Entropy production and heat capacity of systems under time-dependent oscillating temperature

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(Received 20 March 2019; revised manuscript received 19 April 2019; published 28 May 2019)

Using stochastic thermodynamics, we determine the entropy production and the dynamic heat capacity of systems subject to a sinusoidally time-dependent temperature, in which case the systems are permanently out of thermodynamic equilibrium, inducing a continuous generation of entropy. The systems evolve in time according to a Fokker-Planck or a Fokker-Planck-Kramers equation. Solutions of these equations, for the case of harmonic forces, are found exactly, from which the heat flux, the production of entropy, and the dynamic heat capacity are obtained as functions of the frequency of the temperature modulation. These last two quantities are shown to be related to the real and imaginary parts of the complex heat capacity.

DOI: 10.1103/PhysRevE.99.052131

I. INTRODUCTION

The investigation of systems under time-dependent fields of various types is very common in experimental physics. Less common is the investigation of systems under time-dependent temperature. Nevertheless, temperature oscillations are the basis of modulation calorimetry [1–18], which allows the experimental determination of the heat capacity. The method consists in heating a sample by a periodic heating power with an angular frequency ω and measuring the temperature oscillations. This procedure induces a flow of heat from which the dynamic heat capacity C can be obtained as the ratio between the heat flux $\Phi_{\rm q}$ and the time variation of the temperature

$$C = \frac{-\Phi_{\rm q}}{dT/dt}. \tag{1}$$

The heat flux and the heat capacity oscillate in time with the same frequency ω of the temperature oscillations, but with a phase shift. During a cycle the net heat flux vanishes, but not the dynamic heat capacity. Denoting by a bar the time average of a quantity, which is its integral over a cycle divided by the period of the cycle, then $\overline{\Phi}_{\rm q} = 0$ and $\overline{C}$ is nonzero and shows a dispersion, that is, a dependence on ω. The conventional heat capacity C_0, or static heat capacity, is obtained in the limiting value of $\overline{C}$ when $\omega \to 0$.

Under a time-oscillating temperature, the system is permanently out of equilibrium, causing a continuous production of entropy as well as a continuous flux of entropy. The entropy S of the system also varies in time, the time variation being equal to the rate of entropy production Π minus the entropy flux Φ,

$$\frac{dS}{dt} = \Pi - \Phi. \tag{2}$$

According to the second law of thermodynamics, the rate of entropy production is never negative $\Pi \geqslant 0$, but the flux of entropy Φ, given by

$$\Phi = \frac{\Phi_{\rm q}}{T}, \tag{3}$$

may have either sign. Although $\overline{\Phi}_{\rm q} = 0$, this is not the case of $\overline{\Phi}$. In fact, considering that the entropy S is periodic, the left-hand side of (2) vanishes in a cycle and the net flux becomes equal to the entropy produced during a cycle, that is, $\overline{\Phi} = \overline{\Pi} \geqslant 0$.

Our main purpose here is the calculation of the entropy production and the dynamic heat capacity for systems subject to a temperature modulation of the type

$$T = T_0 + T_1 \cos \omega t, \tag{4}$$

where T_1 is the amplitude of modulation and T_0 is the mean temperature. Our calculation is based on stochastic thermodynamics of systems with continuous space of states [19–29]. We restrict ourselves to the case of systems of particles interacting through harmonic forces, in which case the evolution equation can be solved exactly. From its solution we determine the rate of entropy production and dynamic heat capacity as a function of the frequency ω. We also show that the dynamic heat capacity and the entropy production are related to the real and imaginary parts of the complex heat capacity, respectively.

II. FOKKER-PLANCK EQUATION

A. General formulation

We consider a system of interacting particles that is described by a probability distribution $P(x,t)$ of state x at time t, where x denotes the collection of particle positions x_i. We assume that the time evolution of the probability distribution is governed by the Fokker-Planck (FP) equation [19,29]

$$\frac{\partial P}{\partial t} = -\sum_i \frac{\partial J_i}{\partial x_i}, \tag{5}$$

where

$$J_i = \frac{1}{\alpha}\left(f_i P - k_{\rm B} T \frac{\partial P}{\partial x_i} \right), \tag{6}$$

with $f_i = -\partial V/\partial x_i$ the force acting on particle i, V being the potential energy, α a constant, and $k_{\rm B}$ the Boltzmann constant.

The FP equation describes the contact of the system with a heat reservoir at temperature T and corresponds to a description in the overdamped limit [19,30]. Indeed, it is easily shown by replacement into the FP equation that the Gibbs distribution

$$P_0 = \frac{1}{Z} e^{-V/k_B T} \tag{7}$$

is the stationary solution when T is kept constant and in fact the equilibrium solution.

