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A statistical thermal force in a fluid

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Abstract

In 1972, V. Gallina and M. Omini proposed a phenomenological model for thermal diffusion in liquid metals. The authors obtained a formula for the isotope separation provoked by a force which is arising when a thermal gradient is established in the material. Here, we discuss this thermal force and its statistical origin from the bulk. We will see that it could be an entropic force. Keywords: Thermal gradient, Thermal transport, Thermal forces, Entropic forces.

Introduction

In 1972, V. Gallina and M. Omini of the Turin Polytechnic, proposed a model for the thermal diffusion in liquid metals, in the framework of a phenomenological theory [1]. In their study, the aim of the authors was that of giving a formula for the isotope separation in a liquid metal, separation which is observed when a thermal gradient is established in the fluid [2]. In fact, the approach and the related model proposed in [1] 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: $F = -k_B \text{grad}T$ (k_B is the Boltzmann constant and T the temperature). It is a thermal force because it is coming from the energy of the system, not from an external action applied to the fluid. Here, we discuss the thermal force proposed in [1], in order to link it, in some future works, to other thermal and entropic forces that are due to the statistical nature of the systems in which they are observed. We will see that we can find a help for investigating this link in another article that M. Omini published in 1999 [3].

The thermal force

The central part of [1] is discussing the force responsible for the drift velocity of particles in a thermal gradient. The drift of particles, appearing when a thermal gradient exists, is an experimental fact: the observed effect is named as thermodiffusion, thermophoresis, thermomigration or Ludwig-Soret effect [4]. 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 behaviour, 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 [5-8].

In a first approximation, a particle with radius r in a solvent has a drift velocity $w = F/(4\pi\eta r)$ [1]. η is the coefficient of shear viscosity of the solvent. F is the force drifting the particle. To

give an expression of this force, in [1], 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 a 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 $\sigma(\mathbf{q}, \mathbf{q}')$ for an elastic scattering in which a phonon having wave vector \mathbf{q} is deviated into a phonon of wave vector \mathbf{q}' . In fact, this approach would be true only for an impurity scattering: in a perfect lattice, we need at least three phonons involved in scattering processes. However, Gallina and Omini show in the appendix of [1], that using the general theory of phonon-phonon interactions, the same result is obtained.

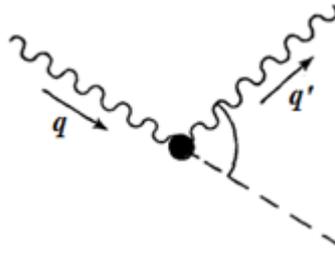


Fig. 1 An atom of the lattice as a scatterer, with transferred momentum equal $\hbar(\mathbf{q} - \mathbf{q}')$.

In the diagram of Fig.1, we can see that the momentum transferred to the atom is clearly $\hbar(\mathbf{q} - \mathbf{q}')$. \hbar is the reduced Planck constant. Adding the contributions of all the scattering processes, which are occurring in unit time, we have the force imparted to the atom by the thermal vibrations. The result is:

$$\bar{F} = \frac{\hbar}{N} \sum_{\mathbf{q}} g_{\mathbf{q}} v_{\mathbf{q}} \bar{q} \frac{1}{\lambda_{\mathbf{q}}} \quad (1)$$

$v_{\mathbf{q}}$ group velocity , $\lambda_{\mathbf{q}}$ mean free path
 $g_{\mathbf{q}}$ deviation from Bose - Einstein function

In (1), N is the total number of atoms. Since the deviation from the Bose-Einstein distribution function, which is the equilibrium one, is proportional to the mean free path in the relaxation-time approximation, we have a result independent of the phonon mean-free path. Therefore, in this approximation, the net force turns out to be simply $F = -k_B \text{grad}T$. 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 [1].

Are we justified in using this force for an atom in the liquid, since it has been deduced for a solid? [1]. 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 neighbours. Imagine we have Σ atoms surrounding O . Since the atom can move isotropically toward any of its Σ 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 neighbours. The time required for an interaction with its i -neighbour, is $t_i = a/v_i$, where a is the nearest-neighbour distance and v_i the speed of i -atom.

After some passages, we can find that the mean force acting on O is [1]:

$$\langle F_O \rangle = -\frac{1}{\Sigma} \sum_i \frac{mv_i^2}{a} \bar{u}_i = -\frac{1}{\Sigma} \sum_i \frac{3k_B T_i}{a} \bar{u}_i \quad (2)$$

\bar{u}_i unit vector from O to i-neighbour
 T_i temp. of i-neighbour, $T_i = T_O + a \bar{u}_i \cdot \nabla T$

Therefore, if we have an isotropic environment, we can average on the solid angle:

$$\langle F_O \rangle = -\frac{1}{a \Sigma} \frac{\Sigma}{4\pi} \int d\Omega 3k_B a (\bar{u}_i \cdot \nabla T) \bar{u}_i = -k_B \nabla T \quad (3)$$

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

$$-4\pi\eta r \bar{w} - k_B \nabla T = 0 \quad (4)$$

$$\bar{w} = -\frac{k_B \nabla T}{4\pi\eta r} \quad (5)$$

As Gallina and Omini 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 [1].

Role of surfaces

Summing the thermal force over all the atoms of the sample, we have $F = -N k_B \text{grad}T$. For $|\text{grad}T| = 1 \text{ }^\circ\text{C/cm}$ and $N=10^{23}$, we have $F \approx 100 \text{ N}$. Why do we not observe this force? [1]. Let us see how the authors answered. In the case of a solid, we can see that on the wall 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 $\text{grad}T$, 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 [1].

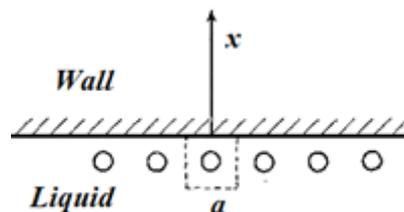


Fig.2. Atoms at the surface of liquid.

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 S is naS . Then the force on the wall is:

$$naS \cdot \frac{2mv_x}{t} = nS m v_x^2 = nS k_B T \quad (6)$$

$$\text{where : } m v_x^2 = \frac{1}{3} m (v_x^2 + v_y^2 + v_z^2) = k_B T, \text{ then}$$

$$F_{\text{surface}} = nS k_B T_1 - nS k_B T_0 = nS L k_B \frac{T_1 - T_0}{L} = N k_B \nabla T \quad (7)$$

In (7), 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 S . 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.

An entropic force

Let us consider the thermal force $F = -N k_B \text{grad}T$. Are we dealing with an entropic force? The Boltzmann constant has the dimensions of an entropy; therefore, dimensionally [9], we have the thermal force as $F = -S \text{grad}T$. An entropy force of this kind is used for the magnetic flux structures in superconductors [10]. However, we can find a more convincing reason for a positive answer in [3]. In this paper, the Debye model is used instead of the Einstein model. In the case of a phononic assembly, the bulk force is [3]:

$$F_{\text{ph. diff}} = -3N k_B \nabla T \times \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} x^4 e^x (e^x - 1)^{-2} dx \quad (8)$$

If we are at low temperatures, the entropy S can be considered as $S = C/3$, where C is the heat capacity [11]. In a Debye model [9]:

$$S \approx \frac{C}{3} = 3N k_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} x^4 e^x (e^x - 1)^{-2} dx \quad (9)$$

Then, the thermal force (8) given by Omini in [3], seems coincident with an entropic force, in the abovementioned approximation. A more refined calculation is of course necessary for a rigorous answer about the coincidence of thermal and entropic forces.

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