Physica A 588 (2022) 126525

Contents lists available at ScienceDirect

Physica A

journal homepage: www.elsevier.com/locate/physa

Entropy changes in crystalline material under phase transition and symmetry breaking

Dhiraj Sinha [a,b,*], Roland Bouffanais [c]

[a] Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, 77, Massachusetts Avenue, Cambridge, MA 02139, United States of America
[b] Plaksha University, Sahibzada Ajit Singh Nagar, Punjab 140306, India
[c] Department of Mechanical Engineering, University of Ottawa, 161, Louis Pasteur, Ottawa ON, Canada K1N 6N5

ARTICLE INFO

Article history:
Received 19 September 2020
Received in revised form 5 September 2021
Available online 21 October 2021

Keywords:
Entropy
Broken symmetry
Phase transition

ABSTRACT

Heat removal from a crystalline material at its critical temperature results in phase transitions which are associated with spontaneous symmetry breaking whereby the final state exhibits infinite degenerate states. Calculations of entropy changes in such systems are not addressed in classical thermodynamics as the system is driven away from equilibrium due to the asymmetric energy landscape of the system. Here, we present a novel mathematical formulation that allows us to calculate entropy changes in such systems while arguing that heat applied to such a system results in an increase in entropy along with the excitation of Goldstone modes. These ideas offer a novel theoretical framework towards understanding the phenomenon of entropy changes in systems driven away from equilibrium.

© 2021 Elsevier B.V. All rights reserved.

1. Introduction

Entropy changes in thermodynamics are defined while assuming the condition of equilibrium associated with the initial and final states of a thermodynamic process [1]. The concept can also be applied, in principle, while calculating entropy changes during phase transitions where each of the successive states are assumed to be in equilibrium during heat transfer [2]. However, phase transition is an irreversible process involving non-equilibrium thermodynamics [3]. Entropy change calculations in non-equilibrium thermodynamics incorporate the rate of change of dissipation energy, entropy production [4] and the nature of the dissipative system [5,6]. Such formulations cannot be applied in calculating entropy changes during a phase transition as it is a non-dissipative process for which the energy landscape of the system undergoes symmetry breaking. Hence, calculation of entropy changes under such conditions would greatly benefit from a mathematical formulation associated with the physics of phase transitions. It must incorporate the role which electromagnetic potentials play at different locations within a crystal and which are physically connected through symmetry relations. The corresponding symmetry of these potentials is defined by the space-group symmetry of the crystal [7] which is transformed or broken under phase transitions and changes in crystal structure [8].

In ferromagnetic materials, there is no finite value of magnetism at room temperature, but below the Curie temperature, there is spontaneous symmetry breaking where the ground state has an infinite number of degenerate states and the system adopts one of the many possible states leading to finite magnetization [9,10]. In a related form of symmetry

* Corresponding author at: Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, 77, Massachusetts Avenue, Cambridge, MA 02139, United States of America.
E-mail address: dhiraj@mit.edu (D. Sinha).

https://doi.org/10.1016/j.physa.2021.126525
0378-4371/© 2021 Elsevier B.V. All rights reserved.

breaking called explicit symmetry breaking, the dynamic equations of the system contain terms which inherently break the symmetry of the system and the final state is uniquely defined by the constraints imposed on the system [11]. Magnetization induced in a certain direction under strong magnetic field is an instance of explicit symmetry breaking in which the final state is uniquely defined by the constraints imposed on the degrees of freedom associated with the final state. As all phase transitions under thermodynamic changes are associated with symmetry transformations, entropy changes should naturally incorporate the nature of symmetry breaking.

The classical notion of phase transition is centered on equilibrium systems and quasistatic processes. In order to capture the physical nature of phase transitions, the concept of dynamical phase transitions was introduced where the entropy production has a non-zero value. Currently, a widely accepted model of dynamic phase transition in quantum systems, argues that the system relaxation time diverges around the critical temperature [12,13]. Another key aspect of dynamical phase transition is that the fluctuations generate small domains creating inhomogeneous orientation of the order parameter [14].

2. Entropy changes under symmetry breaking in ferromagnetic systems

In a ferromagnetic system at high temperature, the microscopic atomic magnets do not have any global orientation due to thermal fluctuations [9]. It can be considered a closed system in thermodynamic equilibrium whose physical state is invariant and has continuous symmetry. Considering a small quantity of heat applied to the system (δQ) or removed from it, such that the existing symmetry remains intact, we can calculate the infinitesimal entropy change, dS using the Clausius' form of the second law of thermodynamics, $dS = \delta Q/T$, where T is temperature.

When the temperature is lowered below the Curie temperature, the role of thermal interactions subside and interactions between atomic magnets dominate, thereby leading to an orientation of the neighboring entities parallel to each other which propagates and yields a net global ordering of the system and a macroscopic finite magnetization [9]. Below the critical temperature, the system undergoes a phase transition with the appearance of an ordered phase. We say that the existing symmetry is spontaneously broken and there is a degenerate ground state associated with the presence of massless modes having continuous symmetry. In other words, the symmetry of the system is reduced and the new state has an infinite number of equivalent symmetric states. A macroscopic order parameter describes the physical nature and degree of broken symmetry. An important underlying assumption is that for a specific value of order parameter, the energy function, which is dependent on order parameter is analytic [10]. In the context of ferromagnetic material, the total average spin or the magnetization is the order parameter as the Hamiltonian is invariant to a change in direction of spin. For a non-interacting superfluid material, the Hamiltonian is invariant to a change in phase of the wavefunction. Hence, the order parameter is the particle wavefunction associated with the particle of the Bose Einstein condensate. For a nematic liquid crystal, a tensor characterizing the anisotropy of the system is the order parameter. The value of order parameter changes continuously up to the critical temperature. In this analysis, the fluctuations are neglected and this approximation is called mean value theory.

The symmetry of the ferromagnetic system above the Curie temperature is illustrated in Fig. 1a using a thermodynamic potential function V, which acquires a minimum value with zero magnetization in the absence of an applied magnetic field above the critical temperature. Below the Curie temperature, the magnetization develops along the minimum values of the thermodynamic potential which illustrate the degenerate ground states as shown in Fig. 1b.

