Stochastic thermodynamics and fluctuations in heat released by magnetic nanoparticles in response to time-varying fields

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Time-varying external magnetic fields can be used to manipulate the dynamics of magnetic nanoparticles. When suspended in viscous media, external fields not only modify the internal Néel relaxation dynamics within the magnetic nanoparticles but also the Brownian particle rotation. For the case of oscillating magnetic fields, Brownian and Néel processes lead to magnetic losses that are dissipated as heat to the neighborhood of the nanoparticle. The mean value of heat dissipated has been studied intensively in recent years, not least because of promising biomedical applications such as magnetic fluid hyperthermia. Here, we use the framework of stochastic thermodynamics to study fluctuations in the dissipated heat. We find that the dynamics of magnetic nanoparticles as modelled by a mesoscopic model obeys the detailed fluctuation theorem in terms of the total entropy production within numerical accuracy. In addition, we observe that the total entropy production is dominated by the dissipated heat and that fluctuations of dissipated heat are rather strong with the standard deviation being of the same order as the mean value. We also find that the probability of observing negative values of dissipated heat is rather large for typical field strengths used in magnetic fluid hyperthermia applications.

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I. INTRODUCTION

Colloidal magnetic nanoparticles (MNPs) provide a fascinating model system for condensed matter physics and statistical mechanics, where field-induced nonequilibrium dynamics can conveniently be studied [1]. The strong response of MNPs to external magnetic fields also opens up a broad range of applications in smart materials, as well as in recording media, efficient refrigeration and medicine [2–5]. For many of these applications, the use of time-varying magnetic fields is of critical importance. Therefore this topic has been studied intensively in recent years, often with a particular view on several emerging biomedical applications [6].

One prominent example of biomedical applications of MNPs is Magnetic Fluid Hyperthermia (MFH) [7–9]. Very recently, further developments of MFH have been investigated to stimulate immune response and in the area of controlled drug release [10,11]. In MFH, magnetic losses are induced inside MNPs due to externally applied oscillating magnetic fields. These magnetic losses are then released as heat which increases the local temperature near the MNP [12].

Many recent studies have investigated the influence of particle and magnetic field parameters on the work done and heat released by MNPs subject to oscillating magnetic fields [13–15]. Magnetic losses in MNPs result from two main modes of relaxation, known as internal or Néel relaxation and Brownian particle rotation, each responding differently to magnetic fields [16,17]. With an eye on MFH applications, a main goal thereby is to find conditions that maximize magnetic losses and heat released [18,19]. Corresponding theoretical and simulation works have helped to understand, interpret and complement experimental results [20–28]. These studies employed different model systems, focusing on Brownian or Néel relaxation or both simultaneously. Some works considered interacting MNPs and the role of structure formation, others focus on individual, noninteracting MNPs.

We note that the above mentioned theoretical and simulation works have all focused exclusively on the mean values of the work done and heat dissipated by MNPs in time-dependent magnetic fields. Knowledge about variations around these mean values, however, is not only of great theoretical interest but also relevant for MFH applications. Recent developments in nonequilbrium statistical physics and stochastic thermodynamics allow us to study such fluctuations in work and heat, even providing exact results in the form of detailed and integral fluctuation theorems that hold under rather general conditions [29–31]. A well-known consequence of fluctuation theorems is the fact that individual trajectories can correspond to positive or negative values of entropy production, with the second law of thermodynamics emerging in the macroscopic limit. Driven colloidal particles have been used as paradigmatic model systems to illustrate these fluctuation theorems [31,32] and more recently to test a generalized differential fluctuation theorem [33]. In this context, also charged particles in magnetic fields [34] and periodically driven systems [35] have been studied theoretically. While it is well-established that thermal fluctuations have pronounced effects on MNPs and the resulting magnetization dynamics [36], to the best of our knowledge, the corresponding fluctuations in work and heat have not been addressed in detail so far.

Here, we use a mesoscopic model [37] to capture thermal fluctuations in MNP dynamics, including both, Brownian and Néel relaxation mechanisms. We use stochastic simulations to numerically solve the model equations. From a large number of simulated trajectories, we study fluctuations in the work done and heat dissipated by MNPs that are subject to oscillating magnetic fields. Besides verifying the detailed fluctuation theorem for the total entropy production for the present case, we also study the variance and skewness of the heat distribution, deviations from Crooks relation, and evaluate the probability of observing negative values of heat dissipation, i.e., where heat is absorbed by the MNP rather than dissipated.

The paper is organized as follows. We start with a brief review of stochastic thermodynamics and its application to field-dependent dynamics of MNPs in Sec. II. In Sec. III, we provide the stochastic formulation of the model equations used in this study. The corresponding macroscopic and stochastic entropy production is discussed in Sec. IV. Results for the statistics of dissipated heat of MNPs in oscillating magnetic fields are presented in Sec. V and some conclusions are offered in Sec. VI.

II. STOCHASTIC THERMODYNAMICS OF MAGNETIC NANOPARTICLES

A. Work and heat related to a single nanoparticle

Consider a MNP with magnetic moment $\mu\mathbf{u}$, where μ denotes the magnitude and $\mathbf{u}$ the orientation defined by a three-dimensional unit vector. In the presence of a time-dependent external magnetic field $\mathbf{H}(t)$, the MNP gains the Zeeman potential energy

$$\Phi(\mathbf{u};t) = -\mu_0\mu\mathbf{u}\cdot\mathbf{H}(t), \tag{1}$$

where μ_0 is the vacuum permeability [1,38–40]. We here consider MNPs with magnetic core small enough so that the magnitude μ of the magnetic moment remains constant. In general, an additional term needs to be added to Eq. (1) to account for the anisotropy energy associated with the misalignment of the magnetic moment with the material's easy axis. Here, we focus on magnetically hard MNPs where the magnetic moment can be considered well aligned with the easy axis of the magnetic material [39,40].

Colloidal systems such as MNPs are suspended in a viscous medium that act as a heat bath. Within stochastic thermodynamics, a single colloidal particle driven by external fields can be viewed as a mesoscopic nonequilibrium system to which increments of applied work $\delta\hat{W}$ and dissipated heat $\delta\hat{Q}$ can be associated [31,46]. Due to random thermal motion of the colloid, the quantities $\delta\hat{W}$ and $\delta\hat{Q}$ show strong fluctuations. The usual macroscopic thermodynamic increments of applied work δW and dissipated hear δQ are obtained from suitable ensemble averages of these quantities. Let us start with defining the incremental work $\delta\hat{W}$ done by the external magnetic field to a single MNP. By changing the external magnetic field $\mathbf{H}$, an amount of work is done to the system that is given by [31]

$$\delta\hat{W} = \frac{\partial\Phi}{\partial t}dt = -\mu_0\mu\mathbf{u}\cdot\dot{\mathbf{H}}dt, \tag{2}$$

where the second equality applies for the particular case of the Zeeman energy (1). Next, stochastic thermodynamics identifies $d\Phi$ with the change in internal energy and uses the analog to the first law of thermodynamics to define the corresponding heat dissipated into the medium by [31]

$$\delta\hat{Q} = \delta\hat{W} - d\Phi = \mu_0\mu\mathbf{H}\cdot d\mathbf{u}. \tag{3}$$

From Eqs. (2) and (3), the work done by the external field and the dissipated heat over the time interval $[t_\mathrm{i}, t_\mathrm{f}]$ is given by

$$\hat{W}[\mathbf{u}_t] = -\mu_0\mu\int_{t_\mathrm{i}}^{t_\mathrm{f}}\mathbf{u}_t\cdot\dot{\mathbf{H}}(t)dt, \tag{4}$$

$$\hat{Q}[\mathbf{u}_t] = \mu_0\mu\int_{t_\mathrm{i}}^{t_\mathrm{f}}\mathbf{H}(t)\cdot d\mathbf{u}_t, \tag{5}$$

respectively. In thermodynamics, it is well known that work and heat are not state variables and therefore depend on the particular path. Here, using stochastic thermodynamics, the path corresponds to a particular trajectory of the orientation of the MNP and this dependence is made explicit in Eqs. (4) and (5). For convenience of notation, in the following we will write $\hat{W}$ instead of $\hat{W}[\mathbf{u}_t]$ and $\hat{Q}$ instead of $\hat{Q}[\mathbf{u}_t]$.

