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Far from Equilibrium Maximal Principle Leading to Matter Self-Organization

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ABSTRACT

In this work an extremal principle driving the far from equilibrium evolution of a system of structureless particles is derived by using the stochastic quantum hydrodynamic analogy. For a classical phase (i.e., the quantum correlations decay on a distance smaller than the mean inter-molecular distance) the far from equilibrium kinetic equation can be cast in the form of a Fokker-Plank equation whose phase space velocity vector maximizes the dissipation of the energy-type function, named here, stochastic free energy.

Near equilibrium the maximum stochastic free energy dissipation (SFED) is shown to be compatible with the Prigogine’s principle of minimum entropy production. Moreover, in quasi-isothermal far from equilibrium states, the theory shows that, in the case of elastic molecular collisions and in absence of chemical reactions, the maximum SFED reduces to the maximum free energy dissipation.

When chemical reactions or relevant thermal gradients are present, the theory highlights that the Sawada enunciation of maximum free energy dissipation can be violated.

The proposed model depicts the Prigogine’s principle of minimum entropy production near-equilibrium and the far from equilibrium Sawada’s principle of maximum energy dissipation as two complementary principia of a unique theory where the latter one is a particular case of the more general one of maximum stochastic free energy dissipation.

Following the tendency to reach the highest rate of SFED, a system relaxing to equilibrium goes through states with higher order so that the matter self-organization becomes possible.

Indexing terms/Keywords

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INTRODUCTION

The research in the field of order generation and matter self-assembling dates back to the thirties [1-8]. Various extremal principles have been proposed for the self-organized régimes governed by classical linear and non-linear non-equilibrium thermodynamic laws, with stable stationary configurations being particularly investigated.

Nevertheless an organic understanding is still not available. In 1945 Prigogine [1,2] proposed the “Theorem of Minimum Entropy Production” which applies only to near-equilibrium stationary state. The proof offered by Prigogine is open to serious criticism [3]. Šilhavý [4] offers the opinion that the extremal principle of [near-equilibrium] thermodynamics does not have any counterpart for far from-equilibrium steady states despite many claims in the literature.

Sawada [5], in relation to the earth's atmospheric energy transport process, postulated the principle of largest amount of entropy increment per unit time. He cited the work in fluid mechanics by Malkus and Veronis [6] as having proven a principle of maximum heat current, which in turn is a maximum entropy production for a given boundary condition, but this inference is not logically ever valid.

The rate of dissipation of energy appeared for the first time in Onsager's work [7] on this subject. An extensive discussion of the possible principles of extrema of entropy production and/or of dissipation of energy is given by Grandy [8]. He finds difficulty in defining the rate of internal entropy production in the general case, showing that sometimes, for the prediction of the course of a process, the extremum of the rate of dissipation of energy may be more useful than that of the rate of entropy production.

Sawada and Suzuky [9] confirmed, both by numerical simulations and by experiments, the maximum rate of energy dissipation in electro-convective instabilities.

Nowadays, the debate about the principle of maximum free energy dissipation (MFED) and the Prigogine one’s is still going on.

An alternative approach to the far from equilibrium evolution can be obtained in term of Langevin equations that in some cases describe the underlying dynamics at a continuous coarse-grained scale. The Langevin equation can be derived by using different techniques, such as the Poisson transformation [10] and the Fock space formalism [11]. Occasionally, exact formulations exist for non-linear reaction kinetics and others few problems. Alternatively, a Langevin equation can be assumed on a phenomenological point of view where it is decided *a priori* what is pertinent to the approximated dynamics. In this context it is really difficult to have a rigorous Langevin description.

The way out is to derive satisfactory Langevin equations from a microscopic model.

In the present work, by using the stochastic quantum hydrodynamic analogy (SQHA) [12-15] as the microscopic model, the classical non-equilibrium kinetics has been derived for the macro-scale limit.

