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A thermal force drifting particles along a temperature gradient

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ABSTRACT. In 1972, V. Gallina and M. Omini of the Polytechnic of Turin proposed a phenomenological model for the thermal diffusion in liquid metals, explaining the isotope separation as provoked by a thermal force which is arising when a temperature gradient is established in the material. Here, we discuss this thermal force and its statistical origin from the bulk. We will see that it can be considered as a force of the form \( F = -S \grad T \), that is as a thermal/entropic force obtained from the derivative of the Helmholtz free energy with respect to the volume.

Keywords: Thermal gradient, Thermal transport, Thermal forces, Entropic forces.

Introduction. With the works of Ludwig Boltzmann, physics and thermodynamics started recognizing the stochastic and probabilistic aspect of natural processes. Besides introducing a fundamental equation widely used for thermal and charge transport [1-5], Boltzmann linked the second law of thermodynamics to the disorder of thermodynamic systems, proposing a fundamental relation between entropy \( S \) and probability through the formula \( S = k_B \ln W \) (\( k_B \) is the Boltzmann's constant and \( W \) is for Wahrscheinlichkeit, that is “probability” in German).

The Boltzmann formulation of entropy was fundamental for the “doctrine of energy and entropy” that rules the thermodynamic world [6], a doctrine where the energy is deterministic and the entropy is favouring randomness. In this framework of natural systems governed by energy and entropy, forces can arise from the Helmholtz free energy \( A = U - T S \), where \( U \) is the internal energy, \( T \) the temperature and \( S \) the entropy. Such as the pressure, the mechanical force divided by a surface, is coming from the derivative of internal energy \( U \) with respect to the volume, the same derivative of the product \( T S \) is giving rise to the thermal and entropic forces. These are forces which are coming from the statistical nature of the system, rather than from a particular microscopic interaction existing in it [6].

Entropic forces had been proposed and used in [7,8] for the Brownian motion and for the elasticity of polymers. For the Brownian motion, the force is in the form of a diffusional driving force or radial force, which has a mean value \( \langle F_r \rangle = T \langle dS/dr \rangle \), where \( r \) is a radial distance [9]. We can understand this mean value considering its dimensionality: the force is an energy - here given by the product \( TS \) - divided by a length. However, besides the entropic force which is coming from a local variation or gradient of entropy, we can have also a force in which it is appearing as the gradient of temperature \( T \) multiplied by an entropy, that is \( F = -S \grad T \). A thermal force of this kind is used for the magnetic flux structures in superconductors [10,11]. In these references, this force is also considered as an entropic force.

In the following discussion, we will show another example of such thermal force, which is concerning the isotope separation in liquid metals driven by a thermal gradient. It was proposed in 1972, by V. Gallina and M. Omini of the Turin Polytechnic in a phenomenological model for the thermal diffusion in liquid metals [12]. In their study, the authors aimed giving a formula for the isotope separation in a liquid metal, separation which is observed when a temperature gradient is
established in the fluid [13]. In fact, the approach and the related model proposed in [12] is more general: it embraces completely the problem of thermal diffusion in fluids.

The focus of authors was in investigating the force that is moving atoms through a liquid when there is a thermal gradient in it. In a good approximation, this force has a simple expression: \( F = -k_B \text{grad} T \), where \( T \) is the temperature. In this paper we will see that it can be consider as the thermal/entropic force \( F = -S \text{grad} T \), [10,11]. It means that this is one of the two partners of a pair of forces coming from the derivative of \( TS \) with respect to volume, the other member being the entropic force \( F = -T \text{grad} S \).

Let us start discussing the thermal force appearing in [12].

The thermal force. The central part of Reference 12 is discussing the force responsible for the drift velocity of particles in a temperature gradient. That the drift of particles, appearing when a thermal gradient exists, is an experimental fact. It appears in observed effects and named as thermodiffusion, thermophoresis, thermomigration or Ludwig-Soret effect [14]. This phenomenon, which we find in mixtures of particles where the different types of particles exhibit different responses to the temperature gradient, has a number of practical applications. In fact, due to the different behavior, the particle types can be separated. Several recent papers on isotope separation in silicate melts for instance, are evidencing the present interest on this subject [15-18].