For the special case of oscillating magnetic fields that we consider in this study,

$$\mathbf{H}(t) = \mathbf{H}\sin(\omega t), \tag{6}$$

and after initial transients, the potential energy (1) is periodic. In this case, we conclude from Eq. (1) that the change of potential energy over one period is zero, $\Delta\Phi = 0$. Therefore the dissipated heat over one period equals the amount of work done over the same period, $\hat{Q}_\omega = \hat{W}_\omega$. Thus

$$\hat{Q}_\omega = \mu_0\mu\oint\mathbf{H}(t)\cdot d\mathbf{u}_t = -\mu_0\mu\oint\mathbf{u}_t\cdot d\mathbf{H}(t). \tag{7}$$

The identity of stochastic work and heat over one cycle is a direct consequence of the definition (3).

B. Connection with macroscopic thermodynamics

For the interpretation of stochastic thermodynamics it is important to note that the MNP is considered as a magnetomechanical system as well as a thermal system that absorbs energy, while the magnetic field $\mathbf{H}$ is an external system, directly acting onto the MNP but without any thermal fluctuations. In this setting, consistency with macroscopic thermodynamics is ensured if the characteristic time scale of the solvent τ_sol is much smaller than timescales of the MNP dynamics and magnetic field variations [41]. While typical time scales of nonmagnetic colloidal particles are indeed much larger than τ_sol [42], the situation is less clear for the internal magnetization dynamics within a MNP. Therefore we here employ a mesoscopic model which ensures that not only the viscous but also the internal magnetization relaxation times are much larger than τ_sol [37]. In addition, frequencies of the magnetic field will be chosen low enough so that the associated time scale is also much larger than τ_sol.

To make contact with macroscopic thermodynamics, we define the macroscopic magnetization as the mean magnetic moment per unit volume, $\mathbf{M} = n\mu\langle\mathbf{u}\rangle$, where $n = N/V$ is the number density of N MNPs in a volume V and angular brackets denote ensemble averages [36,40]. The macroscopic potential energy of a system of N MNPs in a volume V is given by $U = -\mu_0 V\mathbf{M}\cdot\mathbf{H} = N\langle\Phi\rangle$. Taking ensemble averages of Eq. (2) and multiplying with the number N of MNPs in a given volume we obtain

$$\delta W = N\langle\delta\hat{W}\rangle = -\mu_0\mathbf{m}\cdot d\mathbf{H}, \tag{8}$$

where $\mathbf{m} = V\mathbf{M}$ is the ensemble-averaged total magnetic moment in a volume V. Similarly, the mean heat dissipated into the medium is given by

$$\delta Q = N\langle\delta\hat{Q}\rangle = \mu_0\mathbf{H}\cdot d\mathbf{m}, \tag{9}$$

so that the change in the macroscopic internal energy is given by $dE = \delta W - \delta Q$. From Eq. (8), we conclude that the mean work done per unit volume over one cycle is given by

$$\Delta W/V = -\mu_0 \oint \mathbf{M}\cdot d\mathbf{H}(t) \tag{10}$$

which agrees with the commonly used expression [12]. We also note that Eq. (8) agrees with the expression used in Ref. [43]. There, Eq. (9) was given as an "alternative form" for δW. Stochastic thermodynamics does not support such an interpretation. For oscillating magnetic fields, the amount of heat dissipated and work done over one oscillation period are identical. In this context, it is worth to point out a common confusion identified by Callen in that $U = N\langle\Phi\rangle$ represents the change in energy when the material system is introduced and does not include the vacuum contribution [44].

C. Fluctuation theorem for oscillating magnetic fields

Arguably some of the greatest achievements in nonequilibrium statistical mechanics over the past decades have been the discovery of fluctuation theorems [29]. These theorems provide exact relations between changes of work, heat or entropy along forward and backward trajectories when the system is subject to time-dependent forcings. Here, we are particularly interested in systems subject to time-periodic and symmetric forcings which is realized by oscillating magnetic fields (6). For this special case, the time-reversed dynamics coincides with the forward dynamics and the detailed (or transient) fluctuation theorem simplifies to [30,31,45]

$$\frac{p(-\Delta\hat{S}_{\text{tot}})}{p(\Delta\hat{S}_{\text{tot}})} = \exp\left[-\Delta\hat{S}_{\text{tot}}/k_{\text{B}}\right], \tag{11}$$

where $p(\Delta\hat{S}_{\text{tot}})$ denotes the probability density of observing the value $\Delta\hat{S}_{\text{tot}}$ of the total entropy production over one cycle when the system has settled into a periodic steady state and k_{B} Boltzmann's constant. From the detailed fluctuation theorem (11), one readily derives the integral fluctuation theorem [31]

$$\langle\exp\left[-\Delta\hat{S}_{\text{tot}}/k_{\text{B}}\right]\rangle = 1. \tag{12}$$

It is interesting to note that Eq. (12) indeed holds more generally for arbitrary time-dependent fields and lengths of the process [31,46].

The total entropy change $\Delta\hat{S}_{\text{tot}}$ is composed of the entropy change of the system and the surrounding medium, $\Delta\hat{S}_{\text{tot}} = \Delta\hat{S} + \Delta\hat{S}_{\text{med}}$. We can define $\Delta\hat{S}_{\text{med}} = \hat{Q}_\omega/T$ with $\hat{Q}_\omega$ the heat dissipated into the medium over one period, as defined in Eq. (7) and T the temperature of the surrounding medium. If $\Delta\hat{S}$ is negligible (on a logarithmic scale) compared to $\Delta\hat{S}_{\text{med}}$, Eq. (11) can be approximated by

$$\frac{p(-\hat{Q}_\omega)}{p(\hat{Q}_\omega)} = \exp\left[-\hat{Q}_\omega/k_{\text{B}}T\right]. \tag{13}$$

Since $\hat{W}_\omega = \hat{Q}_\omega$ for periodic magnetic fields considered here, Eq. (13) can also be considered as a special case of Crooks relation [30,31] which holds in case the initial and final state are equilibrium states. For the long-time limit approaching a nonequilibrium steady state for constant fields and forcings, $\Delta\hat{S}$ is bounded and can therefore be neglected in several situations [30,31]. For the present case of oscillating magnetic fields, the detailed fluctuation theorem (11) is a rigorous result that applies to the situation considered here, but there is a priori no reason to believe that Eq. (13) holds to a good approximation. We will come back to this point and study deviations from the relation (13) below. In stochastic thermodynamics, $\hat{Q}_\omega$ is a random variable with probability density $p(\hat{Q}_\omega)$. Thus the fluctuation relation (13) connects the probability of finding the value of dissipated heat $\hat{Q}_\omega$ relative to that of $-\hat{Q}_\omega$.