The SQHA, where the structureless molecules are described by a pseudo-Gaussian wave function, allows deriving the far-from-equilibrium phase-space evolutionary criterion for classical gas and fluid phases in term of maximum dissipation of an energy-based function.

THE SQHA EQUATION OF MOTION

The quantum hydrodynamic analogy (QHA) equations are based on the fact that the Schrödinger equation, applied to a wave function $\psi_{(q,t)} = A_{(q,t)}\, exp[\, i \frac{S_{(q,t)}}{\hbar}\,]$, is equivalent to the motion of a fluid owing the particle density $n_{(q,t)} = A^2_{(q,t)} = |\psi|^2$ with a velocity $\dot{q} = \frac{\nabla_q S_{(q,t)}}{m}$, governed by the equations [12-14]

$$\partial_t n_{(q,t)} + \nabla_q \bullet (n_{(q,t)} \dot{q}) = 0 , \tag{1}$$

$$\dot{q} = \nabla_p H , \tag{2}$$

$$\dot{p} = -\nabla_q (H + V_{qu}) , \tag{3}$$

where $\nabla_p = \left(\frac{\partial}{\partial p_i} \right)$, $\nabla_q = \left(\frac{\partial}{\partial q_i} \right)$, H is the Hamiltonian of the system and V_{qu} is the quantum pseudo-potential that reads

$$V_{qu} = -(\frac{\hbar^2}{2m})n^{-1/2}\nabla_q \bullet \nabla_q n^{1/2}. \tag{4}$$

For the purpose of this paper, it is useful to observe that equations (1-3) can be derived by the following phase-space equations [15]

$$\partial_t \rho_{(q,p,t)} + \nabla \bullet (\rho_{(q,p,t)}(\dot{x}_H + \dot{x}_{qu})) = 0 \tag{5}$$

where $\nabla = \left(\frac{\partial}{\partial q_i}, \frac{\partial}{\partial p_i}\right)$ and where

$$n_{(q,t)} = \iiint \rho_{(q,p,t)} d^{3n} p. \tag{6}$$

$$\dot{x}_H = (\nabla_p H, -\nabla_q H) \tag{7}$$

$$\dot{x}_{qu} = (0, -\nabla_q V_{qu}) \tag{8}$$

where the phase space distribution

$$\rho_{(q,p,t)} = n_{(q,t)}\delta(p - \nabla_q S) \quad , \tag{9}$$

where

$$S = \int_{t_0}^{t} dt(\frac{p \bullet p}{2m} - V_{(q)} - V_{qu}), \tag{10}$$

is a Wigner-like distribution since it obeys to the property

$$|\psi|^2 = \int_{-\infty}^{+\infty} d^{3n} p \;\; \rho_{(q,p,t)} . \tag{11}$$

The Madelung approach, as well as the Schrödinger one, are non-local and are not able to give rise to local limit.

When fluctuations are added to the QHA equation of motion, the resulting stochastic-QHA (SQHA) dynamics shows that is possible to obtain a local dynamics on large scale, preserving the quantum behavior on a microscopic one. In a preceding paper [15] the author has shown that in presence of vanishing small stochastic Gaussian noise, the QHA motion equation (at first order of approximation in the noise amplitude Θ) reads

$$\partial_t \rho_{(q,p,t)} = -\nabla \bullet (\rho_{(q,p,t)}(\dot{x}_H + \dot{x}_{qu(n)})) + \eta_{(q,t,\Theta)}\delta(p - \nabla_q S), \tag{13}$$

with

$$\rho_{(q,p,t)} = n_{(q,t)}\delta(p - \nabla_q S), \tag{14}$$

where Θ is a measure of the vacuum noise amplitude (VNA) and

$$< \eta_{(q_\alpha,t)}, \eta_{(q_\beta+\lambda,t+\tau)} >= \underline{\mu}\frac{k\Theta}{\lambda_c^2} exp[-(\frac{\lambda}{\lambda_c})^2]\delta(\tau)\delta_{\alpha\beta} \tag{16}$$

