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

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Abstract

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.

Keywords: energy balance, fluid dynamics, canonical Hamiltonian, statistical mechanics, Lennard-Jones fluid, molecular dynamics

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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 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, 12, 13, 14, 15], which is a powerful numerical method applied much beyond rarefied flows, including thermal radiation [16], thermal conduction [17], combustion [18, 19, 20, 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 thermodynam-

ics, 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. [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, 45, 46, 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 energy. An example would be a one-component, monatomic gas or liquid: Even though water molecules are not spherical, simplified water models are consistent with such an assumption [27]. In classical mechanics the dynamical state of the system at any time-instant is completely specified by the $3N$ coordinates $\mathbf{x}_1$, $\mathbf{x}_2$, ..., $\mathbf{x}_N$ and $3N$ velocities $\mathbf{v}_1$, $\mathbf{v}_2$, ..., $\mathbf{v}_N$ of the particles. The Hamiltonian of this system $\mathcal{H}$ is defined by the sum of the kinetic energy $\mathcal{T}$ and the potential energy $\mathcal{V}$, namely $\mathcal{H} = \mathcal{T} + \mathcal{V}$, where

$$\mathcal{T} = \frac{m}{2} \sum_{n=1}^{N} \mathbf{v}_n^2, \tag{1}$$

$$\mathcal{V} = \sum_{n_1=1}^{N} \sum_{n_2>n_1}^{N} \mathcal{P}(\|\mathbf{x}_{n_1} - \mathbf{x}_{n_2}\|) + \sum_{n=1}^{N} \mathcal{E}(\mathbf{x}_n), \tag{2}$$

$\mathcal{P}(\cdot)$ is the pair potential between particles, $\|\cdot\|$ is the Euclidean norm and $\mathcal{E}(\cdot)$ is the potential energy of a single particle, arising from the interaction with some spatially varying, external field (e.g. the gravitational field).

An essential (and usually critical) step in any molecular dynamics simulation consists in specifying the proper pair potentials between particles, sometimes called (in technical literature) force fields [38]. Force fields consist of two kind of terms: (a) Bonded terms (e.g. covalent bonds) and (b) non-bonded terms (e.g. van der Waals). In the present work, we are mainly interested in fluids and hence we will focus on non-bonded terms only. One of the most important pair interaction is generated by the electrostatic potential among partial charges. For example, this potential is responsible of the

polar nature of water (by hydrogen bonding). If positive and negative partial charges are present in the same molecule (even globally neutral), they realize an electrical dipole. Due to the underlaying quantum dynamics of outer electron shells, even neutral molecules can be subject to temporary induced dipoles. Both permanent and induced dipoles can interact with surrounding dipoles and with further induced dipoles. In particular, the force between two permanent dipoles is called Keesom force, the one between a permanent dipole and a corresponding induced dipole Debye force, and, finally, the one between two instantaneously induced dipoles London dispersion force. All these three forces are attractive (negative potential). In addition, there is a harsh repulsion that appears at short range and has its origin in the overlap of the outer electron shells (positive potential). The van der Waals force (or van der Waals interaction) is the sum of the attractive or repulsive forces between molecules other than those due to covalent bonds or to the electrostatic interaction of ions with one another or with neutral molecules [38]. A popular mathematical description for the van der Waals force is the Lennard-Jones potential (also referred to as 12-6 potential), namely

$$\mathcal{P}(r) = 4\,\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right], \tag{3}$$

where ϵ is the depth of the potential well, σ is the finite distance at which the pair potential is zero and r is the distance between the particles (i.e. $r = \|\mathbf{x}_{n_1} - \mathbf{x}_{n_2}\|$). Eqs (1,2,3) define the Hamiltonian of the Lennard-Jones fluid model [38].

