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Entropy changes in a thermodynamic process under potential gradients

Dhiraj Sinha *

Centre for Advanced Photonics & Electronics, Department of Engineering, University of Cambridge, 9, JJ Thomson Avenue, Cambridge, CB3 0FA, UK

HIGHLIGHTS

- Formulation of entropy as a difference between the changes in Hamiltonian and potential energy.
- Derivation of a new formula of entropy from Boltzmann's formula while incorporating potential energy changes.
- Discussion on symmetry of a thermodynamic system at equilibrium.

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ABSTRACT

Thermal energy applied to particles in conservative vector fields results in an increase in the potential and kinetic energy causing an increase in entropy. However, conservative fields associated with potential energy gradients of the system act in opposition to the kinetic energy gradients reducing the overall accessible states of the system and its entropy. Thus, entropy can be expressed as the ratio of difference between the input energy and potential energy of the system to its temperature. As the input energy represents the changes in Hamiltonian of the system, entropy can also be expressed as the difference in changes of its Hamiltonian and potential energy. Formulation of entropy in terms of the changes in system Hamiltonian and potential energy changes give novel insights on the role of potential fields in determining entropy rate and its impact on order and equilibrium.

1. Introduction

Thermal interaction between particles at molecular level are basically governed by the Newton's laws of motion, however, the impact of their cumulative interaction necessitates application of techniques based on statistical physics to study the empirical aspects of a thermodynamic process. The propagation of physical effects associated with kinetic and potential energy components of a system of particles under thermal interaction are different from each other. The kinetic energy of a system is transferred to a neighbouring system of particles at a less energetic state leading to a uniform distribution of energy with time. But the potential energy of a system remains confined around a central field which is the origin of the system potential. For example, heat applied to a set of gas molecules in a conservative vector field increases the kinetic energy of the molecules and they tend to spread out transferring momentum to less energetic gas molecules while resulting in an increase in entropy, but thermal energy transfer can also induce static charges resulting in development of electromagnetic potentials while strengthening force based interaction among conservative fields resulting in a reduction

* Tel.: +44 7504802846.
E-mail address: sinha.dhiraj@gmail.com.

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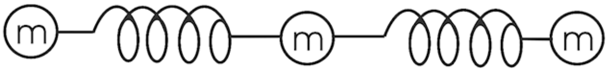

Fig. 1. Heat is applied to the central mass m which results in redistribution of energy and an increase in entropy of the spring mass system. However, the spring elements store energy prior to transferring it to the other masses m and reduce the overall rate of change of entropy depending on the value of spring constant.

in overall accessible states of the system. Thus, the role of potentials and field gradients must be incorporated in calculating entropy changes.

The fundamental laws of thermodynamics are expressed in terms of variables like heat, internal energy, temperature, pressure and volume. However, fields associated with potential energy gradients are not incorporated in the analysis. Besides gravitational and electromagnetic force fields which can influence the evolution of a thermodynamic process, other forms of force fields associated with potential energy gradients viz. elastic energy gradient of an elastic body can influence the thermodynamic process.

2. Entropy in a conservative vector field

The increase in entropy of an isolated system in a spontaneous thermodynamic process under transfer of heat from higher to lower temperature resulting in thermal equilibrium is the basic postulate of the second law of thermodynamics [1]. Heat transfer in a material mainly happens due to transfer of kinetic energy from electrons, molecules and lattice walls of higher temperature to neighbouring systems at lower temperature. The transfer of energy and momentum during thermal transport also results in an increase in finite value of potential energy of the neighbouring particles immersed in different kinds of conservative vector field resulting in energy concentration in localized regions and a reduction in total number of accessible states. For example, when heat is applied to mass m of set of coupled harmonic oscillators through a jet of hot liquid having energetic molecules having an effective mass, μ and acceleration α resulting in a force $F = \mu\alpha$, there is a change in its momentum and the mass gains an acceleration a (Fig. 1). The net force F exerted on mass m results in an acceleration which can be expressed as,

$$m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} = F - kx \tag{1}$$

where k is effective spring constant of springs and x is displacement.

The total work done assuming some displacement of the mass can be expressed as,

$$\int m\frac{\mathrm{d}^2y}{\mathrm{d}t^2}\mathrm{d}x = \int F\mathrm{d}x - \int kx\mathrm{d}x. \tag{2}$$

The work done on the mass m through the jet of liquid is soon dissipated as heat resulting in an increase in entropy which is proportional to the quantity of heat transferred to a system at a specific temperature [2]. It is the input energy to the system and is represented by the positive term on the right hand side of Eq. (2), it results in total change in energy of the system and so it effectively represents the change in Hamiltonian of the system. The negative term in Eq. (2) represents change in potential energy of the system. Its gradient results in a force field which decreases the momentum of the system which reduces the total number of accessible states or the system entropy. The left hand side of Eq. (2) represents the overall kinetic energy of the system which can be transformed into heat at a certain instant of time, thus Eq. (2) can be written as

$$\Delta Q = \Delta H - \Delta U \tag{3}$$

where ΔH is the change in Hamiltonian of the system as a result of input thermal energy, ΔU is the change in potential energy of the system. The entropy of the system at a given instance of time can be expressed as

$$\Delta S = \frac{\Delta Q}{T} = \frac{\Delta H - \Delta U}{T}. \tag{4}$$

Heat is transferred from the central mass to other masses of the harmonic oscillators which are at a lower energy and temperature in accordance to the second law of thermodynamics, but the spring elements of the oscillator store energy from the applied heat resulting in short range order eventually causing a reduction in overall rate of entropy change.

As Lagrangian of a system is the difference between its kinetic and potential energy, hence Eq. (3) can also be expressed as the sum of changes in Lagrangian of the system and its potential energy [3].

$$\Delta S = \frac{\Delta L + \Delta U}{T}. \tag{5}$$

We extend the discussion to include the case of an elastic string of density ρ (mass per unit length) which is subjected to a finite amount of thermal energy at its centre through a certain mass of heated gas. The displacement of string at a certain point x and time t can be represented by $\varphi(x, t)$. Under the impact of force generated by the heated gas molecules, the force