Entropy change calculations in such a system should also incorporate the nature of changes in the system's internal energy where, for instance, heat applied to the given ferromagnetic material can cause oscillations in the magnetization and the resulting modes can propagate along the radial as well as axial direction of the potential energy surface. The curvature of the potential is inverse of the magnetic susceptibility, χ and is a determinant of the energy associated with fluctuations of infinite wavelength which are associated with generation of massive modes. The value of the inverse magnetic susceptibility is zero along the transverse direction of the order parameter, which is magnetization in the current case. Thus, the transverse susceptibility is associated with massless modes which are also called the Goldstone modes and appear under spontaneous symmetry breaking [15,16]. These are also called spin waves or magnons.

According to Landau theory, the Gibbs free energy can be expressed as a power series of the order parameter [17,18]. It incorporates mean-field approximation, where the magnetization is treated as a uniform physical entity in space and the fluctuations are assumed to be negligible. It is assumed that the value of magnetization lies within a narrow range around its equilibrium such that the free energy is minimum. Thus, it offers a framework towards understanding the existence of a critical point and in calculating critical exponents.

It is argued that the derivative of free energy is non-analytic during phase transition, hence, the free energy cannot be truly expressed as a sum of power series at the phase transition [10]. The non-analyticity at phase transition emerges as the partition function involves the sum of all the value of order parameter. However, as the actual free energy is equivalent to some minimum value of the free energy function, hence, Landau's theory of phase transition can still be applied. If the order parameter is fixed, the free energy is analytic. The approximation fails under lower dimensions, renormalization is needed to get correct results.

In a ferromagnetic system, the order parameter is magnetization and the total energy can be expressed as [18]

$$V = a(T - T_C)m^2 + bm^4 + O(m^6), \tag{1}$$

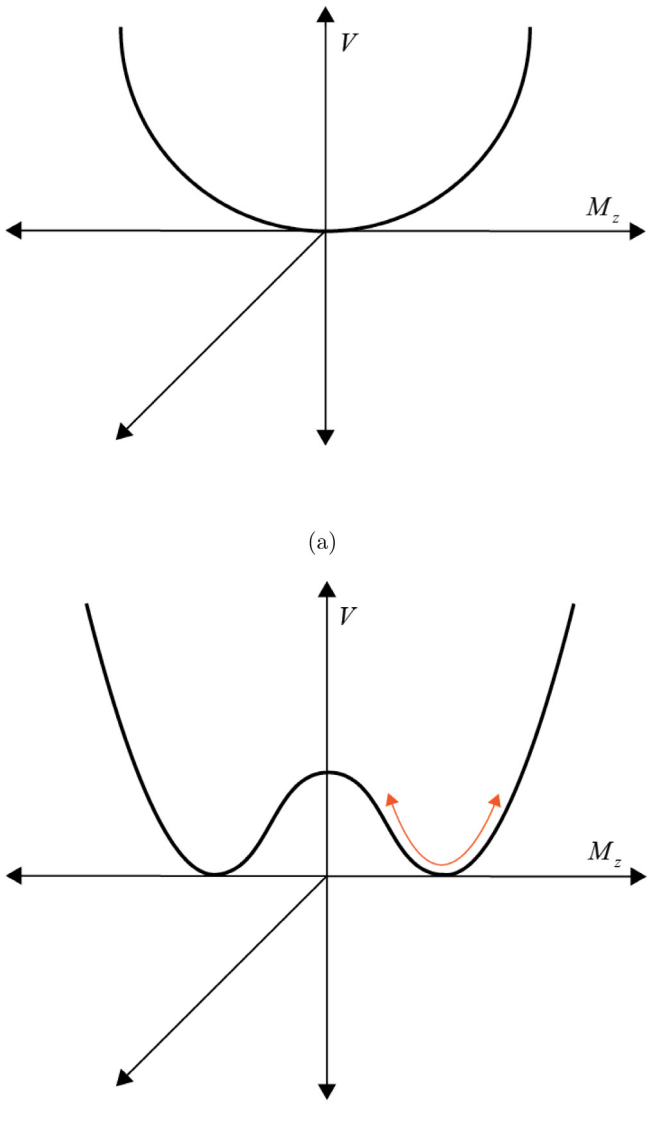


Fig. 1. Magnetization under spontaneous symmetry breaking. a. Relationship between effective thermodynamic potential V and magnetization M above Curie temperature. There is no net magnetization around the minimum value of V. b. For temperatures below the Curie temperature, the minimum values of thermodynamic potential yields magnetization even in the absence of an external magnetic field under spontaneous symmetry breaking. Modes propagating along the direction of the arrow lead to development of an energy gap.

where m is magnetization, a and b are constants, T_C is critical temperature and $O(m^6)$ is a function of higher order terms which can be neglected. The magnetization can be expressed as, $m = \phi_x \boldsymbol{x} + \phi_y \boldsymbol{y}$, where ϕ_x and ϕ_y describe the angle of the atomic magnets and, $m^2 = \phi_x^2 + \phi_y^2$. For $T > T_C$, the system has one minimum potential energy state (Fig. 1a), for $T < T_C$, the minimum is divided into two minimum energy degenerate states (Fig. 1b).

We can also use a single complex function, $\phi = (\phi_x + i\phi_y)/\sqrt{2}$ and obtain the following expression for the energy landscape while neglecting higher order terms,

$$V = \beta^2 \phi^* \phi + \frac{1}{2}\lambda(\phi^* \phi)^2, \tag{2}$$

where $\beta = a(T - T_c)$ and λ is a dimensionless quantity with a positive value. The quartic term, $\lambda(\phi^* \phi)^2/2$ preserves global phase symmetry of the potential function. The potential is bounded from below for a positive value of λ. However, when $\lambda < 0$, the minimum energy state corresponds to a value of $\phi = \phi_0$, where the potential is associated with the following

