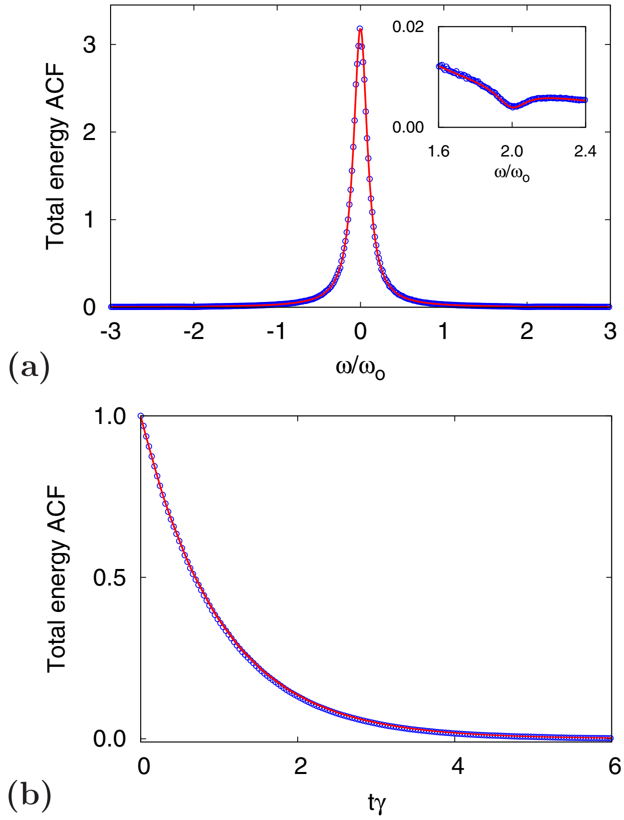

FIG. 5. The total energy ACF in the frequency (a) and time (b) domains for underdamped vibrations with the damping constant $\gamma = 0.1\omega_0$. The points and lines represent MD results and analytical solutions, respectively. The inset shows a zoom into the “antiresonance” region. The functions are normalized according to Eqs. (69) and (70).

where X and Y stand for K, U, or E, with $X \neq Y$ for CCFs and $X = Y$ for ACFs.

Selected results are shown in Figs. 4–6 (for the complete set of figures the reader is referred to the Supplementary Material [6]), plotting the normalized correlation functions (69) or (70) against ω/ω_0 or $t\gamma$ for $\gamma/\omega_0 = 0.1$. Although the spectra only have physical meaning when $\omega \geqslant 0$, the functions are mathematically defined in the entire frequency range $(-\infty,\infty)$ and are shown as such in the figures. The main conclusion of this comparison is that the analytical solutions accurately match the MD results, validating the pair-correlation approximation discussed in Appendix B.

VII. APPLICATION TO THE PROBLEM OF TEMPERATURE FLUCTUATIONS

While fluctuations of extensive parameters, such as energy, are well understood, there are controversies regarding the nature, or even existence [7–9], of temperature fluctuations in canonical systems [10]. The main source of the controversy is the disparity in the definitions of certain fundamental concepts, such as entropy and temperature, in thermodynamics and statistical mechanics. In thermodynamics, temperature is uniquely defined by the fundamental equation of the substance in question as the derivative of energy E with respect to entropy S [11–13]. For a simple substance, the fundamental equation has the form $E = E(S,V,N)$, where V is the system volume and N is the number of particles. By contrast, the statistical-mechanical definition depends on the adopted logical structure of the discipline. For example, if temperature of a canonical system is *defined* as the temperature of the thermostat T_0 (the inverse of β in the standard canonical distribution), then of course the very notion of temperature fluctuations is meaningless [7–9]. From this point of view, the temperature fluctuation relation

$$\overline{(\Delta T)^2} = \frac{kT_0^2}{Nc_v^0} \tag{71}$$

derived in the thermodynamic theory of fluctuations [2,12,14,15] is the result of a mere manipulation of symbols [9,16]. In Eq. (71), $\Delta T = T - T_0$, c_v^0 is the constant-volume specific heat (per particle) at temperature T_0, and k is Boltzmann’s constant. The system volume and number of particles are assumed to be fixed. At best, Eq. (71) is interpreted as a rewriting of the known energy fluctuation relation

$$\overline{(\Delta E)^2} = NkT_0^2 c_v^0 \tag{72}$$

by *formally* defining the nonequilibrium temperature T as $T \equiv T_0 + \Delta E/(Nc_v^0)$ [10]. This makes T a formal parameter essentially identical to energy up to units. Other authors suggest that it is the temperature itself that is not perfectly