The time variation of the energy $U = \langle V \rangle$ of the system can be obtained from the FP equation and is

$$\frac{dU}{dt} = -\Phi_q, \tag{8}$$

where Φ_q is the heat flux *from* the system to outside and is expressed by [19]

$$\Phi_q = \frac{1}{\alpha} \sum_i \left(\langle f_i^2 \rangle + k_B T \langle f_{ii} \rangle\right), \tag{9}$$

where $f_{ii} = \partial f_i / \partial x_i$. Once the heat flux is known, the dynamic heat capacity is determined by (1), if T is time dependent. From the FP equation we can also determine the time variation of the entropy

$$S = -k_B \int P \ln P \, dx, \tag{10}$$

which can be split in two terms, as shown by Eq. (2), where Π, the rate of entropy production, has the form [19]

$$\Pi = \frac{\alpha}{T} \sum_i \int \frac{J_i^2}{P} dx, \tag{11}$$

and Φ, the entropy flux from the system to the environment, is given by (3).

B. Harmonic forces

When the forces are harmonic it is possible to exactly solve the FP equation even for the case of a time-dependent temperature. Here we consider a collection of independent harmonic oscillators in which case it suffices to treat just one oscillator. The potential energy of the oscillator is $V = kx^2/2$, which yields a force $f = -kx$ and the FP equations to be solved is

$$\frac{\partial P}{\partial t} = -\frac{\partial J}{\partial x}, \tag{12}$$

where

$$J = -\frac{k}{\alpha} x P - \frac{k_B T}{\alpha} \frac{\partial P}{\partial x}. \tag{13}$$

The solution of the FP equation for a time-dependent temperature is a Gaussian distribution

$$P = \frac{1}{\zeta} \exp\left\{-\frac{1}{2} b x^2\right\}, \tag{14}$$

where the coefficients b is time dependent. That P is a solution can be checked by replacing it into the FP equation (12). Instead of seeking the coefficients b, we choose to find the averages $B = \langle x^2 \rangle$. Once B is found we may get b, if necessary, from the relation $b = 1/B$.

From the FP equation, we find the equation for B,

$$\alpha \frac{d}{dt} B = -2kB + 2k_B T. \tag{15}$$

For T depending on time like (4), the solution of Eq. (15) is found to be

$$B = \frac{k_B T_0}{k} + 2k_B T_1 \frac{2k \cos \omega t + \alpha\omega \sin \omega t}{\alpha^2 \omega^2 + 4k^2}. \tag{16}$$

C. Entropy production and heat capacity

From Eq. (9) it follows that the heat flux is determined by

$$\Phi_q = \frac{k}{\alpha}(kB - k_B T), \tag{17}$$

or in an explicit form as

$$\Phi_q = k_B T_1 \omega k \frac{2k \sin \omega t - \alpha\omega \cos \omega t}{\alpha^2 \omega^2 + 4k^2}. \tag{18}$$

The entropy flux Φ and the dynamic heat capacity C are determined from Φ_q by the use of Eqs. (3) and (1).

We proceed now to determine the time averages of Φ and C. The time average of the heat flux vanishes $\overline{\Phi}_q = 0$ as expected, but not $\overline{\Phi}$ and $\overline{C}$. Carrying out the integration of Φ and C over a cycle, and considering that $\overline{\Phi} = \overline{\Pi}$, we find

$$\overline{\Pi} = k_B \lambda \frac{\alpha \omega^2 k}{\alpha^2 \omega^2 + 4k^2}, \tag{19}$$

where

$$\lambda = \frac{T_0}{\sqrt{T_0^2 - T_1^2}} - 1, \tag{20}$$

and the dynamic heat capacity is found to be

$$\overline{C} = k_B \frac{2k^2}{\alpha^2 \omega^2 + 4k^2}. \tag{21}$$

D. Harmonic oscillator

The approach we have used above, by employing the FP equation (5) or (12), is appropriate to describe overdamped systems. In this approach the positions were taken into account but not the velocities. However, the oscillations of temperature affect not only the positions, but also the velocities of particles. The treatment of the response of the system concerning the velocities is carried out by setting up the FP equation that gives the evolution of the probability distribution of velocities,

$$\frac{\partial P}{\partial t} = -\frac{\partial J}{\partial v}, \tag{22}$$

where

$$J = -\gamma v P - \frac{\gamma k_B T}{m} \frac{\partial P}{\partial v}, \tag{23}$$

which describes a free particle in contact with a reservoir at a temperature T.