is the VNA variance, where the quantum correlation length λ_c reads[15]

$$\lambda_c = \pi \frac{\hbar}{(2mk\Theta)^{1/2}} \quad , \tag{12}$$

$$S = \int_{t_0}^{t} dt\left(\frac{p \bullet p}{2m} - V_{(q)} - V_{qu(\mathrm{n})}\right) = \int_{t_0}^{t} dt\left(\frac{p \bullet p}{2m} - V_{(q)} - V_{qu(\mathrm{n}_0)} - I^*\right) \tag{17}$$

$$m\overset{\bullet}{q} = p = \nabla_q S = \nabla_q \left\{ \int_{t_0}^{t} dt\left(\frac{p \bullet p}{2m} - V_{(q)} - V_{qu(\mathrm{n}_0)} - I^*\right)\right\} = p_0 + \Delta p_{st} , \tag{18}$$

where

$$\Delta p_{st} = -\nabla_q \left\{ \int_{t_0}^{t} I^* \, dt \right\} , \tag{19}$$

where

$$I^* = V_{qu(\mathrm{n})} - V_{qu(\mathrm{n}_0)} \tag{20}$$

where n_0 is obtained from the zero order of approximation equation (1).

The phase space distribution form (9) imposing the condition $m\overset{\bullet}{q} = p = \nabla_q S$ warrants the wave particle equivalence in the quantum limit.[15].

QUANTUM NON-LOCALITY LENGTH λ_q

In addition to the noise correlation function (12), to obtain the local form of equations (11-18) we need to evaluate the range of interaction of the quantum force $\overset{\bullet}{p}_{qu} = -\nabla_q V_{qu}$ in (15).

As shown in reference [15] the relevance of the quantum potential force at large distance can be evaluated by the convergence of the integral

$$\int_0^{\infty} | q^{-1} \nabla_q V_{qu} | dq < \infty \tag{21}$$

So that the quantum potential range of interaction can be obtained as the mean weighted distance

$$\lambda_q = 2 \frac{\int_0^{\infty} | q^{-1} \frac{dV_{qu}}{dq} | dq}{\lambda_c^{-1} | \frac{dV_{qu}}{dq} |_{(q=\lambda_c)}} \quad . \tag{22}$$

For the interaction of particle pairs (e.g., mono-dimensional case, real gas or a chain of neighbors interacting atoms) expression (22) is quite manageable and leads to very good experimental confirmations [16].

Macroscopic local limiting dynamics

Given ΔL the physical length of the system, the macroscopic local dynamics is achieved for those problems that satisfy the condition

$$\lambda_c \cup \lambda_q << \Delta L \, .$$

From the condition $\lambda_q << \Delta L$ it follows that [15]

$$\lim_{q/\lambda_q \to \infty} -\nabla_q V_{qu(\mathrm{n}_0)} = 0 \tag{23}$$

and the SPDE of motion acquires the form [15]

$$\partial_t \rho_{(q,p,t)} = -\nabla \bullet (\rho_{(q,p,t)} \overset{\bullet}{x}_H) + \eta_{(q,t,\Theta)} \delta(p - \nabla_q S) \tag{24}$$

$$\rho_{(q,p,t)} = \mathrm{n}_{(q,t)} \delta(p - \nabla_q S), \tag{25}$$

$$\partial_t \mathrm{n}_{(q,t)} = -\nabla_q \bullet (\mathrm{n}_{(q,t)} \overset{\bullet}{q}_{cl}) + \eta_{(q_\alpha,t,\Theta)} \tag{26}$$

$$< \eta_{(q_\alpha,t)}, \eta_{(q_\alpha+\lambda,t+\tau)} > = \underline{\mu}\, \delta_{\alpha\beta} \frac{2k\Theta}{\lambda_c} \delta(\lambda)\delta(\tau) \tag{27}$$