Once the Hamiltonian of system is defined, the time evolution of the system is uniquely defined by the Hamilton's equations [48]. Molecular dynamics software (e.g. [39]) solves the Hamilton's equations by robust (explicit)

numerical schemes (e.g. Verlet integration, among others). The outcome of molecular dynamics simulations is given by $3N$ coordinates and $3N$ velocities of particles for every time step, also referred to as trajectory. Clearly, the amount of data in a molecular dynamics trajectory is enormous and definitively impractical for getting some insights on the most of phenomena of practical interest.

Most of the times, we are not interested in all the details of a trajectory. Statistical mechanics is generally used to calculate statistical properties of the trajectory, which can be compared with experimental data, i.e. observable properties. Observable properties can be computed either as time-averages over a solution trajectory (the method of Boltzmann), or as averages over an ensemble of systems, each of which is a replica of the system of interest (the method of Gibbs) [27]. Time averages over trajectory are complex because of the large fluctuations of instantaneous macroscopic quantities. Even though it would seem that enormous times are needed before the fluctuations of the time averages over finite times stabilize around the equilibrium limit value [49], time averages are still popular in many molecular dynamics computations [38]. On the other hand, ensemble averages are extremely powerful from the theoretical point, because they allow one to derive analytical formulas (and sometimes to compute statistical properties in molecular dynamics simulations with less noise). A statistical-mechanical ensemble is an arbitrarily large collection of imaginary systems, each of which is a replica of the physical system of interest and characterized by the same macroscopic parameters [27]. For this reason, it has been said very effectively that ensemble average allows to have thermodynamics without dynamics [49]. Unfortunately, the

ensemble average coincides with time average, only under ergodic hypothesis [49]. More details about the ergodic hypothesis can be found in Ref. [49] and references therein. In this work, we will focus on ensemble averages and we will assume that our systems are ergodic (which is a reasonable assumption for Lennard-Jones fluid models).

First of all, in order to use the ensemble average, we represent the solution trajectory as a time sequence of phase points (defined by $6N$ variables each) in a $6N$-dimensional phase space. The distribution of those points can be described by a phase-space probability density $f_{[N]}$ [27]. The quantity $f_{[N]}\,\Pi_{n=1}^{N} d\mathbf{x}_n \Pi_{n=1}^{N} d\mathbf{v}_n$ is the probability that, at the given time, the physical system is in a microscopic state lying in a specific infinitesimal space element of size $\Pi_{n=1}^{N} d\mathbf{x}_n \Pi_{n=1}^{N} d\mathbf{v}_n$. This definition also implies that $\int\int f_{[N]}\,\Pi_{n=1}^{N} d\mathbf{x}_n \Pi_{n=1}^{N} d\mathbf{v}_n = 1$ at any time. The phase-space probability density $f_{[N]}$ satisfies the Liouville equation [50], although its use is not very practical due to the curse of dimensionality ($6N$, where N can be of the other of Avogadro number). For computing thermodynamic quantities, it proves useful to consider some asymptotic equilibrium limit (determined by attracting low-dimensional manifolds for trajectories in the phase-space [51, 52, 53, 54, 55, 56]), namely $f_{[N]}^{(e)}$, which becomes a function of the time-varying coordinates and macroscopic momenta/quantities. From the practical point of view, in most of the fluid dynamic problems (excluding rarefaction effects), the characteristic time to reach the equilibrium limit is extremely short (in comparison with fluid dynamic ones). This time corresponds to the kinetic stage of the Boltzmann equation [50], even though the latter is formulated for the reduced (single-particle) phase-space distribution

function $f_{[1]}$, which is obtained by integrating $f_{[N]}$ over the coordinates and momenta of the other particles. The equilibrium ensemble average can be defined for any microscopic quantity by means of equilibrium phase-space probability density $f^{(e)}_{[N]}$. For example, the equilibrium ensemble-averaged Hamiltonian is defined as

$$\langle \mathcal{H} \rangle^{(e)} = \int \int \mathcal{H}\, f^{(e)}_{[N]}\, \Pi_{n=1}^{N} d\mathbf{x}_n \Pi_{n=1}^{N} d\mathbf{v}_n. \tag{4}$$