Equation (22) is formally identical to Eq. (12) and we may proceed in a similar way to determine the entropy production and the heat capacities. The result for the heat flux is

$$\Phi_q = k_B T_1 \omega \gamma \frac{2\gamma \sin \omega t - \omega \cos \omega t}{\omega^2 + 4\gamma^2} \tag{24}$$

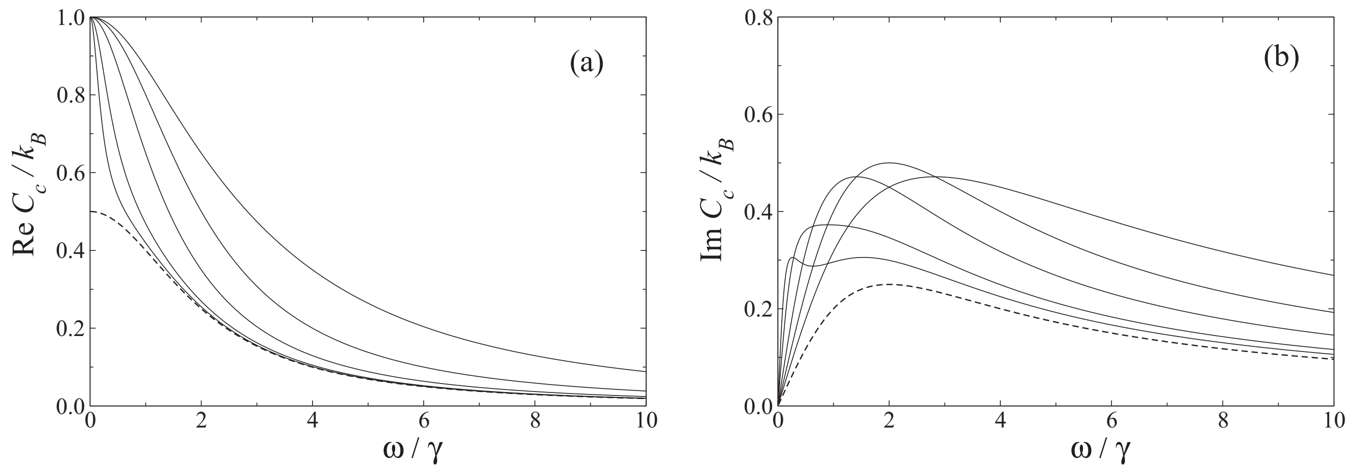

FIG. 1. (a) Real and (b) imaginary parts of the complex heat capacity (32) for the overdamped case as a function of frequency for the following values of κ/γ^2: 0 (dotted line), 0.1, 0.2, 0.5, 1, and 2 (from left to right).

and the time average of the rate of entropy is

$$\overline{\Pi} = k_B\lambda\frac{\gamma\omega^2}{\omega^2+4\gamma^2}, \tag{25}$$

where λ is given by (20), and the dynamic heat capacity is

$$\overline{C} = k_B\frac{2\gamma^2}{\omega^2+4\gamma^2}. \tag{26}$$

To find the entropy production of a harmonic oscillator we should add the entropy production concerning the positions, given by (19), with the entropy production concerning the velocities, given by (25). The result is

$$\overline{\Pi} = k_B\lambda\frac{\gamma\omega^2\kappa}{\gamma^2\omega^2+4\kappa^2} + k_B\lambda\frac{\gamma\omega^2}{\omega^2+4\gamma^2}. \tag{27}$$

Similarly, the dynamic heat capacity is the sum of (21) and (26),

$$\overline{C} = k_B\frac{2\kappa^2}{\gamma^2\omega^2+4\kappa^2} + k_B\frac{2\gamma^2}{\omega^2+4\gamma^2}. \tag{28}$$

The quantities α and γ are related to $\alpha = m\gamma$, and k is related to κ by $k = m\kappa$.