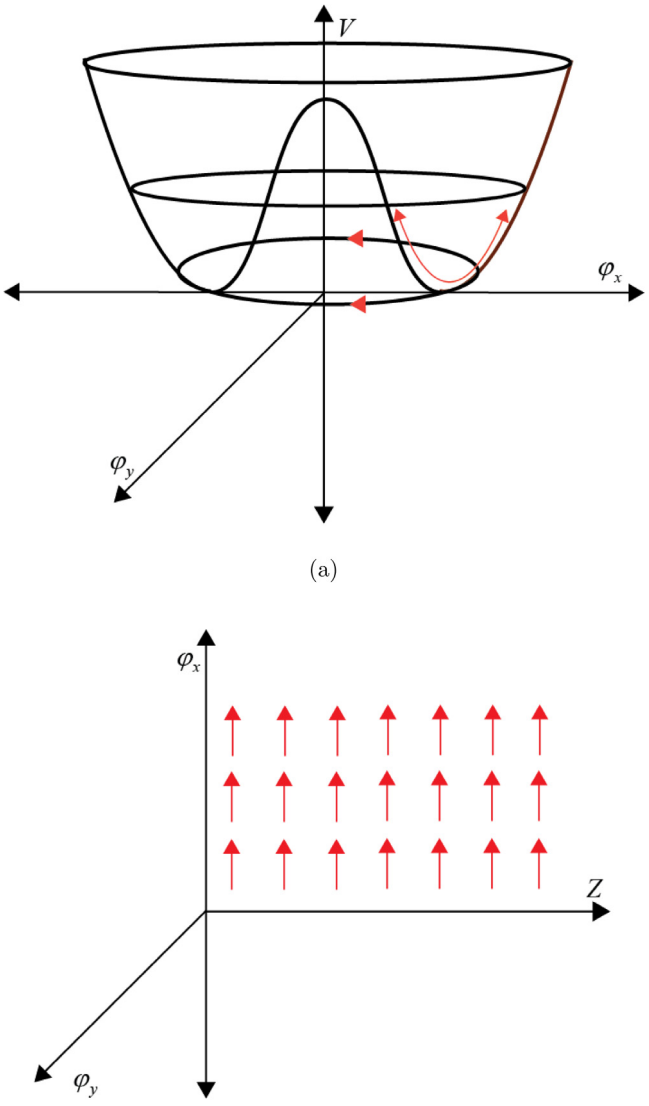


Fig. 2. Mexican hat potential and magnetization. a. Three dimensional Mexican potential hat represents the thermodynamic potential and magnetization. Each point in the valley represents the same value of total magnetization. Fluctuations of magnetization along the vertical arrows lead to massive modes while fluctuation along horizontal arrows lead to Goldstone modes b. The magnetic moments get aligned along a specific direction under spontaneous symmetry breaking.

condition (Fig. 2a),

$$\phi_0^* \phi_0 = \beta^2/\lambda. \tag{3}$$

Eq. (3) represents a circle in the complex ϕ plane, with a radius r, where, $\phi_0 = \beta e^{i\theta}/\sqrt{\lambda} = re^{i\theta}$.

The system has an infinite number of ground states having the same energy for different values of θ, which indicates the phase of the given field. It corresponds to a physical situation where the system was in a state of symmetry initially as represented by a ball at the peak of the Mexican hat potential (Fig. 2a) which drops to the trough spontaneously and rolls along its sides without any additional energy. The dynamics of the system in the initial phase is symmetrical with regard to rotations along the vertical axis. However, the final minimum energy state does not have a symmetry. Thus, the initial symmetry is spontaneously broken which is illustrated by the alignment of magnetic dipole moments in Fig. 2b. The movement of the particle in the potential well does not need any energy and it corresponds to propagation of low energy Goldstone modes.

We need to precisely fix the value of θ and study the dynamics of the ferromagnetic system under variations of the field ϕ in order to evaluate the role of quartic potential in symmetry breaking. When $\lambda \to \infty$, the condition of Goldstone–Sombreao potential occurs and the Lagrangian adopts the least value [19]. The action integral is symmetrical with a change of phase. Here, θ corresponds to exciting the Nambu–Goldstone boson and symmetry transformation results in a phase shift. It does not preserve the ground state. In other words, the transformation, does not annihilate the ground state which has a degeneracy and is not invariant under the condition of spontaneous symmetry breaking.

Heat applied to a ferromagnetic material below its Curie temperature increases the amplitude of fluctuation of the magnetic moments. This would eventually result in an increase in the amplitude of the axial modes or Goldstone modes, inevitably, leading to an increase in entropy. However, there are additional effects which need to be considered in order to calculate the net value of entropy. A part of the input thermal energy would also be absorbed by the radial modes along the direction of increasing potential indicated by the vertical arrows in Fig. 2b. In order to model this mathematically, we define, $\phi_0 = \beta/\sqrt{\lambda}$ and substitute $\phi = \phi_0 + \chi$, to represent the impact of a dynamical field χ generated as a result of thermal energy which momentary excites the magnetization resulting in fluctuations. Thus, we can write the potential energy as,

$$U = U(\phi_0) + \frac{1}{2}\lambda[\phi_0(\chi^* + \chi) + \chi^*\chi]^2. \tag{4}$$

While using $\lambda\phi_0^2 = \beta^2$ and the relation, $\chi = (\chi_1 + i\chi_2)/\sqrt{(2)}$, we get

$$U = U(\phi_0) + \beta^2\chi_1^2 + O(\chi^3), \tag{5}$$

where $O(\chi^3)$ is a function representing the higher order terms. When $\phi = 0$, the system's state is at a vacuum state which is unstable and possesses symmetry along the radial directions. As the system adopts a specific value of $\phi = \phi_0$, the symmetry is lost, or in other words, explicitly broken and there is variation of $\beta/\sqrt{\lambda}$. For the field, χ_1, massive modes with the angular frequency, $\omega = \sqrt{(k^2 + 2\beta^2)}$, where, k is the wave number are generated. It results in an overall change in the magnitude of magnetization as illustrated in Fig. 3a. The associated modes behave like mass which is oscillation of a field when it is homogeneous and has infinite wavelength. If the wavelength of a particular field is infinite, any displacement leads to oscillations of the entire field [20]. The physical situation corresponds to a particle at rest with infinitely long wavelength which is expressed through the relationship $p = h/\lambda$, where, p is momentum, λ is wavelength and h is the Planck's constant. In other words, mass corresponds to oscillation of a field when it is homogeneous and has infinite wavelength. A phonon has no mass as the shift in atoms is not homogeneous. Plasmons have a mass as it corresponds to a homogeneous shift of charges [20]. A massive excitation has a dispersion relation that does not become zero at $k = 0$, but has a curvature. Thus, mass is also connected with the curvature of the potential energy surface at the equilibrium point. As soon as the field is shifted away from the equilibrium point, it starts to oscillate. If $\omega \neq 0$ at $k = 0$, the value of ω at that value of k is the mass. It is worth mentioning that such modes should exist in crystals, however they have not been observed until now. A similar phenomenon leads to mass in high energy physics where the mechanism of generation of an energy gap under explicit symmetry breaking is widely referred to as spontaneously broken gauge symmetry [21–23].