The ensemble average depends on the chosen ensemble, hence on the (fixed) macroscopic parameters defining it. Let us consider a canonical ensemble (the name was introduced for the first time by Gibbs), which is a collection of systems characterized by the same number of particles N, volume V and temperature T. For the first time in this work, we refer to the temperature of a system and we can select the elements of the above ensemble by imposing thermal equilibrium between the system and a thermostat at a fixed temperature T. The equilibrium probability density for a system of identical, spherical particles [27] is now

$$f^{(e)}_{[N]} = \frac{\exp(-\beta\, \mathcal{H})}{\int \int \exp(-\beta\, \mathcal{H})\, \Pi_{n=1}^{N} d\mathbf{x}_n \Pi_{n=1}^{N} d\mathbf{v}_n}, \tag{5}$$

where $\beta = 1/(k_B\, T)$ and k_B is the Boltzmann constant ($k_B = 1.38064 \times 10^{-23}$ m^2 kg s^{-2} K^{-1}).

3. Results

One of the problems in establishing a rigorous link between molecular dynamics and macroscopic computational fluid dynamics is due to the fact that the former (most of the times) deals with systems (on average) at rest,

which is never the case for the latter. This may cause some ambiguities in identifying the quantity $\langle \mathcal{H} \rangle^{(e)}$ from a macroscopic point of view. For example, many textbooks (in chemical physics) identify this quantity as the macroscopic internal energy of the system (for example, see Eq. (2.2.12) in Ref. [27]), which is not correct in general.

Here, we present a simple derivation for overcoming this issue.

First of all, let us introduce the mean velocity vector $\mathbf{u}$, namely

$$\mathbf{u} = \frac{1}{N} \sum_{n=1}^{N} \mathbf{v}_n. \tag{6}$$

In case of particles with different masses, the previous definition would be substituted by a mass-based average. Even though $\mathbf{u}$ is computed by means of all $\mathbf{v}_n$, due to the large number of particles, the dependence of the former on each particle velocity is negligible. This is consistent with kinetic theory, where macroscopic moments (in fluid dynamic regime) do not depend anymore on underlying particle velocity. Moreover, velocity $\mathbf{u}$ does not apply to any particle in general. We can conveniently imagine that this velocity is applied in the center of mass $\mathbf{x}$ of the system, namely $\mathbf{u} \equiv \mathbf{u}(\mathbf{x})$, where

$$\mathbf{x} = \frac{1}{N} \sum_{n=1}^{N} \mathbf{x}_n. \tag{7}$$

Also in this case, $\mathbf{x}$ can be interpreted as a macroscopic coordinate, with negligible dependence on the individual particle position. Combining Eq. (6) with Eq. (1) and taking into account that $\sum_{n=1}^{N} (\mathbf{v}_n - \mathbf{u}) = 0$ yield

$$\mathcal{T} = \frac{m}{2} \sum_{n=1}^{N} (\mathbf{v}_n - \mathbf{u})^2 + M e_k, \tag{8}$$

where $M = m\,N$ is the total mass of the system and $e_k = \mathbf{u}^2/2$ is the macroscopic kinetic energy per unit of mass (of course $e_k \equiv e_k(\mathbf{x})$).

The introduction of the concepts of mean velocity and peculiar velocity $\mathbf{v}_n - \mathbf{u}$ (as in kinetic theory) leads to a shift of the microscopic kinetic energy $\mathcal{T}$ by a constant (with regards to microscopic coordinates).