An immediate consequence of fluctuation theorems of the kind (11) and (13) is the much-debated finding that there is a nonzero (albeit possibly very small) probability of observing processes where entropy is not increasing but decreasing, or heat is not dissipated but absorbed. These results are not in contradiction with macroscopic thermodynamics since the laws of conventional thermodynamics are recovered for the mean values of work, heat and entropy change [29].

III. MESOSCOPIC MODEL FOR DYNAMICS OF MAGNETIC NANOPARTICLES

In the spirit of stochastic thermodynamics, we consider a mesoscopic model for the dynamics of MNPs where the solvent is treated as a viscous medium that also acts as a heat bath. As mentioned in Sec. II B, we can ensure consistency with macroscopic thermodynamics by a proper time-scale separation between solvent and the mechano-magnetic system. Therefore we here employ the so-called diffusion-jump model [37] which captures the field-dependent relaxation arising from Brownian particle rotation and long-time internal (Néel) magnetization reversals. While the Néel relaxation is frequently modeled in terms of the stochastic Landau-Lifshitz-Gilbert equation, this approach is rather inefficient and may even blur the time-scale separation since it includes a microscopic attempt frequency [36]. The coarse-grained diffusion-jump model eliminates the microscopic time scales but still provides a rather accurate approximation to the more detailed model for magnetically hard MNPs [27].

The diffusion-jump model was introduced in Ref. [37] in terms of the master equation for the time-dependent probability density $f(\mathbf{u};t)$ of finding the magnetic moment $\mu\mathbf{u}$ at time t,

$$\frac{\partial}{\partial t} f = (\mathtt{L}_{\text{B}} + \mathtt{L}_{\text{N}}) f. \tag{14}$$

The explicit form of the operators $\mathtt{L}_{\text{B}}$ and $\mathtt{L}_{\text{N}}$ are given in Appendix A. While the formulation (14) in terms of the probability density is very useful for various reasons, it is not ideally suited for discussing the stochastic thermodynamics of MNPs. Therefore we here provide the corresponding stochastic formulation. The three-dimensional unit vector $\mathbf{u}_t$ denotes the stochastic variable that represents the orientation of the magnetic moment of the MNP at time t. From Eq. (1), the dimensionless Zeeman energy can be written as $\Phi/k_{\text{B}}T = -\mathbf{u}_t\cdot\mathbf{h}(t)$, where we introduced the dimensionless field $\mathbf{h}(t) = \mu_0\mu\mathbf{H}(t)/k_BT$. For later use, we also define the Langevin parameter by $h = |\mathbf{h}|$. With τ_B the Brownian rotational relaxation time of the MNP, the dynamics of the diffusion-jump model can be expressed as the stochastic differential equation

$$d\mathbf{u}_t = \mathbf{P}_t \cdot \left[\mathbf{h}(t)\frac{dt}{\tau_B} + d\mathbf{W}_t\right] - \mathbf{u}_t\frac{dt}{\tau_B} - 2\mathbf{u}_t dN_t, \quad (15)$$

where $\mathbf{P}_t = \mathbf{I} - \mathbf{u}_t\mathbf{u}_t$ denotes the orthogonal projector with $\mathbf{I}$ the three-dimensional unit matrix. The three-dimensional Wiener process with zero mean and variance $1/\tau_B$ is denoted by $\mathbf{W}_t$.

The first terms in Eq. (15) merely rewrite the classical model of Martsenyuk *et al* [40] for the rigid dipole approximations of the dynamics of MNPs in terms of a stochastic differential equation and have already been given earlier (see, e.g., Ref. [47]). The last term in Eq. (15) describes additional Néel relaxation by magnetization reversals in terms of a Poisson process N_t. In the absence of external magnetic fields, the Poisson process is homogeneous with a constant rate $\lambda_0 = (2\tau_N)^{-1}$, where τ_N denotes the Néel relaxation time. In the presence of an external magnetic field $\mathbf{h}(t)$, the Poisson process in Eq. (15) becomes nonhomogeneous, where the rate function is a random variable given by $\lambda_t = (2\tau_N)^{-1}\exp[-\mathbf{u}_t \cdot \mathbf{h}(t)]$.

The diffusion-jump model (15) is entirely specified by the two relaxation times τ_B and τ_N and the dimensionless external magnetic field $\mathbf{h}(t)$. For justifications and more details of the model as well as a discussion of possible alternatives to the Arrhenius rate function, we refer the reader to Refs. [27,37].

IV. ENTROPY PRODUCTION IN TIME-VARYING FIELDS

With the one-particle probability density $f(\mathbf{u};t)$, we associate the Boltzmann entropy

$$S(t) = -k_B \int f(\mathbf{u};t)\ln f(\mathbf{u};t)\,d\mathbf{u}. \quad (16)$$

Along solutions of the master equation (14), the Boltzmann entropy (16) changes according to

$$\dot{S} = \sigma_B + \sigma_N + j_B + j_N, \quad (17)$$

where $\sigma_{B,N}$ denote the entropy production due to Brownian and Néel processes, respectively, with $j_{B,N}$ the corresponding entropy fluxes. Note that Brownian and Néel contributions to the system's entropy production are additive. The explicit form of these quantities is given in Appendix A.

In addition to the system entropy S, we follow Ref. [31] and also introduce the entropy of the surrounding medium $S_{\rm med}$ via $dS_{\rm med} = \delta Q/T$, where Q is the dissipated heat given by Eq. (9). Then, the change in the total entropy can be written as $dS_{\rm tot} = dS + dS_{\rm med}$ or

$$\dot{S}_{\rm tot} = \dot{S} + \frac{\dot{Q}_B}{T} + \frac{\dot{Q}_N}{T}. \quad (18)$$

The expressions for the heat production $\dot{Q}_{B,N}$ due to Brownian and Néel processes are given in Appendix A. Inserting the above expressions (17), we arrive at the time rate of change of the total entropy

$$\dot{S}_{\rm tot} = \sigma_N + \sigma_B + \frac{k_B}{\tau_B}\left[\frac{h^2}{3}(1 - S_2) - 2hS_1\right], \quad (19)$$

with the orientational order parameters defined by $S_k = \int P_k(\mathbf{u}\cdot\hat{\mathbf{h}})f(\mathbf{u};t)d\mathbf{u}$, $\hat{\mathbf{h}}$ the unit vector in the direction of the applied field and $P_k(x)$ the kth Legendre polynomial [47]. It is interesting to note that for Néel processes as described here, the entropy flux and heat dissipation perfectly balance each other, $j_N = -\dot{Q}_N/T$. This is not true for Brownian particle relaxation, where the balance of entropy flux and heat generation can be expressed in terms of an effective Brownian angular velocity to rewrite Eq. (19) as

$$\dot{S}_{\rm tot} = \sigma_N + 2\tau_B k_B\langle\boldsymbol{\omega}_B^2\rangle \geqslant 0. \quad (20)$$

Equation (20) verifies that $\dot{S}_{\rm tot}$ is non-negative, which is less obvious from Eq. (19). The definition of the angular velocity $\boldsymbol{\omega}_B$ as well as details of the derivation are given in Appendix B. We note that without the Néel contribution, Eq. (20) is analogous to the case of Brownian translational motion, where $\boldsymbol{\omega}_B$ is replaced by an effective Brownian velocity [31].