$$\begin{aligned} \overset{\bullet}{q} = \frac{p}{m} &= \lim_{\Delta\Omega/\lambda_c \to \infty} \lim_{\Delta\Omega/\lambda_q \to \infty} \frac{\nabla_q S}{m} \\ &= \nabla_q \{ \lim_{\Delta\Omega/\lambda_c \to \infty} \lim_{\Delta\Omega/\lambda_q \to 0} \frac{1}{m} \int_{t_0}^{t} dt \left(\frac{p \bullet p}{2m} - V_{(q)} - V_{qu(\mathrm{n})} - I^* \right) \} \\ &= \frac{1}{m} \nabla_q \{ \int_{t_0}^{t} dt \left(\frac{p \bullet p}{2m} - V_{(q)} - \Delta \right) \} = \frac{p_{cl}}{m} + \frac{\delta p}{m} \cong \frac{p_{cl}}{m} \end{aligned} \tag{28}$$

where δp is a small fluctuation of momentum and

$$\overset{\bullet}{p}_{cl} = -\nabla_q V_{(q)}, \tag{29}$$

Being also $\lambda_c << \Delta L$, I* represents a small energy fluctuation due to the quantum potential [15].

THE KINETIC EQUATION FOR CLASSICAL GAS AND FLUID PHASES

In appendix A the properties of the large-scale coarse-grained quantum mechanical distribution (9) are analyzed and shown to acquire the statistical character.

As derived in appendix B, for a gas or mean-field fluid phases, we can describe our system by a single particle SQHA distribution $\rho_{(1)}$ from which we can extract the statistical single particle distribution ρ^s that obeys to the equation.

$$\lim_{\Delta L >> \lambda_c, \lambda_q} \rho^s < \overset{\bullet}{x}_s > = -\nabla D_{(i)} \rho^s \tag{30}$$

Equation (30) is basically the Fokker-Plank form of the Maxwell equation. The difference with the Boltzmann kinetic equation is that (30) does not give any information about the form of the (phase space) diffusion coefficient D.

In order to obtain from (30) a closed kinetic equation, the standard approach is to introduce additional information about the diffusion coefficient. The local equilibrium approximation is usually achieved by the semi-empirical assumption of linear relation between flows and fluxes.

Here we use (30) since it holds even far from equilibrium and is more general than the Boltzmann kinetic equation (able to give the explicit form of the linear coefficients between flows and fluxes but just near local equilibrium).

The mean phase space molecular volume of WFM

In order to grasp additional information from (30) we observe that (for gasses and meanfield fluids) the SQHA approach shows two competitive dynamics: (a) the enlargements of the molecular DF (given by (B.2- A.?)) between two consecutive collisions, (b) The diffusion of the molecules, in term of their mean position, as a consequence of the molecular collisions (that cause the WFM collapse [16]).

As consequence of free expansions and collapses, the pseudo-Gaussian molecular DF in the phase space cell $\Delta\Omega$ will occupy the mean volume $<\Delta V_m>$ that we pose

$$\lim_{\Delta L >> \lambda_c , \lambda q} <\Delta V_m> = h^3 \, exp[-\phi] \tag{31}$$

where $<\Delta V_m>$ reads:

$$<\Delta V_m> = \frac{\sum\limits_{i \in \Delta\Omega} \left(\int\limits_{\Delta\Omega_{(q,p)}} \rho_{(i)} \, (x_{(i)} - < x_{(i)} >)^2 \, d^3q d^3p \right)^{\frac{1}{2}}}{\sum\limits_{i \in \Delta\Omega} \int\limits_{\Delta\Omega_{(q,p)}} \rho_{(i)} d^3q d^3p} \tag{32}$$

$$< x_{(i)} > = \frac{\int\limits_{\Delta\Omega_{(q,p)}} \rho_{(i)} \, x_{(i)} d^3q d^3p}{\int\limits_{\Delta\Omega_{(q,p)}} \rho_{(i)} d^3q d^3p} \tag{33}$$