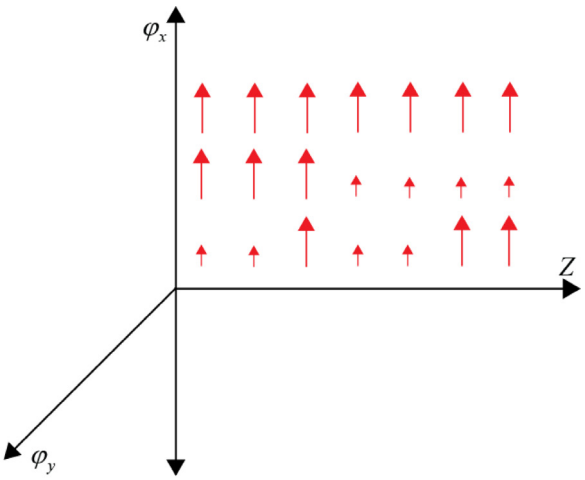
For the field χ_2, there is no quartic term and it corresponds to the existence of a massless boson called Goldstone Boson with the dispersion relationship $\omega = kv$, where v is the velocity (Fig. 3b). It propagates along the path of the minimum potential surface at the bottom of the potential energy surface. This is an instance of Goldstone's theorem, which states that for every spontaneously broken global continuous symmetry, there is a field with massless quanta which is called a Goldstone field [16]. When the angular frequency, ω is a linear function of wavenumber, k, there is no dispersion e.g. unity slope of $\omega - k$. It if is not linear, there is dispersion. A massless excitation is the one with a linear dispersion relation. Thus, application of heat causes fluctuations in the magnetization which leads to massless and massive modes which need to be incorporated in calculations on entropy.

3. Goldstone modes under thermal fluctuations

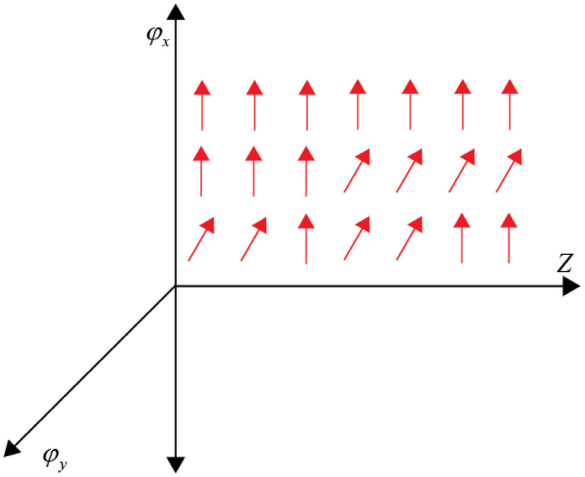
Our current narrative on thermodynamics considers transitions between equilibrium states. The implicit assumption is that if we waited long enough, the system would eventually return to equilibrium [1]. The way a system evolves during the intermediate non-equilibrium phases is not described, which is one of the key goals of the current work.

An important objective of this section is to develop a novel formulation on entropy calculation in systems with low degrees of freedom where fluctuations and non-equilibrium effects dominate the physics. Entropy production under non equilibrium conditions in systems having conservative force fields has not been explored much until now from a deterministic framework, although, there are a number of papers on the subject which address the problem from the perspective stochastic fluctuations. One such example is Crooks fluctuation theorem, which correlates the work done on a system under non-equilibrium transformation to the free energy difference between the two states [24]. It leads to Jarzynski equality which establishes a relation between free energy difference between initial and final non-equilibrium states and irreversible work along the set of trajectories connecting the two states [25].

Landau's mean field theory incorporates an approximation which simplifies the impact of interactions. The effect of neighboring spins on a specific spin is calculated using an averaged physical quantity, called mean field [26]. It does



(a)



(b)

Fig. 3. Generation of modes in ferromagnetic materials a. The excitations along ϕ_x direction represent fluctuation of the magnetization. The corresponding energy does not vanish when the wavelength becomes infinitely large and are massive modes similar to Higgs modes of high energy physics. b. The orientational change of the magnetization do not cost any energy and the corresponding modes can propagate along the valley in the ϕ_y direction. These are Goldstone modes whose energy vanishes as the wavelength becomes infinitely large.

not express the physics of the system when fluctuations, which become dominant near the critical point are taken into account. The correlation length, which indicates the length up to which the interactions have an influence, increases as the temperature is lowered [26]. It tends to diverge around the critical point. The entropy increases logarithmically with an increase in system size, so at low temperatures, energy contribution due to fluctuations is dominant. Microscopic systems are dominated by thermal fluctuations as the system is continuously driven away from equilibrium.

In order to show the role of fluctuations, we consider the statistical interactions defined by the nature of heat bath on the order parameter. The fluctuations can be investigated by considering the response of the magnetization to an external perturbation caused by thermal effect and doing the analysis.

Fluctuation is closely related to dissipation and they are caused by interaction of a system with a heat bath, under which, there is removal of energy as well as addition of energy. At equilibrium, the two terms cancel out and the average energy remains constant. Dissipation is defined as the tendency of systems to move towards equilibrium when different degrees of freedom are allowed to interact with each other. In the process of dissipation of energy, the object's kinetic

energy is redistributed among a huge number of microscopic degrees of freedom, which also generated fluctuations. This is expressed through the fluctuation–dissipation theorem which is also explained in the current work.