In stochastic thermodynamics, a trajectory-dependent entropy of the system is defined by [31,46]

$$\hat{S}(t) = -k_B \ln f(\mathbf{u}_t;t), \quad (21)$$

where $f(\mathbf{u};t)$ denotes the solution of the kinetic model for given initial conditions and $\{\mathbf{u}_t\}$ a corresponding stochastic trajectory. The instantaneous stochastic entropy production is therefore given by [46]

$$\frac{d}{dt}\hat{S}(t) = -k_B \left.\frac{\frac{\partial}{\partial t}f(\mathbf{u};t)}{f(\mathbf{u};t)}\right|_{\mathbf{u}_t} - k_B\dot{\mathbf{u}}_t \cdot \left(\frac{\partial}{\partial \mathbf{u}}f(\mathbf{u};t)\right)_{\mathbf{u}_t}. \quad (22)$$

With $d\hat{S}_{\rm med} = \delta\hat{Q}/T$ the stochastic entropy change of the surrounding medium, we can write the total stochastic entropy production as

$$\frac{d}{dt}\hat{S}_{\rm tot}(t) = -k_B \left.\frac{\frac{\partial}{\partial t}f(\mathbf{u};t)}{f(\mathbf{u};t)}\right|_{\mathbf{u}_t} + 2k_B\tau_B\boldsymbol{\omega}_B(t)\cdot\boldsymbol{\omega}_t, \quad (23)$$

where the stochastic angular velocity $\boldsymbol{\omega}_t$ is defined by $\dot{\mathbf{u}}_t = \boldsymbol{\omega}_t \times \mathbf{u}_t$ and the quantity $\boldsymbol{\omega}_B$ is defined in Eq. (B1). Note that Eq. (23) is formally similar to the case of translational Brownian motion. However, due to the jump processes associated with Néel relaxation, not the total but only the Brownian part of the probability flux $\boldsymbol{\omega}_B$ appears in Eq. (23).

The total stochastic entropy production along a trajectory $\Delta\hat{S}_{\rm tot} = \Delta\hat{S} + \Delta\hat{S}_{\rm med}$ over one period of the magnetic field $T_\omega = 2\pi/\omega$ is given by

$$\Delta\hat{S}_{\rm tot}/k_B = -\ln\frac{f(\mathbf{u}_{t+T_\omega};t+T_\omega)}{f(\mathbf{u}_t;t)} + \frac{\hat{Q}_\omega}{k_BT}. \quad (24)$$

When the system has reached a steady periodic response, we have $f(\mathbf{u};t+T_\omega) = f(\mathbf{u};t)$ and it seems plausible that $\Delta\hat{S}_{\rm tot}$ is dominated by $\hat{Q}_\omega$, such that the fluctuation relation for heat (13) might be a reasonable approximation to the transient fluctuation theorem (11).

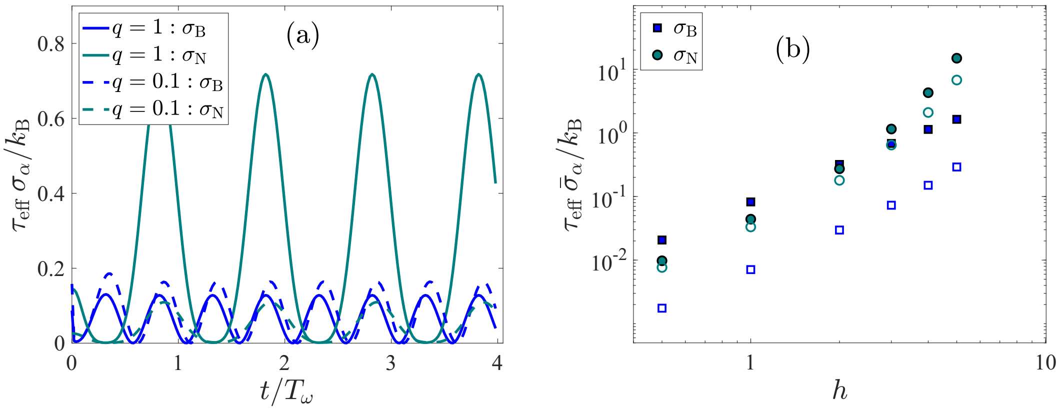

FIG. 1. (a) The transient entropy production due to Brownian (σ_{B}) and Néel (σ_{N}) processes in response to oscillating magnetic fields with frequency $\omega = 1/\tau_{\mathrm{B}}$ and dimensionless amplitude $h = 1$. (b) The entropy production averaged over one cycle is shown versus the amplitude of the applied field. Full and open symbols correspond to frequencies $\omega\tau_{\mathrm{B}} = 1$ and $\omega\tau_{\mathrm{B}} = 5$, respectively, with squares and circles representing $\bar{\sigma}_{\mathrm{B}}$ and $\bar{\sigma}_{\mathrm{N}}$. The ratio of relaxation times was chosen as $q = 0.1$.

V. RESULTS

Here, we consider MNPs that are exposed to oscillating magnetic fields (6). Figure 1 shows the Brownian (σ_{B}) and Néel (σ_{N}) contribution to the entropy production, Eq. (A4) and (A6), respectively. We observe from Fig. 1(a) that σ_{B} oscillates with double the frequency of the applied field, with the minima occurring near the zeros of the applied field. The Néel contribution σ_{N}, on the other hand, oscillates with the same frequency as the applied field, where the minima and maxima of σ_{N} occur near the maxima and minima of the applied field, respectively. For σ_{B}, we find that the effect of changing the ratio $q = \tau_{\mathrm{B}}/\tau_{\mathrm{N}}$ of relaxation times is mainly captured by the effective relaxation time $\tau_{\mathrm{eff}} = \tau_{\mathrm{B}}\tau_{\mathrm{N}}/(\tau_{\mathrm{B}} + \tau_{\mathrm{N}})$. For the Néel contribution, however, increasing q leads to a strong increase of σ_{N}. Figure 1(b) shows the entropy production averaged over one cycle versus the dimensionless amplitude h of the applied field. For the Brownian contribution, we find an approximately quadratic increase of the mean entropy production with h, whereas a stronger increase is seen for the Néel contribution. In both cases, we find that the mean entropy production is larger for $\omega\tau_{\mathrm{B}} = 1$ compared to $\omega\tau_{\mathrm{B}} = 5$ for $q = 0.1$. It is also interesting to note that for strong fields, entropy production is dominated by Néel processes. For weak fields, either Brownian or Néel processes dominate depending on the frequency of the applied field.

Next we turn to the heat dissipated over one cycle, $\hat{Q}_\omega$, as the main quantity of interest in the present study. From Eq. (7), this quantity is identical to the work done by the magnetic field and can be calculated from the associated hysteresis loop.