The situation is not so simple in case of the microscopic potential energy and this may be one of the reasons of confusion. In general, in the case of an inhomogeneous fluid, thermodynamic potentials (in particular the excess parts, see below) depend explicitly on the external potential [27]. This is simply due to the fact that external potential of a single particle $\mathcal{E}(\mathbf{x}_n)$ depends, in general, on the particle position $\mathbf{x}_n$. This determines a correction on the system potential and consequently on the ensemble average. For example, this is unavoidable in case of external electrical fields active on charged particles. However, in most of macroscopic fluid dynamics, the external field is due to gravity and some simplifications apply. Here, the potential of a single particle can be expressed as

$$\mathcal{E}(\mathbf{x}_n) = -G\,\frac{m\,M_G}{\|\mathbf{x}_n - \mathbf{x}_G\|}, \tag{9}$$

where G is the gravitational constant ($G = 6.67384 \times 10^{-11}$ m^3 kg^{-1} s^{-2}), M_G is the mass of the external body acting on the system and $\mathbf{x}_G$ is the location of the external body. If the distance of the external body from the system is much bigger than characteristic size of the system, namely $\|\mathbf{x} - \mathbf{x}_G\| \gg \|\mathbf{x}_n - \mathbf{x}\|$, then the following approximation holds $\|\mathbf{x}_n - \mathbf{x}_G\| \approx \|\mathbf{x} - \mathbf{x}_G\|$ and consequently $\mathcal{E}(\mathbf{x}_n) \approx \mathcal{E}$. This is definitively acceptable for computational fluid dynamics in the proximity of Earth. Thus, Eq. (2) becomes

$$\mathcal{V} = \sum_{n_1=1}^{N} \sum_{n_2>n_1}^{N} \mathcal{P}(\|\mathbf{x}_{n_1} - \mathbf{x}_{n_2}\|) + M e_p, \tag{10}$$

where $e_p = \mathcal{E}/m$ is the macroscopic potential energy due to gravity per unit of mass (of course $e_p \equiv e_p(\mathbf{x})$).

Let us now introduce the relative microscopic kinetic energy $\mathcal{T}' = \mathcal{T} - Me_k$, the relative microscopic potential energy $\mathcal{V}' = \mathcal{V} - Me_p$ and consequently the relative Hamiltonian, namely $\mathcal{H}' = \mathcal{T}' + \mathcal{V}'$. The following correlation holds

$$\mathcal{H} = \mathcal{H}' + Me_m, \tag{11}$$

where $e_m = e_k + e_p$ is the macroscopic mechanical energy per unit of mass. It is easy to prove that, because of the properties of the exponential function, the equilibrium probability density is not affected by the shift in the Hamiltonian due to the macroscopic mechanical energy, namely

$$f^{(e)}_{[N]} = \frac{\exp(-\beta\,\mathcal{H}')}{\int\int \exp(-\beta\,\mathcal{H}')\,\Pi_{n=1}^{N} d\mathbf{x}_n \Pi_{n=1}^{N} d\mathbf{v}_n}. \tag{12}$$

Hence, the previous expression can be used instead of Eq. (5). Taking into account again the properties of the exponential function, the denominator of Eq. (12) can be rewritten as

$$f^{(e)}_{[N]} = \frac{1}{K_N\, Z_N}\, \exp(-\beta\,\mathcal{H}'), \tag{13}$$

where

$$K_N = \int \exp(-\beta\,\mathcal{T}')\,\Pi_{n=1}^{N} d\mathbf{v}_n, \tag{14}$$

while Z_N is the configuration integral [27] given by

$$Z_N = \int \exp(-\beta\,\mathcal{V}')\,\Pi_{n=1}^{N} d\mathbf{x}_n. \tag{15}$$

We are now ready to find out the macroscopic meaning of $\langle \mathcal{H} \rangle^{(e)}$ by substituting Eq. (13) into Eq. (4) and following the standard procedure for

canonical ensemble [27], namely

$$\langle \mathcal{H} \rangle^{(e)} = E_i^{id} + E_i^{ex} + E_m, \tag{16}$$

where $E_m = M e_m$ is the macroscopic mechanical energy of the system and

$$E_i^{id} = \frac{1}{K_N} \int \mathcal{T}' \, \exp(-\beta \, \mathcal{T}') \, \Pi_{n=1}^{N} d\mathbf{v}_n, \tag{17}$$

$$E_i^{ex} = \frac{1}{Z_N} \int \mathcal{V}' \, \exp(-\beta \, \mathcal{V}') \, \Pi_{n=1}^{N} d\mathbf{x}_n. \tag{18}$$