where $x_{(i)} = \begin{pmatrix} q_{(i)} \\ p_{(i)} \end{pmatrix}$. Given that the mean WFM volume (WFMV) per molecule $<\Delta V_m>$ has to be a fraction “□ ” of the phase space volume available per molecule $\frac{\Delta\Omega}{\Delta N_\Omega}$ we can pose

$$<\Delta V_m> = \alpha \frac{\Delta\Omega}{\Delta N_\Omega} \tag{34}$$

where ΔN_Ω is the number of molecules in $\Delta\Omega$.

In the case of stationary states, of classical phases (i.e., λ_c and λ_q << mean inter-particle distance) we can assume that α is proportional to the diffusive enlargement (a) of the WFM with (SQHA) diffusion coefficient $\mathrm{D}_{(\Theta)} = 2\underline{\mu}k\Theta$, and proportional to the time between two consecutive collisions (that generates the collapse of the molecular wave function [?]). Since the time between two consecutive collisions is inversely proportional to the phase space (molecular) diffusion coefficient D, we can formally write

$$\alpha = \alpha' \frac{\mathrm{D}_{(\Theta)}}{D} = \frac{D^*}{D} \quad . \tag{35}$$

where for brevity it has been posed $D^* = \alpha' \mathrm{D}_{(\Theta)}$. As shown in appendix C, the absolute value of the constant α' leads to the re-definition (by a constant) of the free energy at thermodynamic equilibrium. Therefore, defining the constant of the free energy at thermodynamic equilibrium determines α'.

Moreover, by using the definition of ρ^s

$$\rho^s = \frac{\Delta N_\Omega}{\Delta \Omega} \quad , \tag{36}$$

and by using (30), from (34), for stationary states it follows that

$$\lim_{\Delta L >> \lambda_c , \lambda_L} < \Delta V_m > = h^3 \, exp[-\phi] = \frac{D*}{D} \rho^{s^{-1}} \tag{37}$$

$$\lim_{\Delta L >> \lambda_c , \lambda_L} \rho^s = h^{-3} \frac{D^*}{D} exp[\phi] \tag{38}$$

$$\lim_{\Delta L >> \lambda_c , \lambda_q} < \dot{x}_s > = -D\{ \nabla \phi + \nabla \, ln[D*] \} \tag{39}$$

Given that at thermodynamic equilibrium (in absence of external fields) there is the transnational invariance in the phase space, it follows that $\nabla \phi = 0$, as well as $D*$ = constant and hence $\nabla \, ln[D*] = 0$.

The same result holds if the vacuum fluctuations and the thermal ones are decoupled. In this case, we could assume Θ =constant independently by the thermodynamic conditions and hence $\nabla \, ln[D*] = 0$ even out of equilibrium.

In the general case we have a system out of the thermodynamic equilibrium where the vacuum fluctuations and the thermal ones are coupled each other.

The fact that the coupling between matter and vacuum exists is proven by the fact that if we try to reach the zero temperature T, by step of equilibrium, the asymptotical ending state with the T=0 is a non-fluctuating (quantum) state of the system that in the SQHA model can be achieved if and only if $\Theta = 0$ in absence of vacuum fluctuations: if we diminish the thermal energy fluctuation (by step of equilibrium) we will also lower the vacuum ones. It is matter of fact that the open quantum phenomena are elicited by the temperature lowering.