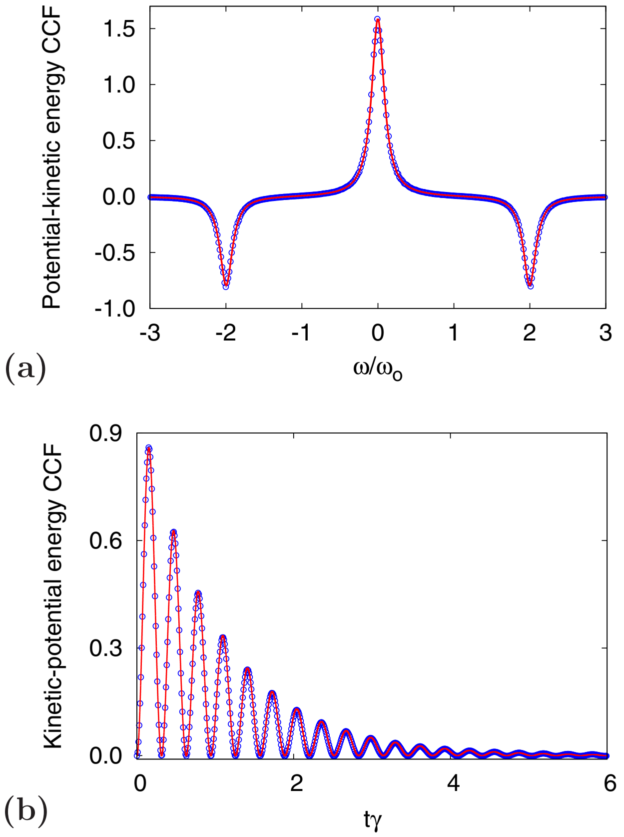

FIG. 6. The kinetic-potential energy CCF in the frequency (a) and time (b) domains for underdamped vibrations with the damping constant $\gamma = 0.1\omega_0$. The points and lines represent MD results and analytical solutions, respectively. The functions are normalized according to Eqs. (69) and (70).

defined, whereas its fluctuation is perfectly well defined within the framework of the statistical estimation theory [16,17].

By contrast, the thermodynamic theory of fluctuations [2,12,14] endows the non-equilibrium temperature with a physical meaning and considers its fluctuations as a real physical phenomenon that can be studied experimentally [18]. The theory recognizes the existence of two different time scales inherent in canonical fluctuations: the time scale of internal relaxation t_r inside the system and the time scale τ_r of relaxation in the compound system consisting of the canonical system and the thermostat.[1] The two relaxation processes are governed by different physical mechanisms and, in most cases, $t_r \ll \tau_r$. Thus, there is an intermediate time scale t_q, such that $t_r \ll t_q \ll \tau_r$, on which the system remains infinitely close to internal equilibrium without being necessarily in equilibrium with the thermostat. Such virtually equilibrium states of the canonical system are called *quasiequilibrium*. On the quasiequilibrium time scale t_q, the system can be described by a fundamental equation, from which its temperature can be found by

$$T = (\partial E/\partial S)_{V,N}. \tag{73}$$

During the equilibration of a system with a thermostat, the system goes through a continuum of quasiequilibrium states. Accordingly, we can talk about the time evolution of its quasiequilibrium temperature T towards T_0 as the system approaches equilibrium with the thermostat. Based on the fluctuation-dissipation relation [2,3,21–25], one can expect that similar quasiequilibrium states arise during fluctuations after the system has reached equilibrium with the thermostat. Such quasiequilibrium states also have a well-defined temperature that fluctuates around T_0. As long as this temperature is properly defined on the quasiequilibrium time scale, its fluctuations will follow Eq. (71).