We start by calculating the mean dissipated heat over one cycle, $Q_\omega = \langle \hat{Q}_\omega \rangle$, where angular brackets denote ensemble averages. Taking the ensemble average of Eq. (7) and multiplying by the number density n of MNPs we arrive at Eq. (10) since $N\langle \hat{Q}_\omega \rangle = \Delta W$. Instead of ΔW, it is more common in the literature to consider the specific loss power defined by $\Delta W/T_\omega$, where $T_\omega = 2\pi/\omega$ denotes the length of the oscillation period of the magnetic field [8,12]. Figure 2 shows the mean dissipated heat per unit time versus the amplitude h of an external oscillating field. Different symbols denote different frequencies ω of the applied field. From Fig. 2, we observe the characteristic quadratic increase of the specific loss power with field strength [see Eq. (C6)]. Strictly speaking, the quadratic increase is restricted to small amplitudes h that remain within the linear response regime. Heuristic arguments are given in Ref. [12] that suggest replacing the factor $h^2/3$ in Eq. (C6) by $hL(h)$ with $L(x) = \coth(x) - 1/x$ the Langevin function. As a quantitative test of our algorithm, we include in Fig. 2 also the results obtained from solving the kinetic equation for the probability density [48]. Very good agreement between both approaches is found. Here and in the following, the size of the symbols is larger than the numerical uncertainties if not indicated otherwise.

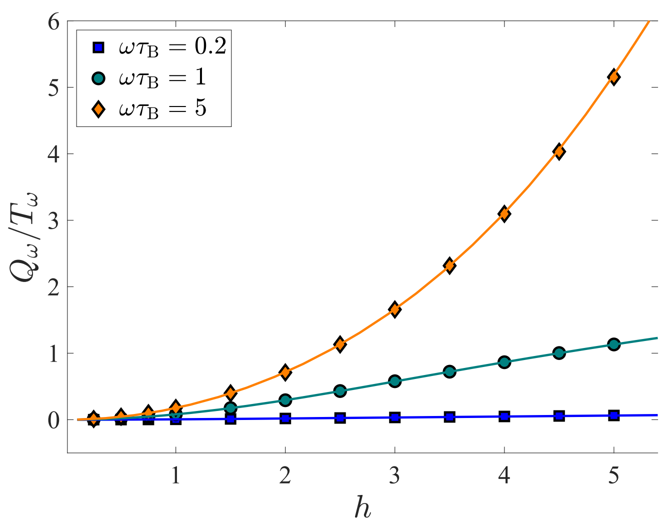

FIG. 2. Mean dissipated heat per unit time as a function of the amplitude h of an oscillating field (6). Different frequencies of the field are applied as indicated in the legend. The ratio of Brownian and Néel relaxation times was chosen as $q = 0.1$. Symbols denote ensemble averages over stochastic simulations, while lines show reference results obtained from solution to the corresponding kinetic equation (14).

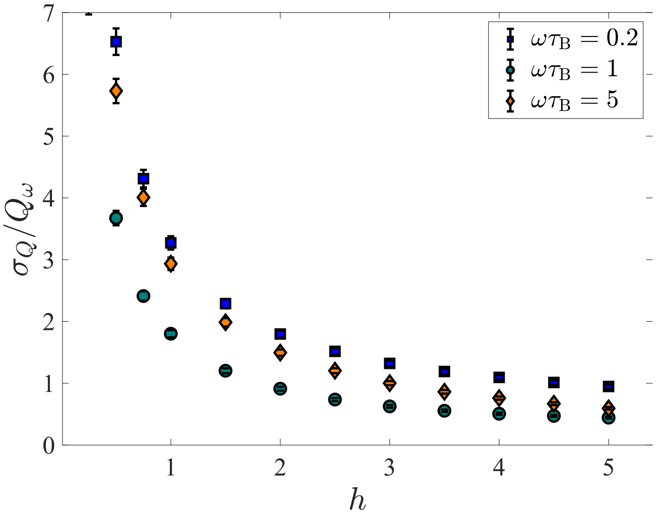

FIG. 3. The coefficient of variation σ_Q/Q_ω is shown as as function of the dimensionless amplitude h of an oscillating magnetic field (6). Various frequencies ω of the field are applied as indicated in the legend. The ratio of Brownian to Néel relaxation time was chosen as $q = 0.1$.

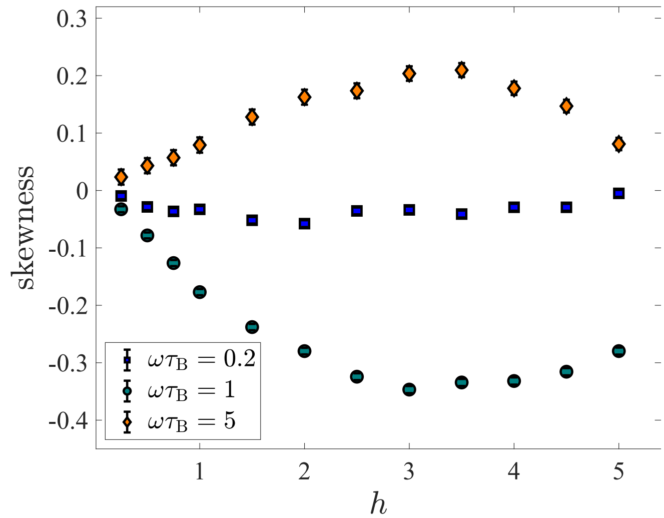

FIG. 4. Normalized skewness coefficient $\tilde{\mu}_3$ defined in Eq. (26) as function of the dimensionless amplitude h of an oscillating magnetic field (6). The same conditions and symbols as in Fig. 3 are used.

Within stochastic thermodynamics, the heat dissipated over one cycle defined in Eq. (7) is a stochastic variable. Therefore we can study not only the mean value as in Fig. 2 but its statistics more generally. To do this, it is convenient to define the centered moments

$$\mu_n = \langle(\hat{Q}_\omega - Q_\omega)^n\rangle \tag{25}$$

for $n = 1, 2, \dots$ By definition $\mu_1 = 0$ and $\mu_2 = \sigma_Q^2$ the variance.

In Fig. 3, we show σ_Q/Q_ω, i.e. the standard deviation normalized with the mean value. This quantity is known as the coefficient of variation and can be interpreted as the relative spread of the random variable around its mean value. Figure 3 shows that σ_Q/Q_ω strongly deceases with increasing amplitude h of the applied field for all frequencies investigated. However, even at relatively large field strengths we find $\sigma_Q/Q_\omega \sim 1$, indicating that the typical spread in $\hat{Q}_\omega$ is comparable to its mean value. This is an important finding, highlighting the importance of considering fluctuations in this situation. It is also interesting to note that the variance and the coefficient of variation depend nonmonotonically on the frequency ω of the applied field. Appendix C shows that such a behavior arises already in a weakly driven system and results from equilibrium magnetization fluctuations.