The physical meaning of the previous quantities will be clarified soon, by elaborating on E_i^{id} in particular. Equation (17) can be rewritten in a more convenient way, namely

$$E_i^{id} = -\frac{1}{K_N} \int \frac{\partial}{\partial \beta} \left[\exp(-\beta \, \mathcal{T}') \right] \, \Pi_{n=1}^{N} d\mathbf{v}_n = -\frac{1}{K_N} \frac{\partial K_N}{\partial \beta} = -\frac{\partial \ln K_N}{\partial \beta}. \tag{19}$$

Moreover K_N can be expressed as

$$K_N = \Pi_{n=1}^{N} \int \exp\left(-\beta \, \frac{m}{2} \, (\mathbf{v}_n - \mathbf{u})^2 \right) d\mathbf{v}_n = \left[\int \exp\left(-\beta \, \frac{m}{2} \, (\mathbf{v} - \mathbf{u})^2 \right) d\mathbf{v} \right]^N, \tag{20}$$

where, in the latter expression, the subscript n has been omitted because $\mathbf{v}$ can be the velocity of any particle in the system at equilibrium (because of the arbitrariness of the labeling). It is easy to recognize that the last term inside the square bracket is proportional to the equilibrium single-particle distribution function $f_{[1]}^{(e)}$ [50], meaning that the system dynamics is ruled by the single-particle dynamics only. Substituting Eq. (20) into Eq. (19) yields

$$E_i^{id} = \frac{M}{\rho} \int \frac{m}{2} \, (\mathbf{v} - \mathbf{u})^2 \, f_{[1]}^{(e)} d\mathbf{v}, \tag{21}$$

where $\rho = \int m \, f_{[1]}^{(e)} d\mathbf{v}$ is the macroscopic local density. The integral at the right-hand side of (21) corresponds to the internal energy definition in kinetic

theory of ideal monatomic gases [50], divided by the system volume V. Hence, E_i^{id} is the ideal part of the macroscopic internal energy of the system. It is possible to prove that, for monatomic gases, $E_i^{id} = 3N\,(k_B T/2)$ [50], where clearly each translational degree of freedom contributes for $k_B T/2$ (similarly happens for rotational and vibrational degrees of freedom). By analogy, E_i^{ex} given by Eq. (18) is the excess part of the macroscopic internal energy of the system, due to the pair interactions between particles [27]. Let us introduce the macroscopic internal energy of the system $E_i = E_i^{id} + E_i^{ex}$. Substituting the latter definition in Eq. (16) yields

$$\langle \mathcal{H} \rangle^{(e)} = E_i + E_m \equiv E_t, \tag{22}$$

where E_t is the macroscopic total energy of the system, which is the most important form of energy in computational fluid dynamics. The previous expression is the main result of the proposed derivation which highlights that the equilibrium canonical-ensemble-averaged Hamiltonian $\langle \mathcal{H} \rangle^{(e)}$ in molecular dynamics corresponds to the macroscopic total energy E_t in computational fluid dynamics.

