The notion of energy through multiple scales: From a molecular level to fluid flows and beyond

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A B S T R A C T

In the present paper, we review the consistent definition of macroscopic total energy in classical fluid mechanics, as a function of the microscopic canonical Hamiltonian field, based on a Lennard-Jones model with some spatially varying external field. The macroscopic total energy (sum of mechanical and internal energy) is proved to be equal to the equilibrium ensemble-averaged Hamiltonian. In particular, the conditions for including the effects of the external field both in the macroscopic potential energy and in the internal energy are discussed. We present the notion of energy as defined in different scientific communities, starting from the standard macroscopic systems all the way down to small ones, which are gaining an increasing popularity.

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1. Introduction and motivation

Energy is a fundamental concept in both physics and engineering. In spite of its tremendous importance and its omnipresence in our modern understanding of Nature, we know very little about it. Energy is usually defined as a conserved extensive property of a physical system, which cannot be observed directly but can be calculated from its thermodynamic state. Hence, the main feature of energy is its conservation, which somehow hides a huge variety of different energies, namely kinetic, potential, mechanical, internal, chemical, electric, magnetic, nuclear, etc. In order to ensure the energy conservation, one could say that, every time that experimental evidences lead to some contradictions, a new form of energy is proposed to re-establish this principle, which is nothing more that the first law of thermodynamics. Moreover, the energy concept pervades many different scientific communities (physics, chemistry, biology and engineering, to mention just few), dealing with extremely different experimental evidences, mathematical approaches and final applications. The interplay between all these varieties inevitably lead to some ambiguities, which represent an essential bottleneck in developing truly multi-scale and multi-physics models, as requested by recent developments in material

science and nanotechnology [1], as well as computational biology and biotechnology [2]. Sometimes it is difficult to compute consistently the same energy by different approaches, simply because of different nomenclatures, conventions, practices, etc. This lack of a common language through multiple scales (and communities) will be elucidated in this paper by an emblematic example through multiple scales, namely energy in molecular dynamics, statistical mechanics, computational fluid dynamics and, finally, engineering design.

Our modern understanding of matter is based on the idea that all macroscopic materials are made of atoms. However this idea have become predominant only very recently. The reason is that, even though nowadays the reality of atoms is considered compatible with religious belief, for long time in the past, atoms presented a challenge for religious belief (see the interesting analysis in Ref. [3]). After Leucippus and his student Democritus proposed the concept of atoms in the fifth century BCE, Epicurus (fourth century BCE) and Lucretius (first century BCE) proposed that the soul is made of atoms as well and dis-aggregates at a later time, meaning that the soul must fall apart after death and hence is not immortal [3]. Of course, the latter point was strongly opposed by Christianity and it might explain the reason why atomism received a negative perception for such a long time. Only from about the middle of nineteenth century, a gradually increasing number of physicists started accepting the reality of atoms, because such a notion enabled (non-obvious) derivation of macroscopic properties of

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substances [4]. The huge number of atoms constituting macroscopic materials requires statistical procedures to fill the gap between atomistic scale and macroscopic scale. Such procedures were beginning to be worked out by a number of physicists in the second half of the nineteenth century, but the outstanding figure among these was Ludwig Boltzmann (see Ref. [4], pertinently entitled 'Ludwig Boltzmann: The Man Who Trusted Atoms'). In 1872, Boltzmann proposed his famous equation which describes the statistical behavior of rarefied particles in non-equilibrium conditions, setting the basis of the non-equilibrium statistical mechanics. The Boltzmann equation is still nowadays the fundamental paradigm to describe rarefied gas dynamics, including both high-speed [5] and low-speed flows (in micro-electro-mechanical systems) [6], vehicular traffic flows [7,8], statistical economics [9] and computational sociology [10]. Moreover, this equation is the theoretical foundation of the lattice Boltzmann method [11–15], which is a powerful numerical method applied much beyond rarefied flows, including thermal radiation [16], thermal conduction [17], combustion [18–21], porous media [22,23], multi-component flows [24,25] and turbulence [26], to mention a few. Remarkably for the present paper, one essential features of the Boltzmann equation is that its collisional kernel, i.e. the mathematical operator describing the collisions between particles, conserves some meaningful quantities (invariants), including particle kinetic energy (elastic collisions).