In the case of sufficiently weak radiative coupling we can write

$$\nabla \, ln[D*] = \underline{\underline{A}} \bullet \nabla \phi + \underline{\underline{\underline{B}}} \bullet \nabla \phi \nabla \phi + O(\nabla \phi^3) \tag{40}$$

In the case of structureless punt-like particles, classically interacting (i.e., the classical gas phase) with central-symmetric potential, the direction of variation of $D*$ must be aligned with $\nabla \phi$ leading to $\underline{\underline{A}} = A\delta_{ij}$ and $\underline{\underline{\underline{B}}} = 0$ and, hence, to

$$\nabla \, ln[D*] = A \nabla \phi + O(\nabla \phi^3) = (A + O(\nabla \phi^2)) \nabla \phi \tag{41}$$

from where it follows that

$$\lim_{\Delta L >> \lambda_c , \lambda_L} < \dot{x}_s > = -D \nabla \phi (1 + A + O(\nabla \phi^2)) \tag{42}$$

that introduced into the FPE (B.24-B.25) leads to the kinetic equation

$$\partial_t \rho^s + \nabla \bullet \rho^s < \dot{x}_{\overline{H}} > = \nabla \bullet \rho^s D \nabla \phi (1 + A + O(\nabla \phi^2)) \tag{43}$$

FAR FROM EQUILIBRIUM RELAXATION AND MAXIMUM STOCHASTIC FREE ENERGY DISSIPATION IN STATIONARY STATES

Even if the ϕ-function is well defined far from equilibrium, the kinetic equations (43,C.1) without the initial and boundary condition of an assigned problem is just a symbolic equation. Nevertheless, the existence of the ϕ-function allows the definition of a formal criterion of evolution.

By writing the irreversible phase space velocity field as follows

$$\lim_{\Delta L >> \lambda_c ,\lambda_q} < \dot{x}_s > = -D\nabla\phi(1+A+O(\nabla\phi^2)) \qquad (46)$$

an evolutionary principle along the relaxation pathway can be formulated in terms of dissipation of the ϕ-function (named here *normalized hydrodynamic free energy* (NHFE) since at equilibrium it converges to the free energy normalized to kT (see appendix C).

Given that, the total differential of the *normalized hydrodynamic free-energy* ϕ can be written as a sum of two terms, such as:

$$\frac{d\phi}{dt} = \frac{\partial\phi}{\partial t} + < \dot{x} > \bullet\nabla\phi = \frac{\partial\phi}{\partial t} + < \dot{\bar{x}}_H > \bullet\nabla\phi + < \dot{x}_S > \bullet\nabla\phi = \frac{d_H\phi}{dt} + \frac{d_S\phi}{dt} \qquad (47)$$

where we name

$$d_H\phi = \lim_{\Delta L_L >> \lambda_c ,\lambda_q} \{ \frac{\partial\phi}{\partial t} + < \dot{\bar{x}}_H > \bullet\nabla\phi \}\delta t \qquad (48)$$

as "*dynamic differential*" and

$$d_S\phi = \lim_{\Delta L >> \lambda_c ,\lambda_q} [< \dot{x}_S > \bullet\nabla\phi]\delta t \qquad (49)$$

as "*stochastic differential*".

Under the range of validity of equation (46) (i.e., structureless punt-like particles, interacting by L-J central symmetric potential that do not undergo to chemical reactions) the stochastic velocity vector evolves through a pathway that follows the ϕ-function negative gradient so that

$$\frac{d_S\phi}{\delta t} \text{ is minimum with respect the choice of } < \dot{x}_S > \qquad (50)$$

and $\frac{d_S\phi}{\delta t} < 0$ since $< \dot{x}_S >$ is anti-parallel to $\nabla\phi$.

Sometime, some authors speak in term of energy dissipation, so that in this case the criterion (50) reads

$$-\frac{d_S\phi}{\delta t} = \left| \frac{d_S\phi}{\delta t} \right| \text{ is maximum with respect the choice of } < \dot{x}_S > \qquad (51)$$

STABILITY AND MAXIMUM STOCHASTIC FREE ENERGY DISSIPATION IN QUASI-ISOTHERMAL STATIONARY STATES

In order to elucidate the significance of the criterion given by (51), we analyze the spatial kinetics far and near equilibrium.

5.1 Spatial kinetic equations

By using a well known method [21] we transform the motion equation (43) into a spatial one over a finite volume V.