Similar theories of temperature fluctuations have been formulated in statistical-mechanical terms by allowing β of the canonical distribution to fluctuate away from β_0 of the thermostat [26,27]. Such theories assume, explicitly or implicitly, the existence of time scale separation and internal equilibration of the system on a certain time scale (which we call here quasiequilibrium) with different values of β. Such approaches are thus perfectly compatible with ours.

While Eq. (73) provides a thermodynamic definition of the quasiequilibrium temperature T, in practice this temperature can be evaluated by utilizing the equipartition relation and the kinetic energy averaged over the quasiequilibrium time scale t_q. This can be readily done in computer simulations and, in principle, in experiments measuring a property sensitive to kinetic energy of the particles. Instead of kinetic energy, other parameters could be used for computing the temperature [28]. This does not imply an ambiguity in the temperature definition but rather the possibility of using different "thermometric properties" for its evaluation. For example, the potential energy could also be used for defining the temperature through the appropriate equipartition relation. A thorough discussion of different definitions of temperature in statistical mechanics can be found, for example, in Refs. [28–30]. This approach obviously assumes ergodicity of the system and classical dynamics.

The Langevin oscillator offers a simple model that can illustrate these ideas. Consider the Einstein model of a solid with a single vibrational frequency ω_0. The $3N$ oscillators describing the atomic vibrations are considered totally decoupled from each other and only interact with a thermostat. Suppose the latter is a Langevin thermostat characterized by a damping constant γ and a random force R satisfying the fluctuation-dissipation relation (5) for a given thermostat temperature T_0. The Langevin thermostat [31] mimics a real thermostat by treating the atoms as if they were embedded in an artificial viscous medium composed of much smaller particles. This medium exerts a drag force as well as a stochastic noise force R that constantly perturbs the atoms. In this model, each vibrational mode can be represented by a single Langevin oscillator. The damping time $\tau_r = 1/\gamma$ sets the time scale of energy exchanges with the thermostat. By contrast to a real solid wherein internal equilibration requires redistribution of energy between different vibrational modes by phonon scattering, in the present model the energy is pumped into or removed from each oscillator individually.

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[1] An illuminating thermodynamic analysis of system-thermostat interactions and the role of dissipation by friction in such interactions can be found in recent papers [19,20].

Thus, the internal equilibration time scale t_r is on the order of $1/\omega_0$.[2] We assume that the vibrations are quasiharmonic and thus $\omega_0 \gg \gamma$ (underdamped regime). Then $t_r \ll \tau_r$ and there is a quasiequilibrium time scale in between on which the temperature can be defined.

We have shown above that kinetic energy fluctuations of an underdamped Langevin oscillator have two components: a fast component due to transformations between the kinetic and potential energies during atomic vibrations (period π/ω_0), and a slow component due to energy exchanges with the thermostat (time scale $1/\gamma$). It is the slow component that should be used to calculate the quasiequilibrium temperature of the system. The fast component can be "filtered out" by averaging K over several vibration periods. Alternatively, the same can be achieved by separating the peaks in the spectrum of the kinetic energy ACF. As was shown above, $\hat{C}_{\Delta K \Delta K}(\omega)$ has two peaks separated by a frequency gap [Figs. 2(a) and 4(a)]. One peak at $\omega = 2\omega_0$ represents the kinetic-potential energy exchanges during the vibrations (fast component) while the other at $\omega = 0$ represents the energy exchanges with the thermostat (slow component). Thus, the separation of the two time scales can be accomplished by splitting the spectrum into two Lorentz peaks described by Eqs. (22) and (19), respectively. As was shown in Sec. II, each peak describes kinetic energy fluctuations with the same variance,

$$\overline{(\Delta K)^2} = (kT_0)^2/4. \tag{74}$$

For a solid composed of $3N$ statistically independent oscillators, we use the low-frequency peak (at $\omega = 0$) to obtain

$$\overline{(\Delta K_{\mathrm{solid}})^2} = \frac{3N(kT_0)^2}{4}. \tag{75}$$

We can now identify the quasiequilibrium temperature with the equipartition value $T = 2K_{\mathrm{solid}}/3Nk$ using the kinetic energy defined by the low-frequency peak. Inserting this temperature into Eq. (75) we have