In a first approximation, a particle with radius \( r \) in a solvent has a drift velocity \( w = F/(4\pi\eta r) \) [12]. \( \eta \) is the coefficient of shear viscosity of the solvent. \( F \) is the force drifting the particle. To give an expression of this force, in [12], the authors evaluated first the net force acting on an atom of a solid lattice when it is subjected to a thermal gradient. Each atom of the lattice is a scatterer of thermal waves (phonons). In the second quantization, the displacements of waves are considered as quasiparticles, the phonons, having energy and momentum. If we consider an atom of the lattice, we can imagine it in a local oscillatory motion. It becomes a phonon scatterer, exhibiting a cross-section \( \sigma(q,q') \) for an elastic scattering in which a phonon having wave vector \( q \) is deviated into a phonon of wave vector \( q' \). In fact, this approach would be true only for an impurity scattering: in a perfect lattice, we need at last three phonons involved in scattering processes. However, Gallina and Omini are showing in [12], that using the general theory of phonon-phonon interactions, the same result is obtained.
In (1), \( N \) is the total number of atoms, \( v_g \) the group velocity, \( \lambda_q \) the mean free path and \( g_q \) the deviation from the Bose-Einstein equilibrium function. Since \( g_q \) is proportional to the mean free path in the relaxation-time approximation [5], we have a result independent of the phonon mean-free path. Therefore, in this approximation, the net force turns out to be simply \( F = - k_B \nabla T \). This force has no real effect if the atom belongs to the solid lattice, because this force is simply transmitted to the centre of mass of the crystal. In a liquid, where the atom is not bound to any particular site of the system, the force becomes a driving force, moving the atom towards the cold end of the sample [12].

Are we justified in using this force for an atom in the liquid, since it has been deduced for a solid? [12]. In the reference, the authors are giving specific arguments for a positive answer. First, we have a phenomenological argument: the thermal force only depends upon the atomic specific heat \( c = 3k_B \), and this is a quantity which is presumed to be almost unaffected by the solid-liquid transition. Second: consider an atom \( O \) in the cage of its neighbors. Imagine we have \( \Sigma \) atoms surrounding \( O \). Since the atom can move isotropically toward any of its \( \Sigma \) surrounding, the probability of one of this atoms of moving toward \( O \) is \( 1/\Sigma \). Thus the atom \( O \), at a certain instant, has the probability \( p = 1/\Sigma \) of being struck by one of its neighbors. The time required for an interaction with its \( i \)-neighbor, is \( t_i = a/v_i \), where \( a \) is the nearest-neighbor distance and \( v_i \) the speed of \( i \)-atom.

After some passages, we can find that the mean force acting on \( O \) is [12]:

\[
< \vec{F}_O > = - \frac{1}{\Sigma} \sum_i \frac{mv_i^2}{a} \hat{u}_i = - \frac{1}{\Sigma} \sum_i \frac{3k_B T_i}{a} \hat{u}_i \tag{2}
\]

In (2), \( \hat{u}_i \) is the unit vector from \( O \) to \( i \)-neighbor. \( T_i \) is the temperature of the \( i \)-neighbor. Moreover, \( T_i = T_O + a \hat{u}_i \cdot \nabla T \). Therefore, if we have a statistical environment which is isotropic, we can average on the solid angle:

\[
< \vec{F}_O > = - \frac{1}{a} \frac{\Sigma}{4\pi} \int d\Omega \ 3k_B a \ (\hat{u}_i \cdot \nabla T) \hat{u}_i = -k_B \nabla T \tag{3}
\]

Let us consider again a particle moving in a solvent; if no other forces are present, the drift velocity is given by:

\[
-4\pi\eta \ r \ \vec{w} - k_B \nabla T = 0 \quad \rightarrow \quad \vec{w} = -\frac{k_B \nabla T}{4\pi\eta \ r} \tag{4}
\]

As the authors are remarking, this force has not to be considered as due to a potential gradient, that is, to an external action; it is a statistical force, originated from the bulk of the material, which accounts for the possibility of an atom of making a random walk in the liquid.
To have (3), an atom which is vibrating at temperature $T$ has an energy $3k_B T$. This is true in the approximation of an atom considered as an Einstein harmonic oscillator. However, this energy has to be modified when an anharmonicity exists [12].