We assume that a given crystalline material is at thermodynamic equilibrium at a temperature $T < T_C$ and all the magnetic moments are perfectly aligned along a given direction. At time, $t = 0$, a finite amount of heat Q is added to the system from a heat bath. It would result in the generation of thermal fluctuations, which can induce momentary changes in the localized values of magnetic field associated with a given set of magnetic moments. Assuming that in a given region, a net magnetic flux density of $\boldsymbol{B}$ has been induced, the net torque generated is $\boldsymbol{\Gamma} = \boldsymbol{\mu} \times \boldsymbol{B}$, where $\boldsymbol{\mu}$ is the magnetic moment. The torque is related to the angular displacement, $\boldsymbol{\theta}$ (expressed in radian), by means of, $\boldsymbol{\Gamma} = Id^2\boldsymbol{\theta}/dt^2$ and the resonant frequency of the system is $\omega_n = \sqrt{\mu B/I}$, where I is the associated moment of inertia. The initial change in angular orientation of the magnetic moment is regained under a resistive torque and the energy is dissipated, we can write the expression of the dynamics of the system using the Langevin equation [27,28],

$$I\frac{d^2\boldsymbol{\theta}}{dt^2} = -\boldsymbol{\beta}\frac{d\boldsymbol{\theta}}{dt} - \omega_n^2\boldsymbol{\theta} + \boldsymbol{\xi}(t), \tag{6}$$

where β denotes the coefficient of viscous friction for torsional motion and $\xi(t)$ represents a fluctuating force field with a net value of zero arising as a consequence of interaction with the heat bath. The correlation function relating the fluctuating force $\xi(t)$ at two instants of time t and $t + \tau$ is expressed as,

$$2\beta k_B T\delta(\tau) = \int_{-\infty}^{\infty} \xi(t+\tau)\xi(t)d\tau. \tag{7}$$

Its Fourier Transform, which also represents its spectral density is defined as,

$$S_\xi(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dte^{-j\omega t}\langle\xi(t_1)\xi(t_2)\rangle. \tag{8}$$

Here $j = \sqrt{-1}$ and ω is the angular frequency associated with the force field generated as a consequence of thermal interactions. From Eqs. (7) and (8), we can write, $2\beta k_B T = 2\pi S_\xi(\omega)$ or $S_\xi(\omega) = 2\beta k_B T/\pi$. The spectral density is related to $\xi(\omega)$ through the relationship, $\langle\xi^2\rangle = \int S_\xi(\omega)d\omega$. Substituting the related values, we get, $\xi(\omega) = \sqrt{4\beta k_B T\Delta f}$ over a bandwidth of Δf. We have used the framework adopted by Nyquist, who derived the formulation on noise voltage in conductors while considering the case of two conductors each of resistance R, interacting through a common heat bath [29].

The Laplace transform and separation of terms in Eq. (6), gives the expression of the angular displacement,

$$\theta(\omega) = \frac{\xi(\omega)}{I(-\omega^2 + 2j\zeta_m\omega\omega_n + \omega_n^2)}. \tag{9}$$

Here $\zeta = \beta/(2I\omega_n)$, represents the damping ratio associated with the torsional couple. Thus, we get the expression of angular displacement over a frequency band of 1 Hz,

$$\theta(\omega) = \frac{\sqrt{4\beta k_B T}}{I(-\omega^2 + 2\zeta\omega_n\omega + \omega_n^2)}. \tag{10}$$

It is graphically illustrated in Fig. 4 where the response of the system is asymptotic around the resonance modes of the system. We have used the context of Somarium Cobalt ($SoCo_5$) which has an atomic mass of 445.01 with a domain size in the range of a couple of hundred nanometers [30]. For the calculations, we considered a magnetic domain of radius 585 nm, which has a mass of around 7 picogram and has around 10^10 molecules. The spectral frequency varies from 10 KHz to 10 MHz and the resonant modes are assumed to lie between 0.6 MHz to 10 MHz.

We can also represent the angular displacement of the magnetic moment using the Green's function defined as,

$$\theta(t) = \int_{-\infty}^{\infty} dt' G(t,t')\frac{\sqrt{2\beta k_B T}}{I}, \tag{11}$$

where $G(t,t')$ is the Green's function defined as,

$$G(t,t') = \int_{-\infty}^{-\infty} \frac{d\omega e^{-i\omega(t-t')}}{-\omega^2 + 2j\zeta\omega\omega_n + \omega_n^2}. \tag{12}$$

The inverse Fourier Transform of Eq. (10) leads to the time domain representation of the angular displacement,

$$\theta(t) = \frac{\sqrt{4\beta k_B T}}{\omega_n I\sqrt{(1-\zeta^2)}} e^{-\zeta\omega_n t}\sin\omega_n\sqrt{(1-\zeta^2)}t \tag{13}$$

where, $0 \le \zeta < 1$. It denotes the amplitude of the Goldstone modes generated by thermal fluctuations which decay with time leading to an increase in entropy. The angular velocity of propagation of the modes is expressed as,

$$\omega(t) = \frac{d\theta}{dt} = \frac{\sqrt{4\beta k_B T}}{I} e^{-\zeta\omega_n t}\left[\cos\omega_n\sqrt{(1-\zeta^2)}t - \frac{\zeta\omega_n}{\sqrt{(1-\zeta^2)}}\sin\omega_n\sqrt{(1-\zeta^2)}t\right]. \tag{14}$$

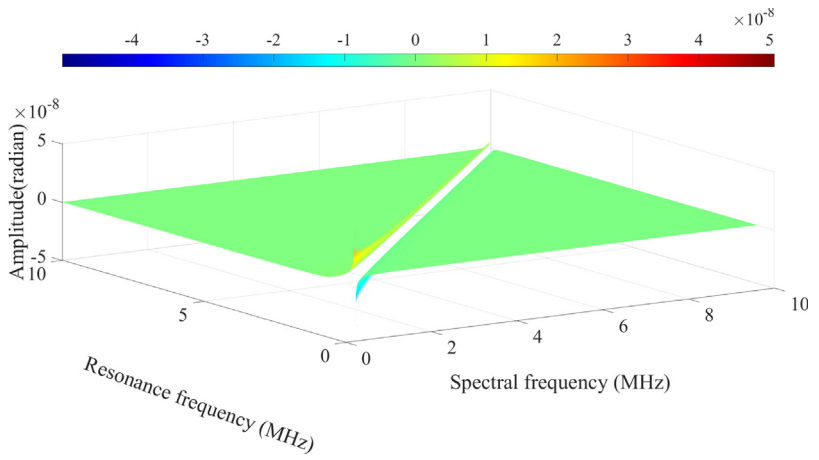


Fig. 4. The frequency domain representation of Goldstone modes which rise asymptotically around the resonant modes. The spectral frequency is assumed to vary from 10 KHz to 10 MHz and the resonant modes are assumed to exist between 0.6 MHz to 10 MHz.