Next, we consider the normalized skewness coefficient defined as

$$\tilde{\mu}_3 = \frac{\mu_3}{\sigma_Q^3} = \frac{\mu_3}{\mu_2^{3/2}}. \tag{26}$$

The skewness vanishes for symmetric distributions, i.e., if positive and negative deviations from the mean value are equally likely. Positive values of the skewness $\tilde{\mu}_3$ imply that the tail towards larger values of $\hat{Q}_\omega$ is stronger, whereas the opposite is the case for negative $\tilde{\mu}_3$. The normalized skewness coefficient (26) is shown in Fig. 4 for different amplitudes h and frequencies ω of an applied magnetic field. It is interesting to observe that the skewness is nonmonotonic in the amplitude as well as in the frequency of the applied field.

Having investigated the mean, variance and skewness of the dissipated heat, Fig. 5 shows the underlying probability density $p(\hat{Q}_\omega)$, estimated from the empirical histogram via kernel smoothing

$$p(\hat{Q}_\omega) \approx \frac{1}{Nb}\sum_{j=1}^{N} K(|\hat{Q}_\omega - \hat{Q}_j|/b), \tag{27}$$

where $\hat{Q}_j$ denote the numerical value for the dissipated heat of ensemble member j and b the smoothing length. We choose

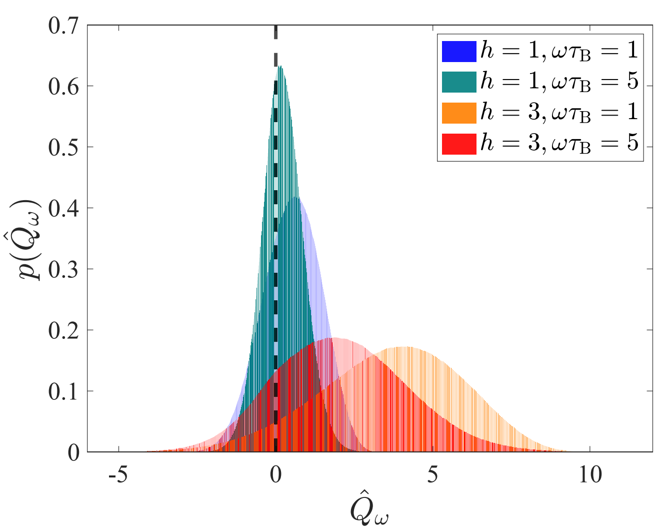

FIG. 5. The probability density $p(\hat{Q}_\omega)$ estimated from stochastic simulations using Eq. (27) for an ensemble size of $N = 10^7$. Different field strengths and frequencies of the applied field were chosen, as indicated in the legend.

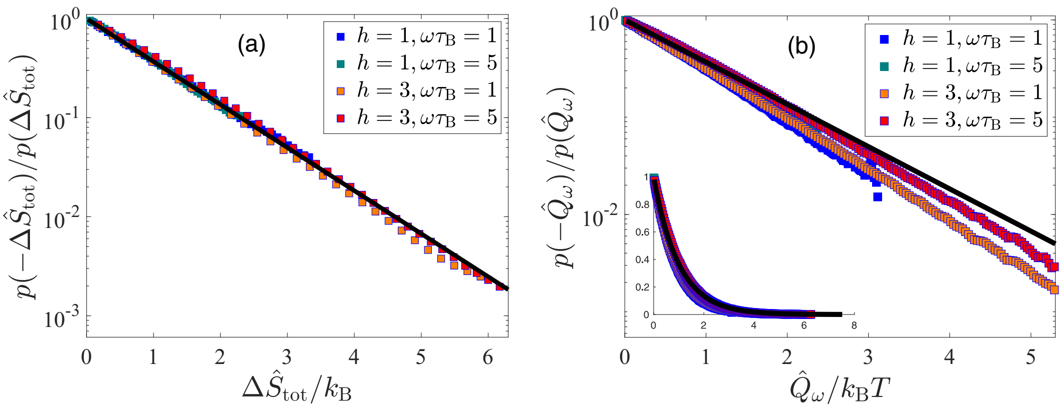

FIG. 6. (a) Test of the detailed fluctuation theorem (11) for the fluctuations of the total entropy change $\Delta\hat{S}_{\rm tot}$ over one period. Symbols denote simulation results for different field amplitudes and frequencies, as indicated in the legend, while the black solid line is the theoretical result. Panel (b) shows a test of the approximate fluctuation relation (13) for the dissipated heat over one cycle. The ratio of the probabilities $p(-\hat{Q}_\omega)/p(\hat{Q}_\omega)$ is shown versus the dimensionless heat $\hat{Q}_\omega/k_BT$. The same color coding as in panel (a) is used. The inset shows the same data on a linear instead of a semi-logarithmic scale.

the Epanechnikov kernel, $K(z) = (3/4)(1 - z^2)$ if $z < 1$ and $K(z) = 0$ else. The ensemble size of the stochastic simulations is chosen as $N = 10^6$. For more accurate estimates of the probability densities, some simulations were performed with $N = 10^7$. Selecting appropriate values for b is known as bandwidth selection problem. For the present case, we choose $b = 2\Delta\hat{q}$ with $\Delta\hat{q}$ the bin width obtained from dividing the interval from minimal to maximal value of $\hat{Q}_\omega/k_BT$ into $N_b = 500$ bins of equal width.

First, it is reassuring to notice from Fig. 5 that the probability density $p(\hat{Q}_\omega)$ is unimodal as one might have intuitively expected. Next, as expected from the mean value shown in Fig. 2, we find that the location of the maximum of $p(\hat{Q}_\omega)$ moves to larger $\hat{Q}_\omega$ with increasing amplitude h of the applied field. In addition, a significant broadening of the peak with increasing h is seen. Together with Fig. 3, we learn that the width of the peaks grows less strong with h compared to the mean value. From Fig. 5 we also learn that the distribution $p(\hat{Q}_\omega)$ depends sensitively on the frequency of the applied field. Finally, Fig. 5 also shows unequivocally the appearance of events with the opposite sign of $\hat{Q}_\omega$, i.e. where heat is not dissipated but absorbed by the MNPs.

As mentioned in Sec. II C, the appearance of microscopic events with both signs of total entropy change, dissipated heat and both signs of work done is implied by stochastic thermodynamics. The detailed fluctuation theorem (11) is a very strong result that connects the probability of observing events with positive and negative total entropy change. On the other hand, we expect deviations from the relation (13) since it does not apply to the present situation.

Having already calculated the trajectory dependent dissipated heat over one cycle $\hat{Q}_\omega$, we use Eq. (24) to find the corresponding total entropy change for every trajectory. To evaluate the corresponding expression, we use an accurate and efficient algorithm for the numerical solution $f(\mathbf{u};t)$ of the kinetic equation (14) of the diffusion-jump model [48]. Figure 6(a) shows that for all magnetic field strengths and frequencies investigated, we find that all our numerical values fall onto the same master curve $\exp[-\Delta\hat{S}_{\rm tot}/k_B]$ over three decades within numerical accuracy. Therefore our numerical simulations agree with the predictions from the detailed fluctuation theorem (11). We also verified that our numerical solution satisfies the integral fluctuation theorem (12) to within 0.4%. Better accuracies can be obtained by further increasing the ensemble size of the stochastic simulations, however at a considerable computational cost.

From the data shown in Fig. 5 we plot in Fig. 6(b) the ratio $p(-\hat{Q}_\omega)/p(\hat{Q}_\omega)$ versus $\hat{Q}_\omega$. From Fig. 6(b) we find that our numerical results agree rather well with the approximate fluctuation relation (13). Upon closer inspection, however, systematic deviations are clearly seen on a semi-logarithmic scale, since the dynamics obeys the detailed fluctuation theorem (11) rather than (13) and the fluctuation relation (13) holds only approximately.