4. Discussion

1. Equation (22), which is rigorously derived in the previous section, represents the key to consistently link disparate scales, as required nowadays in the study of micro- and nano-devices. A schematic view is reported in Figure 1. The equilibrium ensemble-averaged Hamiltonian (in molecular dynamics) and the total energy (in fluid dynamics) are two ways to look at the same quantity. This is the starting point for formulating

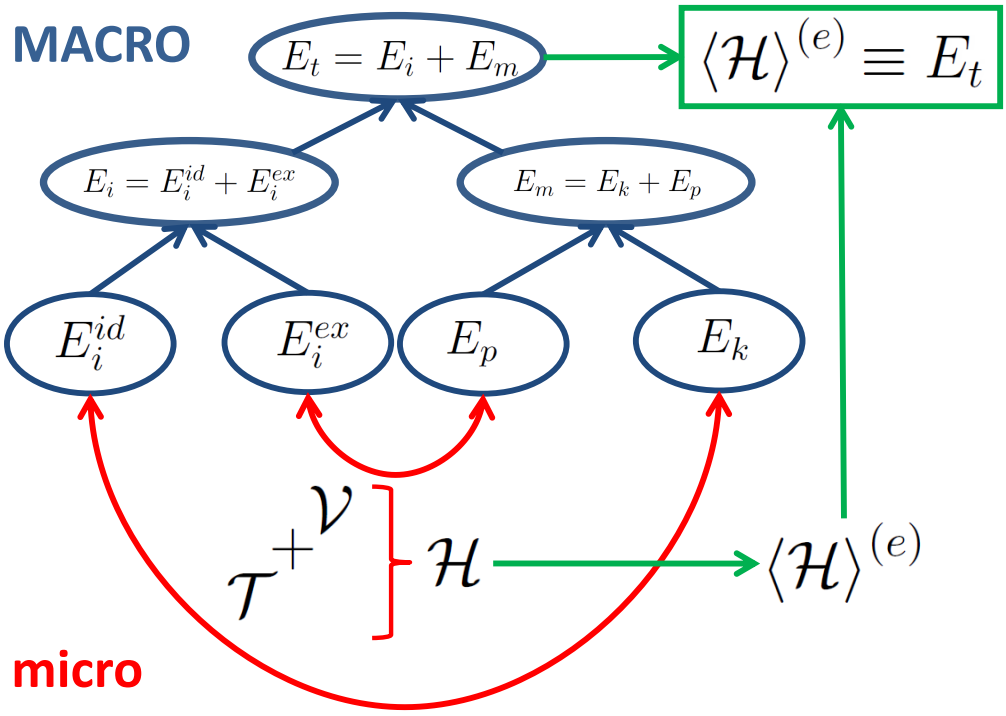

Figure 1: (Color online) Schematic view of the connections among different forms of energy both at macroscopic and microscopic scales: Equation (22) represents the key to link consistently multiple scales, as required nowadays in the theory of small systems.

the first law of thermodynamics in the latter two approaches (see next). Moreover, this allows one to clarify the physical meaning of total energy in the context of macroscopic fluid dynamics. The total energy is the sum of the macroscopic (E_m) and microscopic (E_i) mechanical energy, with thermodynamics being the mechanics of microscopic mechanical energy. The schematic reported in Fig. 1 reminds us that E_i^{id} and E_k have similar microscopic origin (i.e. microscopic kinetic energy), similarly E_i^{ex} and E_p (i.e. microscopic potential energy), even though in fluid dynamics there is a clear distinction between $E_i = E_i^{id} + E_i^{ex}$ (ruling heat transfer) and $E_m = E_k + E_p$ (ruling fluid flow).

2. It is worth the effort to highlight the (often) ambiguous role of the external field $\mathcal{E}$. In the present paper, for the sake of simplicity but without loss of generality, an external field due to a single external source with center $\mathbf{x}_G$ has been considered, namely $\mathcal{E}(\|\mathbf{x}_n - \mathbf{x}_G\|)$. If the distance of the external body from the system is much bigger than a characteristic length of the system, namely $\|\mathbf{x} - \mathbf{x}_G\| \gg \|\mathbf{x}_n - \mathbf{x}\|$, as discussed in the previous section, then the external field will contribute to the macroscopic potential energy E_p. Moreover, in this case, it will not modify the definition of the local equilibrium, as one can realize by comparing Eq. (5) and Eq. (12). As discussed, this is acceptable for gravity. However, in the small systems of interest nowadays in the context of nanotechnology and biotechnology, one can find a huge number of applications where the external field source is very close to the system or even inside it, for example, in presence of functionalized surfaces, surface radicals, surface charges, electro-hydro-dynamics (EHD),