E. Complex heat capacity

The dispersion of the dynamic heat capacity on frequencies, induced by a time-varying temperature, is analogous to the dispersion of susceptibility on frequencies induced by a time-varying field. In the latter case, the response to the field oscillation is described by a complex susceptibility. Analogously, it is also possible to define a complex heat capacity to conveniently describe the response to temperature oscillations. In fact, the complex heat capacity has been the subject of investigation in relation to temperature modulation [5–18]

Suppose that we replace T in Eq. (15) by the complex time-dependent temperature

$$T_c = T_0 + T_1 e^{-i\omega t}. \tag{29}$$

Then, instead of Eqs. (18) and (24), we would get the expression for the heat flux of the harmonic oscillator

$$\Phi_q^c = k_B T_1\left(\frac{i\kappa\omega}{2\kappa - i\omega\gamma} + \frac{i\gamma\omega}{2\gamma - i\omega}\right)e^{-i\omega t}. \tag{30}$$

By analogy with (1), a complex heat capacity C_c can be defined by

$$C_c = \frac{-\Phi_q^c}{dT_c/dt}, \tag{31}$$

from which we find

$$C_c = k_B\left(\frac{\kappa}{2\kappa - i\omega\gamma} + \frac{\gamma}{2\gamma - i\omega}\right), \tag{32}$$

which is time independent. Comparing with expressions (27) and (28), we see that

$$\overline{C} = \mathrm{Re}(C_c), \qquad \overline{\Pi} = \lambda\omega\mathrm{Im}(C_c). \tag{33}$$

These results show that the real part of the complex heat capacity is identified with the dynamic heat capacity and the imaginary part is proportional to the rate of entropy production.

The real and imaginary parts of the complex heat capacity C_c are shown in Fig. 1 as functions of the frequency ω for several values of κ. The real part, which is the dynamic heat capacity $\overline{C}$, becomes the static heat capacity when $\omega \to 0$, which is $C_0 = k_B/2$ if $\kappa = 0$ and $C_0 = k_B$ if $\kappa \neq 0$. In the opposite limit $\omega \to \infty$, it vanishes as $1/\omega^2$. The imaginary part vanishes when $\omega \to 0$ and so does the rate of entropy production $\overline{\Pi}$. In the limit $\omega \to \infty$, the imaginary part vanishes as $1/\omega$ but the rate of entropy production reaches a finite value, which is $\overline{\Pi} = k_B\lambda(\gamma + \kappa/\gamma)$. In Fig. 2 we have plotted $\mathrm{Im}(C_c)$ versus $\mathrm{Re}(C_c)$ and we see that the curves are symmetric.

It is worth determining the real and imaginary part of the complex capacity when the constant κ is small. In this case it is possible to write explicitly an expression that relates these two quantities. Let us define the quantities X and Y by $\mathrm{Re}(C_c) = k_B X$ and $\mathrm{Im}(C_c) = k_B Y$. For small values of κ one

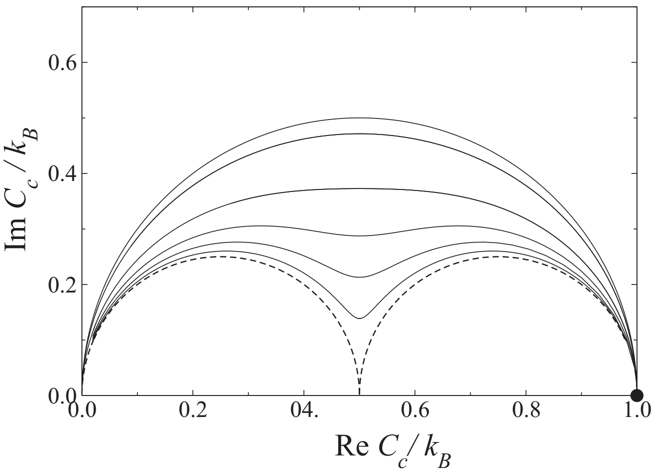

FIG. 2. Imaginary versus real part of the complex heat capacity (32) for the overdamped case for $\kappa \to 0$ (dotted line) and the following values of κ/γ^2: 0.02, 0.05, 0.1, 0.2, 0.5, and 1 (from bottom to top). The thermodynamic equilibrium $\omega = 0$ is indicated by a closed circle.

finds

$$Y = \begin{cases} \sqrt{(1-X)\left(X-\frac{1}{2}\right)}, & X > \frac{1}{2} \\ \sqrt{X\left(\frac{1}{2}-X\right)}, & X < \frac{1}{2}, \end{cases} \tag{34}$$

which are the semicircles shown in Fig. 2.