We have seen above that the fluctuation relation (13) predicts the existence of trajectories with $\hat{Q}_\omega < 0$. To quantify this phenomenon, we define the probability p_- that heat is not released but absorbed,

$$p_- = \int_{-\infty}^{0} p(\hat{Q}_\omega)d\hat{Q}_\omega. \tag{28}$$

Note that p_- can be obtained not only from the probability density shown in Fig. 5 but is available directly from the stochastic simulations via the relative frequency of trajectories with $\hat{Q}_\omega < 0$. Figure 7 shows the probability p_- as a function of the amplitude h of the oscillating magnetic field. We observe that the probability p_- decreases with increasing h. This finding is expected since the mean value increases with h and the relative spread decreases (see Figs. 2 and 3). Therefore large enough fluctuations that lead to negative values of $\hat{Q}_\omega$ are less likely to occur. Interestingly, the values of p_- depend nonmonotonically on the frequency of the applied field. From Fig. 4, we find that the skewness is positive for $\omega\tau_B = 5$ but negative for $\omega\tau_B = 1$, suggesting that the tail of $p(\hat{Q}_\omega)$ to negative values of $\hat{Q}_\omega$ is stronger for the $\tau_B\omega = 1$. However, p_- is found to be smaller for $\omega\tau_B = 1$ compared to $\omega\tau_B = 5$, mainly because the mean value is different in both

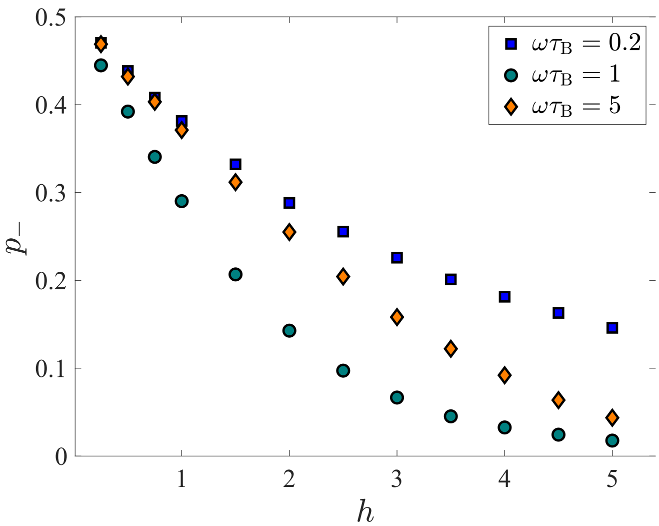

FIG. 7. The quantity p_- defined in Eq. (28) as function of amplitude h of oscillating magnetic field for various frequencies as indicated in the legend. The ratio of the Brownian to the Néel relaxation time is chosen as $q = 0.1$.

cases. Therefore we conclude that the skewness needs to be interpreted carefully and does not provide a reliable measure of quantities like p_-.

VI. DISCUSSION AND CONCLUSIONS

We studied the stochastic dynamics of MNPs in response to oscillating external magnetic fields, taking into account Brownian particle rotation and internal Néel relaxation. Within the framework of stochastic thermodynamics, we analyze fluctuations in magnetic losses and the resulting heat dissipated by the MNPs. The corresponding mean value of dissipated heat is related to the specific loss power or specific absorption rate that has been studied intensively in recent years due to its importance for MFH applications.

Here, we find that fluctuations of the dissipated heat around the mean value are significant, with standard deviations being of the same order as the mean value. For driven colloidal systems, fluctuation theorems relate the probabilities of entropy production, work and heat in forward and reversed processes under rather general conditions. We verify quantitatively the validity of the detailed fluctuation theorem for the total entropy production when applied to the present situation. A corresponding fluctuation relation for the dissipated heat does not apply to oscillating fields, but is found to hold approximately. A consequence of this fluctuation relation is the occurrence of microscopic trajectories with negative values of the dissipated heat, i.e. where heat is absorbed by MNPs rather than dissipated. While the probability of these events depends on the frequency of the applied field, we find them generally to be rather significant for weak and moderate field strengths. The manipulation of dissipated heat via external magnetic fields is not only fascinating from a theoretical point of view, but might also be highly relevant for applications of MNPs such as MFH in particular, where local heating needs to be controlled rather accurately.

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APPENDIX A: ENTROPY AND HEAT IN THE DIFFUSION-JUMP MODEL

The explicit form of the master equation (14) of the diffusion-jump (DJ) model is given by [37]

$$\mathrm{L}_B f(\mathbf{u};t) = \frac{1}{2\tau_B}[\boldsymbol{\mathcal{L}}^2 f(\mathbf{u};t) - \boldsymbol{\mathcal{L}}\cdot[(\mathbf{u}\times\mathbf{h})f(\mathbf{u};t)]], \quad \text{(A1)}$$

$$\mathrm{L}_N f(\mathbf{u};t) = \frac{1}{2\tau_N}[e^{\mathbf{u}\cdot\mathbf{h}} f(-\mathbf{u};t) - e^{-\mathbf{u}\cdot\mathbf{h}} f(\mathbf{u};t)], \quad \text{(A2)}$$

where τ_B and τ_N denote the Brownian and Néel relaxation time, respectively, $\boldsymbol{\mathcal{L}} = \mathbf{u}\times\partial/\partial\mathbf{u}$ the rotational operator and $\mathbf{h} = \mu_0\mu\mathbf{H}/k_BT$ the dimensionless magnetic field. For convenience of notation, we here suppress the explicit time-dependence of $\mathbf{h}(t)$.

Along solutions of the DJ model (14), the rate of change of the Boltzmann entropy (16) can be written as $\dot{S} = \dot{S}_B + \dot{S}_N$, where

$$\dot{S}_\alpha = -k_B \int \ln[f(\mathbf{u};t)]\mathrm{L}_\alpha f(\mathbf{u};t)d\mathbf{u}, \quad \text{(A3)}$$

with $\alpha \in \{B, N\}$ and we used $\int \mathrm{L}_\alpha f d\mathbf{u} = 0$ due to the conservation of the normalization of f.

Inserting the explicit form (A1) for the Brownian contribution and performing partial integration we find $\dot{S}_B = \sigma_B + j_B$, where we defined

$$\sigma_B(t) = \frac{k_B}{2\tau_B}\int \frac{1}{f(\mathbf{u};t)}[\boldsymbol{\mathcal{L}} f(\mathbf{u};t)]^2 d\mathbf{u} \geqslant 0, \quad \text{(A4)}$$

$$j_B(t) = -\frac{k_B}{\tau_B} h S_1(t) \quad \text{(A5)}$$

with the orientational order parameter S_1 introduced after Eq. (19). Note that the Brownian contribution to the entropy flux is given by the Zeeman energy per τ_B. For simplicity of notation, possible time dependence of the external field is suppressed.