Given a quantity per particle

$$\underline{\Upsilon} = \frac{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\rho^s \Upsilon d^3p}{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\rho^s d^3p} \tag{52}$$

its spatial density:

$$n\underline{\Upsilon} = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\rho^s \Upsilon d^3p \tag{53}$$

and its first moment

$$n\underline{\Upsilon\dot{q}} = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\rho^s \Upsilon < \dot{q} > d^3p \tag{54}$$

by using the motion equation (43) it is possible to obtain the spatial differential equation:

$$\begin{aligned}\partial_t n\underline{\Upsilon} + \nabla \bullet n\underline{\Upsilon\dot{q}} - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\rho^s\{\partial_t\Upsilon + < \dot{x}_{<H>} > \bullet\nabla\Upsilon\}d^3p \\ = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\Upsilon\{\nabla\bullet\rho^s D\nabla\phi(1+A+O(\nabla\phi^2))\}d^3p\end{aligned} \qquad 55)$$

That by choosing

$$\Upsilon = kT\phi, \tag{56}$$

where T is the “mechanical” temperature defined as

$$T = \gamma\frac{< E_{cin} + E_{pot} >}{k} = \gamma\left(\frac{\frac{< p_i >< p_i >}{2m} + < \overline{V}_i >}{k}\right), \tag{57}$$

where γ is defined at thermodynamic equilibrium.

After some manipulations (see appendix D) for a system at thermal equilibrium (i.e., small thermal gradients) but far from equilibrium in terms of concentrations and mechanical variables, at constant volume, we obtain

$$\begin{aligned}\frac{d\Phi}{dt} - \frac{d\Phi_{sup}}{dt} - \frac{d(E_{cin} + E_{int})}{dt} + \frac{dTS^s{}_{vol}}{dt} \\ = -\iiint_V \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT\frac{(\phi-1)}{\phi}\rho^s\left(\frac{d_s\phi}{dt}\right)d^3p\ d^3q + \Delta_0 + \Delta_1\end{aligned} \tag{58}$$

where Δ_0 represents the “source” term

$$\Delta_0 = \{ \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \phi^2 (\nabla \bullet \nabla \phi)(1 + A + O(\nabla \phi^2))d^3 p \}, \tag{59}$$

and Δ_1 the out of equilibrium contribution

$$\begin{aligned} \Delta_1 = & \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \rho^s \{ \partial_t \Delta \Upsilon + < \dot{x}_{\overline{H}} > \bullet \nabla(\Delta \Upsilon) \} d^3 p \\ & + \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \rho^s \{ T \partial_t \Delta S + < \dot{x}_{\overline{H}} > \bullet T \nabla \Delta S \} d^3 p \end{aligned} \quad . \qquad 60)$$

(where $\Delta S = S^s - S$ and $\Delta \Upsilon = \Upsilon^s - \Upsilon^{eq}$, where S and Υ^{eq} are the (local) equilibrium entropy and free energy, respectively)

$$\frac{d\Phi_{sup}}{dt} = \oint\!\!\oint n \underline{\Upsilon \dot{q}} \bullet d\sigma \tag{61}$$

where $d\sigma$ is a vector perpendicular to the infinitesimal element of the boundary surface, and where

$$\frac{d\Phi}{dt} = \iiint_V \frac{\partial(n\underline{\Upsilon})}{\partial t} d^3 q \tag{62}$$

$$\frac{dTS^s{}_{vol}}{dt} = \frac{\gamma}{k} \iiint_V \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \rho^s S^s F \bullet < \dot{q} > d^3 p \, d^3 q = \frac{\gamma}{k} \iiint_V F \bullet \underline{S^s \dot{q}} \, d^3 q \tag{63}$$

where

$$S^s = -k \ln \rho^s . \qquad 64)$$

$$\underline{S^s \dot{q}} = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \rho^s S^s < \dot{q} > d^3 p , \tag{65}$$

where for potentials that are not function of momenta, the term $F = < \dot{p} >_{(q)}$ can be brought out of the integral in (63) and where $E_{int\,t}$ and E_{cin} are the internal energy and the macroscopic kinetic energy of the system, respectively.