etc.. In all these cases, the external field would contribute to the internal energy of the fluid E_i by E_i^{ex}. In particular, in these cases, the internal energy is no more a simple function of the temperature, but it depends also on the microscopic details of the interaction between the fluid and the external field. For example, this feature is very important for studying the nanoconfinement of water [57].

3. As recognized by Gibbs in 1902, canonical ensemble is appropriate for describing a closed system (i.e. unable to exchange particles with its environment), which is into weak thermal contact with other systems that are described by ensembles with the same temperature [49]. If the system is also isolated (i.e. unable to exchange particles and energy with its environment), then the equilibrium ensemble-averaged Hamiltonian, i.e. the total energy of the system because of Eq. (22), is constant. Let us consider a mass M enclosed into a fixed volume Ω and let E_t be its total energy. If this system is closed and isolated, then $\partial E_t/\partial t = 0$, meaning that the total energy is not created nor destroyed within Ω. In fluid dynamics, the previous property is expressed by saying that total energy is a conserved quantity of the system.
   On the other hand, if the system is not isolated, then the total energy can vary inside the volume because of the fluxes at the border, namely

$$\frac{\partial E_t}{\partial t} = \frac{\partial}{\partial t}\int_\Omega \rho e_t \, dV = -\oint_{\partial\Omega} \mathbf{f}\cdot\hat{\mathbf{n}}\, dS, \tag{23}$$

   where $\mathbf{f}$ is the flux of total energy, $\partial\Omega$ is the closed border surface of Ω, $\hat{\mathbf{n}}$ is the (outgoing) versor of the surface $\partial\Omega$ and S is the parameterization of the surface $\partial\Omega$. Recalling that the volume Ω is arbitrary and it does

not change in time, the Gauss theorem yields

$$\frac{\partial(\rho e_t)}{\partial t} + \nabla \cdot \mathbf{f} = 0. \tag{24}$$

Next, let us remove the last constraint and let us consider also the possibility to exchange particles at the border, at least as far as the particles remain the same (neither chemical nor nuclear reactions are considered here). This is a typical procedure used in engineering thermodynamics in order to extend to open system the applicability of the results derived by canonical ensemble for non-reactive systems [41]. Let us allow Ω to be permeable. The particles that at time $t = 0$ were in Ω can now move and they will occupy the volume Ω' at time $t = \delta t \ll 1$ with a total energy E'_t. The quantity $E'_t - E_t$ allows one to quantify the total energy flux at the border of the original volume Ω, i.e. $\mathbf{f}$ in (24). Three terms can contribute to $\mathbf{f}$: (a) advection flux $\rho e_t \mathbf{u}$; (b) thermal flux $\mathbf{q}_\alpha$ and (c) mechanical flux $\mathbf{\Pi} \cdot \mathbf{u}$, where $\mathbf{\Pi}$ is the total stress tensor (sum of the hydrostatic and hydrodynamic parts). Putting together these results yields

$$\frac{\partial(\rho e_t)}{\partial t} + \nabla \cdot (\rho e_t \, \mathbf{u} + \mathbf{q}_\alpha + \mathbf{\Pi} \cdot \mathbf{u}) = 0, \tag{25}$$

which accounts for the energy balance in the Navier-Stokes-Fourier system of equations. This section aims at stressing that the total energy equation in the Navier-Stokes-Fourier system of equations immediately follows from Eq. (22).