For the Néel contribution to the entropy change, we find from Eq. (A2) again that the rate of entropy change can be separated in a production and flux term, $\dot{S}_N = \sigma_N + j_N$, with

$$\sigma_N(t) = \frac{k_B}{4\tau_N}\int [e^{\mathbf{u}\cdot\mathbf{h}} f(-\mathbf{u};t) - e^{-\mathbf{u}\cdot\mathbf{h}} f(\mathbf{u};t)] \times \ln\frac{e^{\mathbf{u}\cdot\mathbf{h}} f(-\mathbf{u};t)}{e^{-\mathbf{u}\cdot\mathbf{h}} f(\mathbf{u};t)} d\mathbf{u} \geqslant 0 \quad \text{(A6)}$$

and

$$j_N(t) = \frac{k_B}{\tau_N}\int \mathbf{u}\cdot\mathbf{h}\, e^{-\mathbf{u}\cdot\mathbf{h}} f(\mathbf{u};t)\, d\mathbf{u}. \quad \text{(A7)}$$

Note that the form (A6) of the entropy production due to Néel relaxation is well-known for Markov processes [29].

Next we calculate the dissipated heat. From Eqs. (9) and (14), we find that also the dissipated heat can be separated into Brownian and Néel contributions, $\dot{Q} = \dot{Q}_{\mathrm{B}} + \dot{Q}_{\mathrm{N}}$, with

$$\dot{Q}_{\alpha} = N k_{\mathrm{B}} T\, \mathbf{h} \cdot \int \mathbf{u}\, \mathrm{L}_{\alpha} f(\mathbf{u};t)\, d\mathbf{u}. \tag{A8}$$

Inserting the explicit form (A1), (A2) of the operators $\mathrm{L}_{\mathrm{B,N}}$ into Eq. (A8), we find

$$\dot{Q}_{\mathrm{B}} = \frac{k_{\mathrm{B}}T}{\tau_{\mathrm{B}}}\left[-hS_1 + \frac{h^2}{3}(1 - S_2)\right], \tag{A9}$$

$$\dot{Q}_{\mathrm{N}} = -\frac{k_{\mathrm{B}}T}{\tau_{\mathrm{N}}}\int (\mathbf{u}\cdot\mathbf{h}) e^{-\mathbf{u}\cdot\mathbf{h}} f(\mathbf{u};t)\, d\mathbf{u}. \tag{A10}$$

We note that $\dot{Q}_{\mathrm{N}}(t) = -T j_{\mathrm{N}}(t)$. Moreover, $\dot{Q}_{\mathrm{B}}$ and $\dot{Q}_{\mathrm{N}}$ vanish in equilibrium as they should.

APPENDIX B: EFFECTIVE BROWNIAN ANGULAR VELOCITY

In kinetic theory, it is common to define an effective velocity v from the relation $\partial f/\partial t = -\nabla_x (v f)$ [29,42]. For the present case, we can define an effective Brownian angular velocity $\boldsymbol{\omega}_{\mathrm{B}}$ from the Brownian contribution to the time evolution (14) via the relation $\mathrm{L}_{\mathrm{B}} f = -\boldsymbol{\mathcal{L}} \cdot (\boldsymbol{\omega}_{\mathrm{B}} f)$. From the explicit form (A1) of L_{B} we can read off

$$\boldsymbol{\omega}_{\mathrm{B}} = \frac{1}{2\tau_{\mathrm{B}}}[\mathbf{u}\times\mathbf{h} - \boldsymbol{\mathcal{L}} \ln f]. \tag{B1}$$

Calculating $\boldsymbol{\omega}_{\mathrm{B}}^2$ from Eq. (B1) and performing averages with respect to $f(\mathbf{u};t)$, we find after integration by parts

$$\langle \boldsymbol{\omega}_{\mathrm{B}}^2 \rangle = \frac{1}{(2\tau_{\mathrm{B}})^2}\left[\frac{2h^2}{3}(1 - S_2) - 4hS_1 + \frac{2\tau_{\mathrm{B}}}{k_{\mathrm{B}}}\sigma_{\mathrm{B}}\right], \tag{B2}$$

where we used the definition (A4) and the orientational order parameters S_k.

APPENDIX C: HEAT FLUCTUATIONS FOR WEAKLY DRIVEN SYSTEM

To better understand fluctuations in heat dissipated due to oscillatory magnetic fields, we start from Eq. (7) and define fluctuations in the heat dissipated over one period $T_\omega = 2\pi/\omega$ as

$$\delta\hat{Q}_\omega = -k_{\mathrm{B}} T h\omega \int_0^{T_\omega} [u_t - \langle u_t\rangle] \cos\omega t\, dt \tag{C1}$$

where u_t and $\langle u_t\rangle$ are the components of $\mathbf{u}_t$ and $\langle \mathbf{u}_t\rangle$ parallel to the direction of the applied field, respectively. Then, the variance $\sigma_Q^2 = \langle \delta\hat{Q}_\omega^2\rangle$ can be written as

$$\sigma_Q^2 = (k_{\mathrm{B}} T h\omega)^2 \langle \delta u^2\rangle \int_0^{T_\omega}\int_0^{T_\omega} C(t_1,t_2)\cos\omega t_1 \cos\omega t_2 \mathrm{d}t_1 \mathrm{d}t_2 \tag{C2}$$

with the magnetization auto-correlation function

$$C(t_1,t_2) = \frac{\langle [u_{t_1} - \langle u_{t_1}\rangle][u_{t_2} - \langle u_{t_2}\rangle]\rangle}{\langle [u - \langle u\rangle]^2\rangle}. \tag{C3}$$

After initial transients, we expect time-translational invariance, $C(t_1,t_2) = C(t_1 - t_2)$. We note that the correlation function (C3) describes nonequilibrium fluctuations in a periodically driven system. Therefore expressions for C are in general expected to be rather involved. For sufficiently weak external driving, however, we may approximate Eq. (C3) with the same form as the equilibrium correlation function,

$$C(t_1,t_2) = \exp[-|t_1 - t_2|/\tau], \tag{C4}$$

with an effective relaxation time τ. Inserting Eq. (C4) into Eq. (C2), we obtain an explicit expression for the variance,

$$\sigma_Q^2 = 2\pi (k_{\mathrm{B}}T)^2 h^2 \langle \delta u^2\rangle \frac{\omega/\tau}{1+(\omega\tau)^2} \times\left[1 - \frac{\omega\tau/\pi}{1+(\omega\tau)^2}(1 - e^{-2\pi/\omega\tau})\right]. \tag{C5}$$

In general, we expect the relaxation time τ introduced in Eq. (C4) to depend on the field amplitude h and frequency ω. For weak driving, for which Eq. (C4) is better justified, τ is approximately constant and can be identified with the effective relaxation time τ_{eff} introduced above. Even in this regime, the fluctuations (C5) show an intricate and non-monotonic dependence on the frequency ω of the applied field.

For weak fields, the linear response result for the mean dissipated heat over one cycle is [12]

$$\langle \hat{Q}_\omega\rangle = \frac{\pi}{3} k_{\mathrm{B}} T h^2 \frac{\omega\tau}{1+(\omega\tau)^2}. \tag{C6}$$

The coefficient of variation is defined as $\sigma_Q/\langle\hat{Q}_\omega\rangle$. From Eqs. (C5) and (C6), we find that the coefficient of variation first decreases with increasing frequency ω, reaching a minimum near $\omega\tau = 1$ before increasing again. This behavior is in qualitative agreement with the results shown in Fig. 3.

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