III. FOKKER-PLANCK-KRAMERS EQUATION

A. General formulation

We consider again a system consisting of several interacting particles in contact with a temperature reservoir at temperature T, with which it exchanges heat. The time evolution of the probability distribution $P(x, v, t)$, where x denotes the collection of the positions x_i and v the collection of velocities v_i of the particle, is governed by the Fokker-Planck-Kramers (FPK) equation [20,28,29]

$$\frac{\partial P}{\partial t} = -\sum_i \left(v_i \frac{\partial P}{\partial x_i} + \frac{1}{m} f_i \frac{\partial P}{\partial v_i} + \frac{\partial J_i}{\partial v_i} \right), \tag{35}$$

where

$$J_i = -\gamma v_i P - \frac{\gamma k_B T}{m} \frac{\partial P}{\partial v_i}. \tag{36}$$

Here m is the mass of each particle, γ is the dissipation constant, and f_i is the force acting on the particle i, given by $f_i = -\partial V/\partial x_i$.

If the temperature T is kept constant, then for large times the probability distribution approaches the Gibbs equilibrium distribution

$$P^e(x, v) = \frac{1}{Z} e^{-E/k_B T}, \tag{37}$$

where $E = mv^2/2 + V$ is the energy of the system. This result shows that the FPK equation (35) indeed describes the contact of a system with a heat reservoir at a temperature T.

The time variation of the energy $U = \langle E \rangle$ is obtained from the FPK equation and is

$$\frac{dU}{dt} = -\Phi_q, \tag{38}$$

where the heat flux Φ_q from the system to outside is expressed as [20,28]

$$\Phi_q = \sum_i \left(\gamma m \langle v_i^2 \rangle - \gamma k_B T \right), \tag{39}$$

where the first and second terms are understood as the heating power and the power of heat losses, respectively, with γk_B being the heat transfer coefficient [2]. The entropy S of the system is determined from the Gibbs expression

$$S = -k_B \int P \ln P \, dx \, dv. \tag{40}$$

Using the FPK equation, one finds that its time derivative can again be split into two terms, as shown by Eq. (2), where the rate of entropy production Π can be written as [20,28]

$$\Pi = \frac{m}{\gamma T} \sum_i \int \frac{J_i^2}{P} dx \, dv \tag{41}$$

and the flux of entropy Φ can be written in the form (3), where Φ_q is the heat flux given by (39). If T is time dependent then the dynamic heat capacity is obtained from (1).

B. Harmonic oscillator

We consider here the case of just one harmonic oscillator. When the temperature or the external force is time dependent, the probability distribution (37) is no longer the solution of the Fokker-Planck equation for long times and we should seek a solution. When the force is harmonic, which we write as $f = -m\kappa x$, the FPK equation can be solved exactly. The solution is a Gaussian distribution in x and v of the type

$$P(x, v) = \frac{1}{\zeta} \exp\left\{ -\frac{1}{2}(av^2 + bx^2 + 2cxv) \right\}, \tag{42}$$

where the parameters a, b, and c depend on time. That this Gaussian distribution is a solution can be checked by substituting it into the FPK equation. The solution is reduced to the determination of the time dependence of the parameters.

From the Gaussian distribution (42) we see that the parameters a, b, and c are related to the averages $A = \langle v^2 \rangle$, $B = \langle x^2 \rangle$, and $C = \langle xv \rangle$ as

$$a = \frac{B}{AB - C^2}, \quad b = \frac{A}{AB - C^2}, \quad c = \frac{C}{AB - C^2}. \tag{43}$$

The method we use here rests on setting up equations for A, B, and C, from whose solutions we can find the coefficients a, b, and c of the Gaussian distribution as functions of temperature, if needed.

From the FPK equations the following set of equations is found for A, B, and C:

$$\frac{dA}{dt} = -2\kappa C - 2\gamma A + \frac{2\gamma k_B T}{m}, \tag{44}$$

$$\frac{dB}{dt} = 2C, \tag{45}$$

$$\frac{dC}{dt} = A - \kappa B - \gamma C. \tag{46}$$

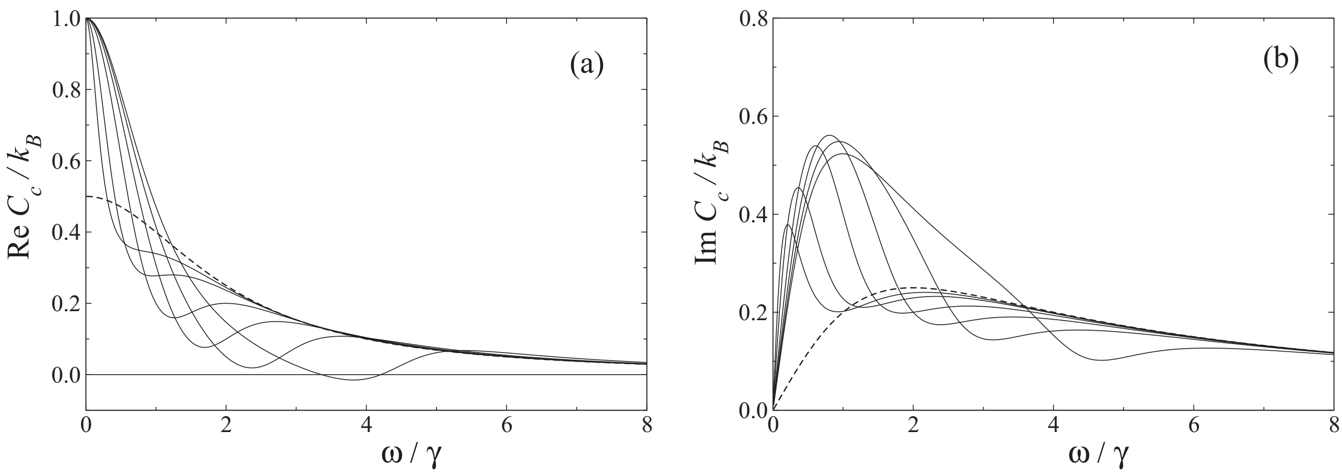

FIG. 3. (a) Real and (b) imaginary parts of the complex heat capacity (57) as a function of frequency for the following values of κ/γ^2: 0 (dotted line), 0.1, 0.2, 0.5, 1, 2, and 5 (from left to right).

Equations (44)–(46) are coupled linear differential equations whose solution can also be found for a temperature modulation of the type (4). The solution of the set of equations (44)–(46) gives the result for A,

$$A = \frac{k_B T_0}{m} + \frac{k_B T_1}{m}(A_1 \cos\omega t + A_2 \sin\omega t), \tag{47}$$

where

$$A_1 = \frac{4\gamma^2(\omega^4 - 3\kappa\omega^2 + 4\kappa^2 + \gamma^2\omega^2)}{(\omega^2+\gamma^2)[(\omega^2-4\kappa)^2 + 4\gamma^2\omega^2]}, \tag{48}$$

$$A_2 = \frac{2\gamma\omega(\omega^4 - 6\kappa\omega^2 + 8\kappa^2 + \gamma^2\omega^2)}{(\omega^2+\gamma^2)[(\omega^2-4\kappa)^2 + 4\gamma^2\omega^2]}. \tag{49}$$

C. Entropy production and heat capacity

Using the result (47) for A, we can write the heat flux

$$\Phi_q = \gamma(mA - k_B T) \tag{50}$$

in the explicit form

$$\Phi_q = k_B T_1 \gamma[(A_1 - 1)\cos\omega t + A_2 \sin\omega t]. \tag{51}$$

The entropy flux Φ and the dynamic heat capacity C are obtained from this expression for Φ_q and by the use of Eqs. (3) and (1). To get the time averages of Φ and C we should integrate them over one cycle. Carrying out the integration and taking into account that $\overline{\Phi} = \overline{\Pi}$, we find

$$\overline{\Pi} = k_B\lambda\gamma(1 - A_1), \tag{52}$$

or in a explicit form

$$\overline{\Pi} = k_B\lambda\frac{\gamma\omega^2(\omega^4 - 8\kappa\omega^2 + 16\kappa^2 + 4\kappa\gamma^2 + \gamma^2\omega^2)}{(\omega^2+\gamma^2)[(\omega^2-4\kappa)^2 + 4\gamma^2\omega^2]}, \tag{53}$$

where λ is given by Eq. (20), and

$$\overline{C} = k_B\frac{\gamma}{\omega}A_2, \tag{54}$$

or in a explicit form

$$\overline{C} = k_B\frac{2\gamma^2(\omega^4 - 6\kappa\omega^2 + 8\kappa^2 + \gamma^2\omega^2)}{(\omega^2+\gamma^2)[(\omega^2-4\kappa)^2 + 4\gamma^2\omega^2]}. \tag{55}$$

The results above were obtained for the case of a harmonic oscillator. It is possible to find the results for a free particle by formally setting $\kappa = 0$. Using this procedure, we recover the results (25) and (26) for a free particle.