$$\overline{(\Delta T)^2} = \frac{T_0^2}{3N}. \tag{76}$$

This fluctuation relation matches Eq. (71) if $c_v^0 = 3k$, which is exactly the classical specific heat of the solid. We emphasize that this result was obtained by defining the quasiequilibrium temperature using the kinetic energy and without any reference to the behavior of the total energy during the fluctuations. This fundamentally differs from the approach mentioned above wherein T is defined as a formal quantity strictly proportional to E. That approach also leads to Eq. (76), except that the latter simply reflects the temperature definition. As mentioned above, potential energy could also be used to define the temperature, which would lead to exactly the same temperature fluctuation (76).

To show that the foregoing derivation of Eq. (76) is nontrivial, suppose we ignore the different time scales and define the temperature from the same equipartition rule but now using *instantaneous* values of the kinetic energy, as is often done in MD simulations. The mean-square fluctuation of this "instantaneous temperature" $\tilde{T}$ is obtained by averaging over both time scales or, which is equivalent, by including both peaks of $\hat{C}_{\Delta K \Delta K}(\omega)$. As discussed in Sec. II, the respective kinetic energy fluctuation of an oscillator is then $\overline{(\Delta K)^2} = (kT_0)^2/2$. This leads to the temperature fluctuation

$$\overline{(\Delta \tilde{T})^2} = \frac{2T_0^2}{3N}. \tag{77}$$

The specific heat extracted from this fluctuation relation is $c_v^0 = 3k/2$, which is factor of two off. It is only the temperature defined on the quasiequilibrium time scale that satisfies the fluctuation relation (71) with the correct specific heat.

VIII. CONCLUDING REMARKS

The main result of this work is the derivation of the analytical solutions for the energy correlation functions of a Langevin oscillator. The derivation was enabled by approximating the quadruple correlation functions by a sum of products of pair correlation functions as explained in Appendix B. In other words, the derivations neglect all correlations between stochastic properties beyond pairwise. The accuracy of this approximation has been validated by comparison with MD simulations, which were found to be in excellent agreement with the analytical solutions.

Given the role of the Langevin oscillator model in various areas of physics, the results obtained here might be useful for addressing diverse physics problems involving energy fluctuations in systems coupled to a thermostat. As one example of possible applications, we have presented a simple model illustrating the existence and the meaning of the temperature fluctuations in canonical systems. Temperature fluctuations is a controversial subject with many conflicting views published over the past century (see the references in Ref. [10]).

One of the oldest and, in our opinion, most fruitful approaches recognizes the existence of quasiequilibrium states that arise during canonical fluctuations and exist on a particular time scale [2,12,14]. The temperature calculated on this quasiequilibrium time scale by treating the system as if it were equilibrium is a well-defined physical property whose fluctuations follow the relation (71). By considering an Einstein solid composed of Langevin oscillators, we have demonstrated the existence of the quasiequilibrium time scale and verified that the temperature computed on this time scale indeed satisfies Eq. (71). Although rather simplistic, this model captures the essential physics. A more realistic MD study of temperature fluctuations in a crystalline solid modeled with an accurate many-body atomistic potential will be published elsewhere [15].

ACKNOWLEDGMENTS

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[2] Perhaps a more accurate measure is the half-period, π/ω_0, which is sufficient for the kinetic energy to transform to potential. But since we are only interested in orders of magnitude, $1/\omega_0$ is a suitable estimate of the relevant time scale.

APPENDIX A

The Fourier resolution of a function of time $f(t)$ is

$$f(t)=\int_{-\infty}^{\infty}\hat{f}(\omega)e^{i\omega t}d\omega,$$

with the Fourier amplitude

$$\hat{f}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}f(t)e^{-i\omega t}dt.$$

The Fourier transform of a product of two functions is the convolution of their Fourier transforms and vise versa: If $R(t)=f(t)g(t)$, then

$$\hat{R}(\omega)=\int_{-\infty}^{\infty}\hat{f}(\omega-\omega')\hat{g}(\omega')d\omega', \quad \text{(A1)}$$

and if $\hat{R}(\omega)=\hat{f}(\omega)\hat{g}(\omega)$, then

$$R(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}f(t-t')g(t')dt'. \quad \text{(A2)}$$

Calculations involving Dirac's δ function utilize the relations $\hat{1}(\omega)=\delta(\omega)$ and $\hat{\delta}(\omega)=1/2\pi$. Spectral calculations often employ the residue theorem of complex analysis. The residues can be found analytically or with the help of the *Wolfram Mathematica* function `Residue[]`.