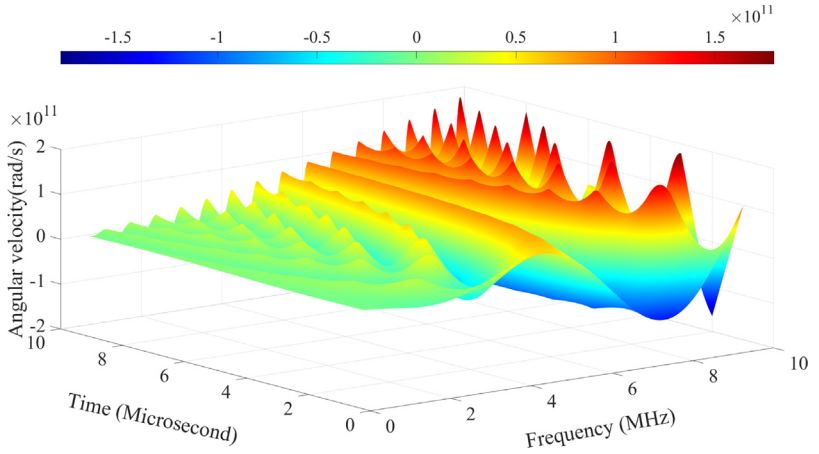


Fig. 5. Time dependence of angular velocity. The Goldstone modes propagate with an angular velocity before finally decaying. The wave evolves from 0 to 10 μs and the resonant modes are assumed to exist between 0.6 MHz to 10 MHz. For the calculations, a sample of around 7 picogram of Somarium Cobalt ($SmCO_5$) with an atomic mass of 445.01 and a magnetic domain of radius 585, was considered.

It is graphically illustrated in Fig. 5 where the angular frequency appears to be attenuated with time. The frequency is in the range of THz, which corresponds to measured values of magnons in ferromagnetic materials [31]

When the damping ratio, is, $\zeta = 1$, the angular displacement of the magnetic moment is,

$$\theta(t) = \frac{\sqrt{2\beta k_B T}}{2\omega_n I\sqrt{(\zeta^2-1)}}\left[e^{-(\zeta-\sqrt{\zeta^2-1})\omega_n t} + e^{-(\zeta+\sqrt{\zeta^2-1})\omega_n t}\right]. \tag{15}$$

The corresponding angular velocity is,

$$\omega(t) = \frac{d\theta}{dt} = -\frac{\sqrt{2\beta k_B T}}{2\omega_n I\sqrt{(\zeta^2-1)}}\left[(\zeta-\sqrt{\zeta^2-1})\omega_n e^{-(\zeta-\sqrt{\zeta^2-1})\omega_n t} + (\zeta+\sqrt{\zeta^2-1})\omega_n e^{-(\zeta+\sqrt{\zeta^2-1})\omega_n t}\right]. \tag{16}$$

This time dependence of angular displacement and angular velocity associated with magnetic moments can be used in calculating the total entropy change under heat transfer in a ferromagnetic system. The damping coefficient is a constant for a given system under a given set of physical conditions, which implies that at a certain temperature, the orientation of the magnetic moments can be calculated using a deterministic framework, which offers a pathway towards calculation of entropy changes under phase transition, which are associated with non-equilibrium force fields.

4. Entropy changes under Goldstone modes

When heat is applied to a system with a state of spontaneous symmetry breaking, the thermal energy excites the Goldstone modes. This can also be interpreted as an increase in entropy of the system.

A process driven away from equilibrium is a process where entropy is produced. The issue of entropy production can be understood from the perspective of generation and propagation of Goldstone modes in a magnetic material. The energy stored at a certain instant of time is $(1/2)\omega_n^2 I\theta^2$ and the total energy dissipated over a differential time, dt, is $(1/2)\beta\omega^2 dt$. Thus, if an input heat δQ is transferred to a material, the total entropy change is, $dS = \delta Q/T$. A part of the input energy increases the energy of Goldstone modes expressed as, $(1/2)\omega_n^2 I\theta^2$ or $(1/2)k\theta^2$, where k is the force constant, and the other part is dissipated as heat. The rate of heat dissipation is expressed as, $(1/2)\beta\omega^2$. Thus, the total entropy change over a period of time dt can be expressed as,

$$dS = \frac{\beta\omega^2 dt - k\theta^2}{2T}. \tag{17}$$

The net change in thermal energy can be correlated to the energy of the Goldstone modes, thus, heat, $Q = \Delta H$, where ΔH is the total Hamiltonian of the Goldstone modes and it can be written as, $\Delta H = \int \Gamma d\theta$, where Γ is the net torque on the magnetic atoms which are displaced by infinitesimally by an angle $d\theta$. The Goldstone modes are Fourier transform obtained from the torque. The entropy change can be expressed as, $\Delta S = \int \delta Q/T = \Delta H/T$, where T is the temperature of the crystal.

Under explicit symmetry breaking, a part of the input thermal energy is annihilated by the generation of Higgs like modes which propagate in a direction orthogonal to the Goldstone modes. An effective energy gap ΔU is associated with these massive modes which can reduce the total amplitude of Goldstone modes. For example, in a crystalline solid at room temperature conditions, the Goldstone modes in the solid correspond to phonons [32]. When heat is applied, the increase in entropy eventually appears as an increase in amplitude of the phonons which can be represented by a change in its Hamiltonian, ΔH. However, the associated massive modes do not result in an increase in entropy. Thus, when a part of the input thermal energy is transformed into massive modes, it results in a relative decrease in entropy. Considering this, the net change in the thermal energy can be expressed as, $\delta Q = \Delta H - \Delta U$ and the entropy change can be written as, $\Delta S = \int \delta Q/T = (\Delta H - \Delta U)/T$.