**Role of surfaces.** Summing the thermal force over all the atoms of the sample, we should have $F = -N k_B \nabla T$. For $|\nabla T| = 1^\circ C/cm$ and $N=10^{23}$, we have $F \approx 100$ N. Why do we not observe this force? [12]. Let us see how the authors answered. In the case of a solid, we can have that on the wall which is at higher temperature, there is an excess of phonon pressure with respect to the wall at lower temperature. This extra pressure gives rise to a force directed along $\nabla T$, which is exactly counterbalanced by the resultant of the thermal forces. In the case of a fluid, we can see that atoms at the surface of the material give different pressures; there is a force on surfaces which is equal and opposite to the thermal force [12].

![Fig.2. Atoms at the surface of liquid.](image)

For a liquid, let us take an atom of the liquid near the wall (Fig. 2). It makes a random oscillation in a cage of the order of the atomic volume $a^3$. The atom oscillates. If $t$ is the period of the oscillation, we can write $v_x t \approx 2a$, where $v_x$ is the average velocity normal to the wall. Whenever the atom arrives at the wall, we assume an elastic reflection. The transferred momentum is $2mv_x$. If $n$ is the number density of atoms in the liquid, the total number of atoms facing the wall with surface $\Sigma$ is $na\Sigma$. Then the force on the wall is:

$$n a \Sigma \cdot \frac{2mv_x}{t} = n \Sigma m v_x^2 = n \Sigma k_B T$$

where $m v_x^2 = \frac{1}{3} m \left(v_x^2 + v_y^2 + v_z^2\right) = k_B T$ (5)

$$F_{surface} = n \Sigma k_B T_1 - n \Sigma k_B T_0 = n \Sigma L k_B \frac{T_1 - T_0}{L} = N k_B \nabla T$$ (6)

In (6), we have that an unbalanced force on surfaces exists. However, the bulk thermal force balances this surface force. It happens when the two walls at different temperatures have the same surface $\Sigma$. If we have different surfaces, we need to consider the role of the lateral surface, in order to have a net force equal to zero. The conservation of momentum tells us that the net force must be zero.

**Thermal and entropic forces.** Let us consider the Helmholtz free energy $A = U - TS$, and its derivative with respect to the volume $V$. Then, let us multiply this derivative by the surface $\Sigma$. We can consider a generalized force as $F = \Sigma dA/dV = \Sigma dU/dV - \Sigma \dot{S} dT/dV - T \Sigma dS/dV$. The first term is the pressure multiplied by the surface, that is, the mechanical force.
In the case that we assume the volume variation $dV$ as equal to $\Sigma dx$, we have a force $F$ given by three terms, $F = \Sigma p - S dT/dx - T dS/dx$. Then, besides the term containing the pressure, we have the two thermal/entropic terms.

Is the thermal force $F = -N k_B \nabla T$ previously discussed the term $-S dT/dx$? The Boltzmann constant has the dimensions of an entropy $S$; therefore, dimensionally [19], we have the thermal force $F = -N k_B \nabla T$ as $F = -S \nabla T$, and a thermal/entropic force of this kind was used for the magnetic flux structures in superconductors [11,12]. However, we can find a more convincing reason for a positive answer in [20]. In this paper, the Debye model is used instead of the Einstein model. In the case of a phononic assembly, the bulk force is [20]:

$$F_{\text{ph,diff}} = -3N k_B \nabla T \times \left( \frac{T}{\theta_D} \right)^3 \int_{0}^{\theta_D/T} y^4 e^y (e^y-1)^{-2} dy \quad (7)$$

If we are at low temperatures, the entropy $S$ can be considered as $S = C/3$, where $C$ is the heat capacity [21]. In a Debye model [19]:

$$S \approx C/3 = 3N k_B \left( \frac{T}{\theta_D} \right)^3 \int_{0}^{\theta_D/T} y^4 e^y (e^y-1)^{-2} dy \quad (8)$$

Then, the thermal force (7) given by Omini in [20], seems coincident with a thermal/entropic force, in the abovementioned approximation. In fact, using (8) in (7), we have:

$$F_{\text{ph,diff}} = -S \nabla T \quad (9)$$

Also in the case of Eq.3, we can repeat the same observation given above on heat capacity and entropy and have a force $F = -S \nabla T$.

However, besides having the force $F = -S \nabla T$, when we derive the Helmholtz energy we can have $F = -T \nabla S$ too. It means that in the cases discussed in [12] and [20], this entropic force could exist. It is possible because entropy is depending on temperature, and temperature is a function of the spatial coordinates. Therefore a gradient of entropy exists and consequently an entropic force. Since this force could be written as $F = -T (dS/dT) \nabla T$, its effective role in the system requires a further evaluation.

References