The pair correlation function of two (generally, complex) stochastic variables y and z is defined by

$$C_{yz}(t)=\overline{y(t')z(t'+t)}=\overline{y(0)z(t)}, \quad \text{(A3)}$$

where we assumed that the process is stationary and thus independent of the initial time t'. Obviously, $C_{yz}(t)=C_{zy}(-t)$. The Fourier transform

$$\hat{C}_{yz}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}C_{yz}(t)e^{-i\omega t}dt \quad \text{(A4)}$$

has the property $\hat{C}_{yz}(\omega)=\hat{C}_{zy}(-\omega)$. The inverse transformation recovers $C_{yz}(t)$:

$$C_{yz}(t)=\int_{-\infty}^{\infty}\hat{C}_{yz}(\omega)e^{i\omega t}d\omega. \quad \text{(A5)}$$

Taking $t=0$ we obtain

$$\overline{yz}=C_{yz}(0)=\int_{-\infty}^{\infty}\hat{C}_{yz}(\omega)d\omega. \quad \text{(A6)}$$

It can be shown that

$$\overline{\hat{y}(\omega)\hat{z}(\omega')}=\delta(\omega+\omega')\hat{C}_{yz}(\omega')=\delta(\omega+\omega')\hat{C}_{yz}(-\omega). \quad \text{(A7)}$$

Integrating the last equation with respect to ω' we find

$$\hat{C}_{yz}(\omega)=\int_{-\infty}^{\infty}\overline{\hat{y}(\omega')\hat{z}(\omega)}d\omega'. \quad \text{(A8)}$$

In the particular case when $y(t)\equiv z(t)$, we obtain the ACF

$$C_{yy}(t)=\overline{y(0)y(t)} \quad \text{(A9)}$$

and its Fourier transform $\hat{C}_{yy}(\omega)$. Both functions are symmetric: $C_{yy}(t)=C_{yy}(-t)$ and $\hat{C}_{yy}(\omega)=\hat{C}_{yy}(-\omega)$. Equations (A6), (A7), and (A8) become, respectively,

$$\overline{y^2}=\int_{-\infty}^{\infty}\hat{C}_{yy}(\omega)d\omega, \quad \text{(A10)}$$

$$\overline{\hat{y}(\omega)\hat{y}(\omega')}=\delta(\omega+\omega')\hat{C}_{yy}(\omega), \quad \text{(A11)}$$

$$\hat{C}_{yy}(\omega)=\int_{-\infty}^{\infty}\overline{\hat{y}(\omega')\hat{y}(\omega)}d\omega'. \quad \text{(A12)}$$

APPENDIX B

For two (generally, complex) stochastic properties $a(t)$ and $b(t)$, let us evaluate the ACF of $F(t)=a(t)b(t)$ relative to its average value $\overline{F}=\overline{ab}$. Denoting $\Delta F=F-\overline{F}$, we have

$$C_{\Delta F\Delta F}(t)=C_{FF}(t)-(\overline{ab})^2. \quad \text{(B1)}$$

It will suffice to find the Fourier transform $\hat{C}_{\Delta F\Delta F}(\omega)$, which can be then inverted to $C_{\Delta F\Delta F}(t)$.