D. Complex heat capacity

Again we may set up a complex heat capacity. If Eqs. (44)–(46) are solved by replacing the temperature T by the complex temperature (29), then instead of expression (51) we would get

$$\Phi_q^c = k_B T_1 \gamma(A_1 - 1 + iA_2)e^{-i\omega t} \tag{56}$$

and the complex heat capacity

$$C_c = k_B\frac{\gamma}{i\omega}(A_1 - 1 + iA_2), \tag{57}$$

which is time independent. The real and imaginary parts of C_c are

$$\mathrm{Re}(C_c) = k_B\frac{\gamma}{\omega}A_2, \quad \mathrm{Im}(C_c) = k_B\frac{\gamma}{\omega}(1 - A_1), \tag{58}$$

and using relations (52) and (54) we find

$$\mathrm{Re}(C_c) = \overline{C}, \quad \mathrm{Im}(C_c) = \overline{\Pi}/\lambda\omega. \tag{59}$$

Again, these results show that the real part of the complex heat capacity is the dynamic heat capacity and the imaginary part is proportional to the rate of entropy production.

The real and imaginary parts of the complex heat capacity C_c are shown in Fig. 3 as functions of the frequency ω for several values of κ. The real part, which is the dynamic heat capacity $\overline{C}$, becomes the static heat capacity when $\omega \to 0$, which is $C_0 = k_B/2$ if $\kappa = 0$ and $C_0 = k_B$ if $\kappa \neq 0$. In the opposite limit $\omega \to \infty$, it vanishes as $1/\omega^2$. The imaginary part vanishes when $\omega \to 0$ and so does the rate of entropy production $\overline{\Pi}$. In the limit $\omega \to \infty$, the imaginary part vanishes as $1/\omega$ but the rate of entropy production reaches a finite value, which is $\overline{\Pi} = k_B\lambda\gamma$. In Fig. 4 we have plotted $\mathrm{Im}(C_c)$ versus $\mathrm{Re}(C_c)$.

When the constant κ is small, the plot of the imaginary versus the real part of the complex heat capacity approaches the function given by (34) and thus coincides with the result for the overdamped case, as shown by the two semicircles in

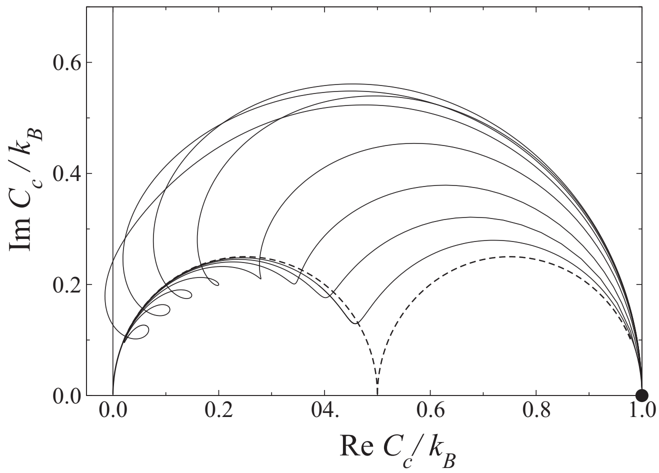

FIG. 4. Imaginary versus real part of the complex heat capacity (57) for $\kappa \to 0$ (dotted line) and the following values of κ/γ^2: 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, and 5 (from right to left). The thermodynamic equilibrium $\omega = 0$ is indicated by a closed circle.

Fig. 4. The semicircle behavior of the imaginary and real parts of the complex heat capacity is found in many experimental results of temperature-modulated systems [31,32].

IV. COMPLEX HEAT CAPACITY

During a small interval of time Δt, the heat introduced equals $-\Phi_q \Delta t$, which divided by the increment ΔT in temperature gives $\Phi_q \Delta t/\Delta T$. The heat capacity is obtained by taking the limit $\Delta t \to 0$,

$$C = \frac{-\Phi_q}{dT/dt}, \tag{60}$$

which is the expression of the dynamic heat capacity that we have used. Other definitions of nonequilibrium heat capacity have been advanced [33,34], but (60) seems to be a natural extension of the equilibrium heat capacity if we consider the significance of this quantity as being the ratio of the heat introduced and the variation in temperature. In the absence of external work, which is the case of the present analysis, $-\Phi_q = dU/dt$ and the heat capacity is related to the energy by $C = (dU/dt)/(dT/dt)$. Notice that the expression (60) is not $T(dS/dt)/(dT/dt)$ because $T\,dS/dt$ is not equal to Φ_q on account of the production of entropy.

The dynamic heat capacity does not share with the static heat capacity C_0 the property $C_0 \geqslant 0$. Generically, the heat flux is not in phase with the variation of temperature. A flux of heat to the outside could happen while the temperature is increasing, or a flux toward the system could happen while the temperature is decreasing. In both cases the dynamic heat capacity has a negative sign. This peculiar but not illegitimate behavior is shown in Fig. 3(a) for a small interval of frequencies for one of the curves and is shown by other definitions of nonequilibrium heat capacity [33]. Notice, on the other hand, that the rate of entropy production is always non-negative, as illustrated in Fig. 3(b).