Even though kinetic equations represent the typical example of mesoscopic description between molecular dynamics and fluid dynamics, clearly kinetic energy is not enough when the interaction potentials among particles become complex, leading to a classical N-body problem. In these cases, the potential energy due to all pairwise interactions among particles is crucial and it allows one to describe much more fluids with realistic rheology [27]. The classical tools, e.g. the system mechanical energy (Hamiltonian), of equilibrium statistical mechanics have been very successful for relating the microscopic properties of individual atoms and molecules to the macroscopic bulk properties of materials. However, modern frontiers of small systems [28] (in material science, nanotechnology, drug discovery, etc.) raise an increasing attention towards non-equilibrium phenomena, where theory has (usually) much less to say. Mesoscopic non-equilibrium thermodynamics, or extended irreversible thermodynamics [29,30], is an active field of research, trying to formulate and rationalize general properties which are common to all non-equilibrium systems, where even the concept of temperature becomes ambiguous [31]. Some of the most significant results of the modern trends in thermodynamics are the so-called fluctuation-dissipation theorems [32]. Very briefly, in 1993 Evans, Cohen and Morriss [33] considered the fluctuations of the entropy production rate in a shearing fluid, and proposed the so called Fluctuation Relation. This represents a general result concerning systems arbitrarily far from equilibrium. Moreover it is consistent with the Green-Kubo and Onsager relations, when equilibrium is approached. This pioneering work has experienced an extensive development by different authors (see Ref. [32] and references therein). The original result has been extended to many different cases and it is now a whole new theoretical framework which encompasses the previous linear response theory and goes beyond that, to include far from equilibrium phenomena, such as turbulence and the dynamics of granular materials [32]. In spite of these exciting achievements, the formulation of a mesoscopic non-equilibrium thermodynamics theory able to analyze irreversible processes at very small scales is still problematic [34,35]. The theory of small-system thermodynamics was developed by Hill [36], mainly dealing with isolated nanoparticles, and, even though it has been successfully applied since then [37], a universal framework is still out of sight. Hence from the practical point of view, molecular dynamics simulations still represent the most viable alternative [38], boosted by very sophisticated softwares (e.g. Ref. [39] among many others), which nowadays allows to handle huge molecular systems (up to $\sim 10^{10}$ atoms).

Even though (conceptually) the theoretical foundations of classical molecular dynamics simulations are clear and mechanical energies of the system (and its sub-parts) are immediately available, the link with macroscopic quantities, which is essential for scaling-up the results, is sometimes underestimated and poorly discussed. For example, many textbooks (in chemical physics) identify the equilibrium ensemble-averaged Hamiltonian as the macroscopic internal energy of the system (for example, see Eq. (2.2.12) in Ref. [27]), which is not correct in general. Moreover, where the effects of the external field end up at the macroscopic scale (if in the macroscopic potential energy or in the macroscopic internal energy) can not be universally stated, because it depends on some properties of the external field (discussed later on, in this paper). The latter point is crucial because, if external effects go into the macroscopic potential energy, they would not contribute to entropy production, otherwise they would. Hence, the assumption that external field never contribute to entropy production may produce large errors, particularly in small systems. The need to clarify such elementary issues in the fluid dynamics community should not surprise. The mathematical theory of fluids is in a very primitive state and the fluid dynamic equations do not have a fundamental nature [40]. In spite of those difficulties, the engineering community largely relay upon fluid dynamic equations and uses them extensively for design and optimization [41]. Moreover, the analysis of the entropy generation is becoming a popular paradigm for design and optimization [42,43], covering a wide variety of applications [44–47].

Taking into account the previous discussion, the present paper can be placed at the intersection between molecular physics and fluid dynamics, which are two disciplines with an increasing overlap (e.g. in microfluidics, lab-on-chips, functionalized interfaces, etc.). Hence, it is of fundamental importance for the future of nanotechnology and biotechnology to clearly define the basic notions underlying their foundations. Of course, the energy concept is first in the list.

The paper is organized as follows. In Section 2, the materials and methods which represent the starting point of our analysis are briefly summarized. In Section 3 the main results are reported, including the fundamental link between the microscopic canonical Hamiltonian and the macroscopic total energy in classical fluid mechanics. In Section 4 some consequences are derived from the fundamental result. Finally, in Section 5, the conclusions are reported.

2. Materials and methods

The main goal of this work is to elucidate and rationalize the link between molecular dynamics simulations and macroscopic computational fluid dynamics. The key idea is to use the concept of total energy of the system both at microscopic and macroscopic level. In particular, classical Hamiltonian mechanics looks particularly promising for this goal because it is a theory both physics and engineering communities are familiar with. Hamiltonian mechanics was first formulated by William Rowan Hamilton in 1833 [48], starting from Lagrangian mechanics, a previous reformulation of classical mechanics introduced by Joseph Louis Lagrange in 1788. By means of more general concepts, Hamiltonian mechanics allows more easily to generalize Newtonian mechanics to N-body systems.

Consider an isolated, macroscopic system consisting of N identical, spherical particles of mass m enclosed in a volume V. The assumption of spherical particles enables to focus only on translational kinetic energy, neglecting rotational and vibrational