According to statistical thermodynamics, the entropy of a macroscopic system is given by $S = k_B \ln \Omega(E)$ where, $\Omega(E)$ is the total number of accessible states and is a function of energy E and K_B is Boltzmann constant [1]. The entropy change can be expressed using a Taylor expansion,

$$\Delta S = k_b \ln \Omega(E + \Delta H - \Delta U) - k_B \ln \omega(E) = k_B\left(\frac{\partial \ln \Omega}{\partial E}\right)(\Delta H - \Delta U) + K\frac{1}{2}\frac{\partial^2 \ln \Omega}{\partial E^2}(\Delta H - \Delta U)^2 + \cdots\cdots. \tag{18}$$

We substitute $\partial \ln \Omega(E)/\partial E$ by a constant η, in order to simplify the expression, and obtain,

$$\Delta S = k_B \ln \Omega(E + \Delta H - \Delta U) - k_B \ln \omega(E) = k_B \eta(\Delta H - \Delta U) + k_B\frac{1}{2}\frac{\partial \eta}{\partial E}(\Delta H - \Delta U)^2 + \cdots\cdots. \tag{19}$$

The source of heat is a large thermal reservoir which indicates that η does not change significantly enough to warrant inclusion of higher order terms in the equation. Here, the underlying assumption is that it is an isothermal process. We substitute η by $1/(k_B T)$, where k_B is Boltzmann constant and T is temperature, finally obtaining the expression of entropy change at a given temperature as the ratio of change in thermal energy and temperature. Thus, entropy at a given instance of time, while incorporating the role of conservative force fields at a temperature T, can be expressed as $\Delta S = \Delta Q/T = (\Delta H - \Delta U)/T$. The issue of entropy reduction in a thermodynamic process under conservative force fields in a classical systems under conservative force field has also been discussed elsewhere [33].

Thus, the net value of entropy change under the impact of thermal energy is determined by the symmetry changes associated with phase transitions. Fig. 1a and b show the potential energy landscapes associated with the phase transitions above and below the critical temperature.

If the final energy state has many degenerate states, it would lead to spontaneous symmetry breaking similar to ferromagnetic transitions. The key point of the argument is that the potential energy landscape defines the nature of symmetry breaking during phase transitions — whether spontaneous or explicit.

It is worth adding that the ideas on entropy reduction have been discussed in the context of ferromagnetic materials but can be applied to all crystalline materials. For example, a piezoelectric crystal has a finite value of polarization below critical temperature. Transfer of heat to such a system excites the Goldstone modes which are polarization waves or polarons. However, the Higgs like massive mode would also be generated leading to a finite vale of entropy reduction.

In non-ferroelectric solids, the electromagnetic potentials at different locations in a crystal are associated through symmetry relations which are defined by the space-group symmetry of the crystal [2]. Under the application of heat, the symmetry of the potential is transformed or broken under phase transitions and changes in crystal structure. The entropy calculations should incorporate the generation of Goldstone and Higgs like modes around the broken symmetries of the potential energy landscape.

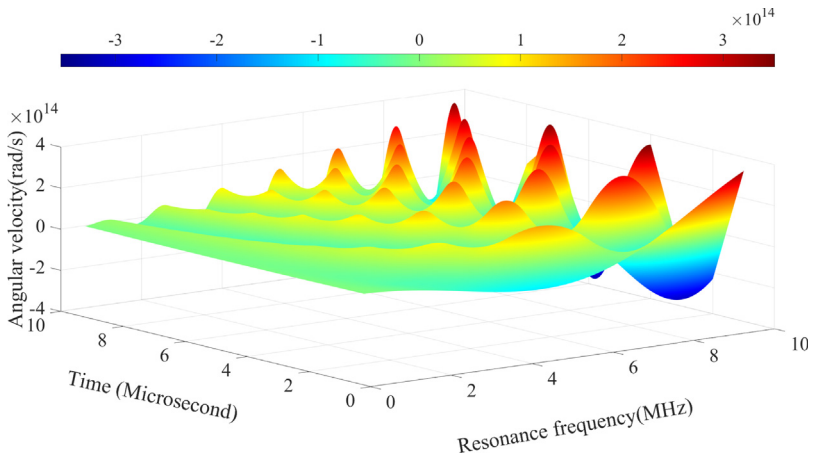


Fig. 6. The Goldstone modes can generate specific changes in the energy profile of a material imparting a specific pattern to it at a given instant of time generating complex patterns. The wave evolves over a period of 0 to 10 μs and the resonant modes are assumed to exist between 0.6 MHz to 10 MHz. Each of the resonant mode can impart a specific crest in the resultant pattern.

5. Entropy reduction in dissipative systems

Entropy reduction in thermodynamic systems during a phase transition should reveal itself in the form of generation of order at some time and length scales under thermodynamic fluctuations induced by heat. However, entropy reduction and order generation under thermal fluctuations are generally observed in the context of dissipative systems leading to self-organization [34,35]. Such systems are associated with a potential energy function $V(x)$ whose values change when heat is applied to the system. Thus, despite the word 'dissipative systems', such systems are characterized by conservative force fields with a continuous potential energy function. According to Prigogine, if a closed system with an entropy S_0 is perturbed around its equilibrium, its stability can be described using a Lyapunov function. As all Lyapunov functions can be expressed in terms of potential energy functions [36], the entropy changes can be associated with an energy gap generated by the massive modes, which can have a negative values leading to a net order and entropy reduction around the perturbation leading to the formation of a specific pattern. Fig. 6 depicts a snapshot of a Goldstone mode in a block of Somarium Cobalt, a ferromagnetic material, under a relatively high damping coefficient which can impart a specific pattern to a system under a given condition of heat transfer. Although a sinusoidal wave propagation has been illustrated, in more complex cases, a Gaussian wave packet could be generated under thermal impact while generating more complex patterns along temporal and spatial dimensions. The kinetic energy of the Goldstone modes has a potential energy component, which can play a key role in inducing other related modes while generating more complex patterns in a physical system under heat transfer.

Prigogine highlighted the role of fluctuations in entropy production and irreversibility in the context of systems driven far away from equilibrium [34]. An important aspect of Prigogine's work is on the generation of order from non-equilibrium systems [35]. However, the phenomenological level of entropy production or the rise of order, both remain unexplained.

In recent years, stochastic formulations have been used to define the nature of entropy changes at the microscopic level. According to the Fluctuation Theorem, in the context of a system driven away from equilibrium, the ratio between probability P, that the system results in production of an average positive entropy, $S = A$, to its probability of production of negative entropy over a period of time t, is given by $P(S = A)/P(S = -A) = e^{At}$ [37]. In a related work, Wang et al. trapped beads in optical tweezers in fluid medium and the system showed entropy reduction over short time scales in apparent violation of the second law of thermodynamics [38]. Evans et al. in their initial paper, argued that shearing forces are associated with thermodynamic fluctuations [37] which were empirically verified by Wang et al. through the optical tweezer experiments, where an optical tweezer generates a potential energy valley which applies a force on the molecules [5] defined as $\boldsymbol{F}_{grad} = -n_m^3 r_p^3 (n_c^2 - 1)/(n_c^2 + 2)\nabla \boldsymbol{E}^2/2$, where n_m is medium refractive index, n_c is relative index of the particle, r_p is radius of the particle and $\boldsymbol{E}$ is the electric field [37]. During that process, work is transferred to the bead, leading to entropy reduction. A microparticle being levitated by a laser beam in fluid is a complex example of an interplay between conservative and non-conservative force fields where distinction between heat to work transformation gets blurred. Hence, the physical results, which Evans et al. interpreted as entropy reduction due to fluctuations and violation of the second law of thermodynamics under fluctuations, could be interpreted as entropy reduction under work transfer induced by the potential well of the optical beam. Thus, an alternative explanation is that a part of the input energy is temporarily absorbed in the massive modes around the potential energy gradient generated by optical tweezers leading to short-term order which is eventually transformed into the corresponding Goldstone modes leading to an increase in entropy.