Let us assume that in general the heat flux Φ_q behaves as

$$\Phi_q = \Phi_1 \cos\omega t + \Phi_2 \sin\omega t. \tag{61}$$

As we have seen above, this is correct for harmonic forces as shown by Eqs. (18), (24), and (51). For any type of force this is also expected if T_1/T_0 is small, a condition that we assume here. In fact, this condition is fulfilled in experiments on temperature modulation. Replacing Φ_q in the definition (1) of the dynamic heat capacity and calculating $\overline{C}$, we find

$$\overline{C} = \frac{\Phi_2}{T_1\omega}. \tag{62}$$

Analogously, replacing Φ_q in the definition (3) of the entropy flux $\Phi = \Phi_q/T$ and calculating $\overline{\Phi}$ which equals $\overline{\Pi}$, we find

$$\overline{\Pi} = -\frac{\Phi_1\lambda}{T_1}, \tag{63}$$

where λ is given by (20).

The complex heat capacity C_c is defined by (31), where

$$\Phi_q^c = (\Phi_1 + i\Phi_2)e^{-i\omega t} \tag{64}$$

is the complex heat flux, and T_c is given by (29), from which we get

$$C_c = \frac{1}{iT_1\omega}(\Phi_1 + i\Phi_2). \tag{65}$$

Comparing this expression with Eqs. (62) and (63), we find the results

$$\mathrm{Re}(C_c) = \overline{C}, \tag{66}$$

$$\mathrm{Im}(C_c) = \frac{1}{\lambda\omega}\overline{\Pi} \tag{67}$$

and may conclude that the imaginary part of the complex heat capacity is proportional to the rate of entropy production.

When $\omega \to 0$, the denominator of (62) vanishes and at first sight $\overline{C}$ seems to become singular. However, in this limit Φ_q also vanishes because in the absence of temperature modulation there is no heat flux. Considering that in this limit the dynamic heat capacity should approach the static heat capacity C_0, it follows, in view of (62), that Φ_2 should behave as $\Phi_2 = \omega T_1 C_0$. Indeed, this is confirmed by the results of $\overline{C}$ for the harmonic oscillator, if we recall that $C_0 = k_B$.

The dynamic heat capacity C defined above by Eq. (60) can be understood, within the linear response theory [9,12,16,35], as a response function. Defining $h = -dT/dt$, we write Eq. (60) as $\Phi_q = Ch$ and it becomes clear that h plays the role of the input and Φ_q of the output and C is the response function to the time-varying temperature. Considering that $h = \omega T_1 \sin\omega t$, it follows that the Fourier transforms $\hat{\Phi}_q$ and $\hat{C}$ are related by

$$\hat{\Phi}_q = i\omega T_1 \hat{C}. \tag{68}$$

Comparing this relation with (65), we may conclude that the complex heat capacity C_c is in fact the Fourier transform $\hat{C}$ of the dynamic heat capacity C. In addition, the Fourier transform of the heat flux is $\hat{\Phi}_q = \Phi_1 + i\Phi_2$. The connection of the present problem with the linear response theory makes the results obtained here easier to understand and may give insights into a possible extension to nonlinear models.

V. CONCLUSION

We have determined the entropy production and the dynamic heat capacity of systems under time-varying temperature by the use of stochastic thermodynamics. The systems that we have analyzed evolve in time according to the Fokker-Planck equation, for the overdamped case, or to the Fokker-Planck-Kramers equation. Exact solutions were possible to find for the cases of harmonic forces and temperature modulation of the sinusoidal type. The heat flux also varies sinusoidally, but with a phase shift with respect to temperature. From the heat flux, the rate of entropy production $\overline{\Pi}$ and the dynamic heat capacity $\overline{C}$ could be determined as functions of the frequency ω of the temperature modulation. In the limit of small frequencies, $\overline{C}$ approaches the equilibrium heat capacity, which is non-negative, and vanishes for large frequencies. The dynamic heat capacity may not be a monotonic decreasing function of ω and might even be negative. The rate of entropy production is always non-negative, vanishing for zero frequency, when the system is in equilibrium. For large values of ω it approaches a nonzero value. Finally, $\overline{C}$ and $\overline{\Pi}$ were shown to be related to the real an imaginary parts of the complex heat capacity.

ACKNOWLEDGMENT

C.E.F. acknowledges the financial support from FAPESP under Grant No. 2018/02405-1.

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