



Criteria for validity of thermodynamic equations from non-equilibrium molecular dynamics simulations

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ABSTRACT

The assumption of local equilibrium is validated in four different systems where heat and mass are transported. Mass fluxes up to 13 kmol/m² s and temperature gradients up to 10¹² K/m were used. A two-component mixture, two vapor–liquid interfaces, a chemical reaction in a temperature gradient and gas adsorbed in zeolite were studied using non-equilibrium molecular dynamics simulations. In all cases, we verified that thermodynamic variables obeyed normal thermodynamic relations, with an accuracy better than 5%. The heat and mass fluxes, and the reaction rate were linearly related to the driving forces. Onsager's reciprocal relations were validated for two systems. Equipartition of kinetic energy applied to all directions. There was no need to invoke any dependence of the thermodynamic variables on the gradients. Away from global equilibrium, the local velocity distribution was found to deviate from the Maxwell distribution in the direction of transport. The deviation was in a form that is used by the Enskog method to solve the Boltzmann equation. New general criteria were formulated for thermodynamic state variables, P . In order to obey local equilibrium, the relative fluctuation in the state variable needs only to fulfill $\delta P/P \lesssim 1/\sqrt{N}$, where N is the number of particles in the volume element. The variation of the variable in the direction of transport needs to fulfill $\Delta P/P = \ell_x \nabla P/P \ll 1$, where the length of the volume element in direction of transport, ℓ_x , is of the order of the diameter of a molecule. These criteria are much less restrictive than proposed earlier, and allows us to use thermodynamic equations in open volume elements with a surprisingly small number (8–18) of particles.

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1. Introduction

In the modeling of chemical and mechanical processes in typical engineering problems, it is normally taken as granted that thermodynamic equations apply and can be used in any volume element of the system. But systems of interest to engineering are now becoming smaller. Microfluid processes and nanoscale control volumes are being investigated at large fluid velocities and gradients. It is therefore of interest to examine when our normal thermodynamic equations apply. How far can we go down in dimensions and time, and still use these equations? Can criteria be formulated such that we know that they hold?

It is thus of great practical interest to have quantitative criteria for the validity of the assumption of local equilibrium. Such can be

obtained by asking how big can the gradients be, or how small can the system be, in terms of the number of interacting particles, before thermodynamic relations stop being valid. When can we expect deviations in the presence of chemical reactions, or during chemisorption of reactants on a surface? And how can the system be characterized, when local equilibrium applies, in a system that is clearly out of global equilibrium?

In the field of non-equilibrium thermodynamics, the assumption of local equilibrium is of fundamental importance. When the equations of thermodynamics hold in local volume elements, we can use the Gibbs relation and calculate entropy fluxes and entropy production in the presence of irreversible processes. The assumption is crucial for the proof of the Onsager relations [1–3].

Knowledge of conditions for local equilibrium will therefore not only have a practical consequence for the use of thermodynamic equations on a macroscopic level [3] but also on a mesoscopic [4–7] level and thus for the development of thermodynamic theories, so as to be able to deal with nanosystems. To our knowledge these issues have not been thoroughly addressed before. This work attempts to summarize and to expand on some earlier works on this topic [9–24].

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Nomenclature Roman symbols

a_{ij}	parameter in Lennard-Jones potential
b_{ij}	parameter in Lennard-Jones potential
c	concentration, mol/m ³
$\Delta_r G$	reaction Gibbs energy, J/mol
$f(v)$	velocity distribution function
\mathbf{F}_{ij}	force acting on i due to j , N
H_i	partial molar enthalpy of i , J/mol
H_B	Boltzmann H function
k_B	Boltzmann constant, J/K
k_f	reaction constant for forward reaction
J	mass flux, mol/m ² s
J_q, J'_q	total heat flux, measurable heat flux J/m ² s
ℓ	mean free path, m
l_x	cell thickness, m
L_x, L_y, L_z	box dimensions, m
m_i	mass of i , kg
N_A	Avogadro's number
N	number of particles
p	pressure, Pa
P	thermodynamic variable
R	gas constant, J/K mol
r	reaction rate, mol/m ³ s
r_{ij}	distance between particle i and j , m
T	temperature, K
t	time, s
U	internal energy, J
u_{ij}	Lennard-Jones pair potential, J
x, y, z	cartesian coordinates, m