6. Conclusion

Thermal energy applied to a crystalline material with spontaneously broken symmetry results in excitation of the Goldstone modes along with an increase in entropy. The process is associated with generation of Higgs like modes and an energy gap which reduce the overall entropy of the system. The ideas can be equally applied to general crystalline solids where phase transitions are associated with symmetry breaking. At an experimental level, generation of order under thermal excitation have been observed in dissipative systems, stochastic resonance and particles trapped in optical tweezers where potential energy wells similar to a system having broken symmetries are present. The current work offers new perspectives towards understanding the phenomenon of entropy reduction and generation of order in diverse systems under the thermodynamic fluctuations generated by heat transfer.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

All authors have read and approved the manuscript.

Funding

The work is supported by SUTD-MIT Fellowship.

References

[1] F. Reif, Fundamentals of Statistical and Thermal Physics, McGraw Hill, New York, 1965.
[2] Glasser L., Lattice and phase transition thermodynamics of ionic liquids, Thermochim. Acta 421 (2004) 87–93.
[3] Malte Hankel, Haye Hinrichsen, Sven Lübeck, Michel Pleimling, Non-Equilibrium Phase Transitions, Springer, Berlin, 2008.
[4] L. Onsager, Phys. Rev. 37 (1931) 405–426.
[5] P. lansdorff, I. Prigogine, Thermodynamic Theory of Structure, Stability, and Fluctuations, Wiley-Interscience, London, 1971.
[6] G. Lebon, D. Jou, J. Casas-Vázquez, Understanding non-equilibrium thermodynamics: Foundations, applications, in: Frontiers, Springer-Verlag, Berlin, 2008.
[7] John Clarke Slater, Quantum Theory of Molecules and Solids, Vol. 4, McGraw-Hill, New York, 1974.
[8] M.E. Fisher, Phase Transitions, Symmetry and Dimensionality, Vol. 4, New York, pp. 43–89, 1972, 1972.
[9] L.D. Landau, Phys. Z. Sowjet. 11 (1937) 26.
[10] M. Kardar, Statistical Physics of Fields, Cambridge University Press, Cambridge, 2007.
[11] D. Sinha, G.A.J. Amaratunga, Phys. Rev. Lett. 114 (2015).
[12] M. Heyl, A. Polkovnikov, S. Kehrein, Dynamical quantum phase transitions in the transverse-field Ising model, Phys. Rev. Lett. 110 (13) (2013) 135704.
[13] Heyl M., Scaling and universality at dynamical quantum phase transitions, Phys. Rev. Lett. 115 (14) (2015) 140602.
[14] B. Žunkovič, A. Silva, M. Fabrizio, Dynamical phase transitions and Loschmidt echo in the infinite-range XY model, Phil. Trans. R. Soc. A 374 (2069) (2016) 20150160.
[15] J. Goldstone, Nuovo Cimento 19 (1961) 154.
[16] J. Goldstone, A. Salam, S. Weinberg, Phys. Rev. 127 (1962) 965.
[17] H.T. Stoof, K.B. Gubbels, D.B. Dickerscheid, Ultracold Quantum Fields, Springer, Amsterdam, Dordrecht, 2009.
[18] L.D. Landau, Selected works (nauka, moscow, 1969, in: D. ter Haar (Ed.), Collected Papers of L.D. Landau, Vols, 1, 2, Pergamon Press, London, 1965, (in Russian).
[19] Dhiraj Sinha, Gehan A.J. Amaratunga, Explicit Symmetry Breaking in Electrodynamic Systems and Electromagnetic Radiation, Morgan & Claypool Publishers, 2016.
[20] P. Anderson, Phys. Rev. 130 (1963) 439.
[21] P. Higgs, Phys. Rev. 145 (1966) 1156.
[22] G.S. Guralnik, C.R. Hagen, T.W.B. Kibble, Phys. Rev. Lett. 13 (1964) 585.
[23] F. Englert, R. Brout, M. Thiry Il, Nuovo Cimento 43 (1966) 244.
[24] G. Crooks, Phys. Rev. E 60 (1999) 2721.
[25] C. Jarzynski, Phys. Rev. Lett. 78 (1997) 2690.
[26] D.I. Uzunov, Introduction To the Theory of Critical Phenomena: Mean Field, Fluctuations and Renormalization, World Scientific, Singapore, 1993.
[27] A. Einstein, Ann. Der Phys. 17 (1905) 549.
[28] Paul Langevin, CR Acad. Sci.(Paris) 146 (1908) 530–533.
[29] H. Nyquist, Phys. Rev. 32 (1928) 110.
[30] M. Duerrschnabel, et al., Nat. Commun. 8 (2017) 1–7.
[31] A.V. Chumak, A.A. Serga, B. Hillebrands, Nature Commun. 5 (2014) 1–8.
[32] H. Wagner, Z. Phys. 195 (3) (1966) 273.
[33] D. Sinha, Physica A 416 (2014) 676–683.
[34] P. lansdorff, I. Prigogine, Thermodynamic Theory of Structure, Stability, and Fluctuations, Wiley-Interscience, London, 1971.
[35] I. Prigogine, Physica 31 (5) (1965) 719–724.
[36] A.M. Lyapunov, The general problem of motion stability, Annal. Math. Stud. 17 (1892).
[37] D.J. Evans, E.G.D. Cohen, G.P. Morriss, Phys. Rev. Lett. 71 (1993) 2401.
[38] G.M. Wang, E.M. Sevick, E. Mittag, D.J. Searles, D.J. Evans, Phys. Rev. Lett. 89 (2002) 050601.