By the product rule of the Fourier transformation,

$$\hat{F}(\omega)=\int_{-\infty}^{\infty}\hat{a}(\omega')\hat{b}(\omega-\omega')d\omega'. \quad \text{(B2)}$$

Applying this rule twice and averaging over the ensemble, we obtain

$$\overline{\hat{F}(\omega)\hat{F}(\omega')}=\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\overline{\hat{a}(\omega'')\hat{b}(\omega-\omega'')\hat{a}(\omega''')\hat{b}(\omega'-\omega''')}d\omega''d\omega'''. \quad \text{(B3)}$$

We will assume that the quadruple correlation function appearing in this equation can be broken into a sum of products of pair correlation functions. Only three distinct products can be formed, which are obtained by permutations of the $\hat{a}$'s and $\hat{b}$'s:

$$\overline{\hat{a}(\omega'')\hat{b}(\omega-\omega'')}\;\overline{\hat{a}(\omega''')\hat{b}(\omega'-\omega''')},$$

$$\overline{\hat{a}(\omega'')\hat{a}(\omega''')}\;\overline{\hat{b}(\omega-\omega'')\hat{b}(\omega'-\omega''')},$$

$$\overline{\hat{a}(\omega'')\hat{b}(\omega'-\omega''')}\;\overline{\hat{a}(\omega''')\hat{b}(\omega-\omega'')}.$$

Applying Eq. (A7), these functions become, respectively,

$$\delta(\omega)\delta(\omega')\hat{C}_{ab}(\omega-\omega'')\hat{C}_{ab}(\omega'-\omega'''),$$

$$\delta(\omega''+\omega''')\delta(\omega+\omega'-\omega''-\omega''')\hat{C}_{aa}(\omega''')\hat{C}_{bb}(\omega'-\omega'''),$$

$$\delta(\omega'+\omega''-\omega''')\delta(\omega-\omega''+\omega''')\hat{C}_{ab}(\omega'-\omega''')\hat{C}_{ab}(\omega-\omega'').$$

Inserting their sum into Eq. (B3), we obtain

$$\begin{aligned}\overline{\hat{F}(\omega)\hat{F}(\omega')}&=\delta(\omega)\delta(\omega')\left(\int_{-\infty}^{\infty}\hat{C}_{ab}(-\omega'')d\omega''\right)\left(\int_{-\infty}^{\infty}\hat{C}_{ab}(-\omega''')d\omega'''\right)\\&\quad+\delta(\omega+\omega')\int_{-\infty}^{\infty}\hat{C}_{aa}(\omega''')\hat{C}_{bb}(\omega'-\omega''')d\omega'''\\&\quad+\delta(\omega+\omega')\int_{-\infty}^{\infty}\hat{C}_{ba}(\omega'')\hat{C}_{ab}(\omega-\omega'')d\omega''.\end{aligned} \quad \text{(B4)}$$

By Eq. (A6), the first line gives $\delta(\omega)\delta(\omega')(\overline{ab})^2$.

Integrating Eq. (B4) with respect to ω' and applying Eq. (A12) we obtain

$$\hat{C}_{FF}(\omega) = \delta(\omega)(\overline{ab})^2 + \int_{-\infty}^{\infty} \hat{C}_{aa}(\omega'')\hat{C}_{bb}(\omega-\omega'')d\omega'' + \int_{-\infty}^{\infty} \hat{C}_{ba}(\omega'')\hat{C}_{ab}(\omega-\omega'')d\omega''. \tag{B5}$$

On the other hand, the Fourier transform of Eq. (B1) is

$$\hat{C}_{\Delta F\Delta F}(\omega) = \hat{C}_{FF}(\omega) - \delta(\omega)(\overline{ab})^2. \tag{B6}$$

Comparing Eqs. (B5) and (B6), we obtain

$$\hat{C}_{\Delta F\Delta F}(\omega) = \int_{-\infty}^{\infty} \hat{C}_{aa}(\omega')\hat{C}_{bb}(\omega-\omega')d\omega' + \int_{-\infty}^{\infty} \hat{C}_{ba}(\omega')\hat{C}_{ab}(\omega-\omega')d\omega'.$$

Next, we will take the same stochastic properties $a(t)$ and $b(t)$, form two new properties $G(t) = a^2(t)$ and $H(t) = b^2(t)$, and evaluate the CCF $C_{\Delta G\Delta H}(t)$, where $\Delta G = G - \overline{G}$ and $\Delta H = H - \overline{H}$. It will suffice to find the Fourier transform

$$\hat{C}_{\Delta G\Delta H}(\omega) = \hat{C}_{GH}(\omega) - \delta(\omega)\overline{G}\,\overline{H}. \tag{B7}$$