V	volume, m ³
\mathbf{v}	velocity, m/s

Greek symbols

α, β	symbols for directions
δ	describes size of fluctuation
γ	surface tension, N/m
ε_{ij}	minimum of potential between particle i and j , J
Φ	potential surface for a chemical reaction, J
ϕ_i	potential energy of particle i in the field of all other particles, J
$\phi_{k,l}$	a function defined by Eq. (22)
ρ	overall particle density in the simulation box, kg/m ³
σ_{ij}	distance between particles i and j when the potential is zero, m

Subscripts, superscripts

c	cut-off distance in Lennard-Jones potential
i	particle i
k, v	component k in layer no. v
\parallel	parallel component
\perp	normal component
H	high
L	low
s	switch distance in Lennard-Jones potential
2	pair potential for a reaction
3	triplet potential for a reaction

The method of non-equilibrium molecular dynamics (NEMD) simulation is well suited to examine such questions, see [8] and references therein. The technique is invaluable in its ability to give assumptions made in the theory a quantitative and molecular footing. In NEMD simulations, one does not a priori assume validity of thermodynamic relations. Thermodynamic properties are being derived from a purely mechanical description, described in Section 2.2. The method will therefore serve as an independent verification of thermodynamic relations.

The NEMD method has already been used in some studies that examine the basic assumption of non-equilibrium thermodynamics. This work gives a review of what has been done so far using this technique, in homogeneous mixtures [9–17], in systems with interfaces [18–21] and on chemical reactions [22–24]. We shall add new results on heterogeneous microporous systems for further substantiation.

With the NEMD technique one is able to generate large temperature gradients, as high as 6×10^{11} K/m [9,22], and use large mass fluxes, around 13 kmol/m² s [20]. These are extreme conditions that seldom appear in engineering problems, so one would expect deviations from local equilibrium near these values. Deviations have so far only been found for even larger temperature gradients, as we shall see.

One would expect that non-equilibrium statistical mechanics gives criteria for validity of local equilibrium. As discussed extensively by Kreuzer in his book [25] such criteria were given rigorously only for a dilute gas. For such gases Meixner [26,27] used the Enskog solution method of the Boltzmann equation and found that local equilibrium is valid when the temperature variation ΔT over a mean free path ℓ is much smaller than the absolute temperature, $\Delta T = \ell \nabla T \ll T$. Similar conditions applied to

other thermodynamic variables. Kreuzer argued that the difference ΔP in a variable across a cell with thickness l_x is at most of the order of the fluctuation of the variable, δP , in the cell. The fluctuation should be much smaller than the average value of the variable P . Combining these two criteria, Kreuzer gave as basic criterion for the validity of local equilibrium:

$$\Delta P = l_x \nabla P \lesssim \delta P \ll P \quad (1)$$

For a gas $l_x = \ell$ was the mean free path. In a liquid or a solid there is no natural way to choose l_x . Kreuzer proceeded to give arguments to prove the general validity of his criterion and to establish the size of l_x . We refer to his book for the details. On the basis of the results from the NEMD simulations, to be discussed below, we shall conclude, like Tenenbaum et al. [9] and Hafskjold and Ratkje [13], that his criterion is much too restrictive.

Orban and Bellemans [28] as well as Haile [29] proposed that the velocity part of Boltzmann's H_B function

$$H_B = \int f(\mathbf{v}) \ln f(\mathbf{v}) d\mathbf{v} \quad (2)$$

can be used as a criterion for local equilibrium. (Subscript B has been added to separate H_B from the enthalpy.) Here $f(\mathbf{v})$ is the velocity distribution of the particles in the system. By comparing H_B to the value found from the Maxwell distribution one has a measure of how close a volume element is to equilibrium. We shall come back to how to choose the size of a volume element in a liquid or a solid.

NEMD simulations allow us to characterize non-equilibrium systems on the molecular scale, and one purpose of these studies has been to develop a molecular understanding of the properties of a system that obeys local equilibrium. Hafskjold and Ratkje [13]

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