4. A general expression of the first law in engineering thermodynamics for open systems [58] can be derived from Eq. (25). Splitting the stress

tensor into hydrostatic and hydrodynamic parts, namely $\mathbf{\Pi} = p\,\mathbf{I} - \mathbf{\Pi}_\nu$ where p is the pressure and $\mathbf{I}$ is the identity matrix, yields

$$\nabla \cdot (-\mathbf{q}_\alpha + \mathbf{\Pi}_\nu \cdot \mathbf{u}) = \frac{\partial(\rho e_t)}{\partial t} + \nabla \cdot (\rho e_t\,\mathbf{u} + \rho\, pv\,\mathbf{u}), \tag{26}$$

where $v = 1/\rho$ is the specific volume per unit of mass. Integrating the previous equation over the control volume Ω yields

$$\sum_j \Phi_j - W_t^* = \left.\frac{\partial E_t}{\partial t}\right|_\Omega + \sum_i G_i \left(e_t + pv\right)_i \tag{27}$$

where Φ_j is the thermal flux through the j-th portion of the border $\partial\Omega$ called $\partial\Omega_j^\Phi$, namely

$$\Phi_j = -\oint_{\partial\Omega_j^\Phi} \mathbf{q}_\alpha \cdot \hat{\mathbf{n}}\, dS, \tag{28}$$

W_t^* is the gross mechanical power done by the system on its surroundings, namely

$$W_t^* = -\oint_{\partial\Omega} (\mathbf{\Pi}_\nu \cdot \mathbf{u}) \cdot \hat{\mathbf{n}}\, dS, \tag{29}$$

G_i is the mass flow rate through the i-th portion of the border called $\partial\Omega_i^G$, namely

$$(e_t + pv)_i = \frac{1}{G_i} \oint_{\partial\Omega_i^G} \rho(e_t + pv)\mathbf{u} \cdot \hat{\mathbf{n}}\, dS, \tag{30}$$

and $(e_t + pv)_i$ is the average quantity on the surface $\partial\Omega_i^G$, namely

$$G_i = \oint_{\partial\Omega_i^G} \rho\mathbf{u} \cdot \hat{\mathbf{n}}\, dS. \tag{31}$$

Sometimes it is common [58] to remove the contribution of the environment on the mechanical power. Introducing the net mechanical power $W_t = W_t^* - p_0\, dV/dt$, where p_0 is the environmental pressure the system works in, yields

$$\sum_j \Phi_j - W_t = \left.\frac{\partial(E_t + p_0 V)}{\partial t}\right|_\Omega + \sum_i G_i \left(e_t + pv\right)_i. \tag{32}$$

5. Conclusions

In the present paper, we clarify 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 in the presence of spatially varying external field. The macroscopic total energy E_t (sum of mechanical and internal energy) is proved to be equal to the equilibrium ensemble-averaged Hamiltonian $\langle \mathcal{H} \rangle^{(e)}$, as expressed by Eq. (22). This result clarifies some ambiguities (for example, see Eq. (2.2.12) in Ref. [27]), which is an essential step in developing a consistent theoretical framework for the study of engineering systems characterized by a wide range of scales. A schematic view of the connections among different forms of energy both at macroscopic and microscopic levels is reported in Fig. 1. Four main comments follow from the derived result. First of all, even though macroscopic fluid dynamics makes a distinction between internal energy E_i and mechanical energy E_m as the quantities for describing heat transfer and fluid flow respectively, they have a common microscopic origin rooted in the underlying (canonical) system Hamiltonian. Moreover, the effects of the external field can be included either in the macroscopic potential energy or in the internal energy, depending on the location of the external field source with regards to the considered domain. The latter point is crucial in the analysis of nanoconfinement. Finally, once the fundamental link is established, it is easy to derive the corresponding equations prescribing the conservation of energy in fluid dynamics (given by Eq. (25)) and thermal systems engineering (given by Eq. (32)). We hope this work can contribute in clarifying the link among the several notions of energy as used in the different scientific

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