Applying the product rule of Fourier transformations we have

$$\overline{\hat{G}(\omega)\hat{H}(\omega')} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \overline{\hat{a}(\omega'')\hat{a}(\omega-\omega'')\hat{b}(\omega''')\hat{b}(\omega'-\omega''')}d\omega''d\omega'''. \tag{B8}$$

As above, we break the quadruple correlation function into a sum of products of pair correlation functions. The three distinct products are

$$\overline{\hat{a}(\omega'')\hat{a}(\omega-\omega'')}\;\overline{\hat{b}(\omega''')\hat{b}(\omega'-\omega''')} = \delta(\omega)\delta(\omega')\hat{C}_{aa}(\omega'')\hat{C}_{bb}(\omega'''),$$

$$\overline{\hat{a}(\omega'')\hat{b}(\omega''')}\;\overline{\hat{a}(\omega-\omega'')\hat{b}(\omega'-\omega''')} = \delta(\omega''+\omega''')\delta(\omega+\omega'-\omega''-\omega''')\hat{C}_{ab}(\omega''')\hat{C}_{ab}(\omega'-\omega'''),$$

$$\overline{\hat{a}(\omega'')\hat{b}(\omega'-\omega''')}\;\overline{\hat{b}(\omega''')\hat{a}(\omega-\omega'')} = \delta(\omega'+\omega''-\omega''')\delta(\omega-\omega''+\omega''')\hat{C}_{ab}(\omega'-\omega''')\hat{C}_{ab}(\omega''').$$

Inserting the sum of these terms in Eq. (B8) we have

$$\begin{aligned}\overline{\hat{G}(\omega)\hat{H}(\omega')} &= \delta(\omega)\delta(\omega')\left(\int_{-\infty}^{\infty}\hat{C}_{aa}(\omega'')d\omega''\right)\left(\int_{-\infty}^{\infty}\hat{C}_{bb}(\omega''')d\omega'''\right)\\ &\quad +2\delta(\omega+\omega')\int_{-\infty}^{\infty}\hat{C}_{ab}(\omega''')\hat{C}_{ab}(\omega'-\omega''')d\omega'''\\ &= \delta(\omega)\delta(\omega')\overline{G}\,\overline{H} + 2\delta(\omega+\omega')\int_{-\infty}^{\infty}\hat{C}_{ab}(\omega''')\hat{C}_{ab}(\omega'-\omega''')d\omega'''.\end{aligned}$$

Comparing this equation with Eq. (A7) and applying Eq. (B7), we obtain

$$\hat{C}_{\Delta G\Delta H}(\omega) = 2\int_{-\infty}^{\infty}\hat{C}_{ab}(\omega')\hat{C}_{ab}(\omega-\omega')d\omega'. \tag{B9}$$

The foregoing results can be summarized as the following statement:
If only pair correlations are taken into account, then for any two stochastic properties $a(t)$ and $b(t)$,

$$\hat{C}_{\Delta F\Delta F}(\omega) = \int_{-\infty}^{\infty} \hat{C}_{aa}(\omega')\hat{C}_{bb}(\omega-\omega')d\omega' + \int_{-\infty}^{\infty} \hat{C}_{ba}(\omega')\hat{C}_{ab}(\omega-\omega')d\omega', \tag{B10}$$

$$\hat{C}_{\Delta G\Delta H}(\omega) = 2\int_{-\infty}^{\infty}\hat{C}_{ab}(\omega')\hat{C}_{ab}(\omega-\omega')d\omega', \tag{B11}$$

where $F(t) = a(t)b(t)$, $G(t) = a^2(t)$, and $H(t) = b^2(t)$.

In the particular case when $a(t) \equiv b(t)$, we have $F(t) = a^2(t)$ and Eq. (B10) gives

$$\hat{C}_{\Delta F\Delta F}(\omega) = 2\int_{-\infty}^{\infty}\hat{C}_{aa}(\omega')\hat{C}_{aa}(\omega-\omega')d\omega'. \tag{B12}$$

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