Maximum free energy dissipation in far from equilibrium quasi-isothermal systems at constant-volume

The importance of stationary quasi-isothermal states far from equilibrium comes from the fact that living systems operate in such a condition.

If we consider the overall system (environment plus system) sometime the energetic reservoir is able to maintain the system (even for a long laboratory time scale) in a stationary state even the global system (system plus reservoirs) is relaxing toward the global equilibrium.

Moreover, assuming that the system is at constant volume and the energetic reservoir is both at constant volume and thermally isolated (without loss of generality, we can assume the energetic reservoirs are much bigger than the system and that they work on it in a reversible manner) the decrease of reservoirs free energy is equal to the free energy transferred to the system by means of volume forces.

Given that for stationary states in quasi-isothermal condition at constant volume (fixed wall) it holds that

$$\frac{d\Phi}{dt}=0 \text{, and } \frac{dE_{int}}{dt}=0 \text{, } \frac{dE_{cin}}{dt}=0 \Rightarrow \frac{dTS^{s}{}_{vol}}{dt}=0 \qquad 66)$$

and that

$$\frac{dE_{sup}}{dt}=0 \qquad (67)$$

$$\frac{d\Phi_{sup}}{dt}=\frac{dE_{sup}}{dt}-\frac{dTS^{s}{}_{sup}}{dt}=-\frac{dTS^{s}{}_{sup}}{dt}\text{ ,} \qquad (68)$$

where the suffix “*sup*” and “*vol*” refer to contributions coming from the boundary surface and volume of the system , respectively, from (58) it follows that

$$\frac{dTS_{sup}}{dt}+\frac{dT\Delta S_{sup}}{dt}-\Delta_0-\Delta_1=-\iiint\limits_V \int\limits_{-\infty}^{+\infty}\int\limits_{-\infty}^{+\infty}\int\limits_{-\infty}^{+\infty} kT\frac{(\phi-1)}{\phi}\rho^{s}\left(\frac{d_s\phi}{dt}\right)d^3p\ d^3q \qquad (69)$$

Moreover, by the quasi-isothermal condition we can infer that the local thermal equilibrium exists even if the local domains $\Delta\Omega_q{}^{s}$ are far from mechanical chemical equilibrium and hence and that

$$\Delta_0 \cong 0\text{,} \qquad (70)$$

$$\Delta S = S^{s}-S \cong 0\text{,} \qquad (71)$$

$$\Delta \Upsilon = \Upsilon^{s}-\Upsilon^{eq} \cong 0 \quad (71) \qquad (72)$$

and hence that $\Delta_1 \cong 0$. So that (72) reads

$$\frac{dTS_{sup}}{dt}\cong-\iiint\limits_V \left\{ \int\limits_{-\infty}^{+\infty}\int\limits_{-\infty}^{+\infty}\int\limits_{-\infty}^{+\infty} kT\frac{(\phi-1)}{\phi}\rho^{s}\left(\frac{d_s\phi}{dt}\right)d^3p \right\} d^3q \qquad (73)$$

Moreover, assuming that the reservoir (free) energy E_{res} transferred to the system, $-\frac{dE_{res}}{dt}$, is then dissipated by the system in heat $\frac{dTS_{sources}}{dt}$ (reversibly transferred to the environment (defined positive outgoing) through the surface at constant temperature so that

$$\frac{dTS_{sup}}{dt}=\frac{dQ_{sup}}{dt} \text{ and } \frac{dT\Delta S_{sup}}{dt}\cong 0) \qquad (74)$$

for the energy conservation it follows that

$$\frac{dE_{res}}{dt}=-\frac{dTS_{sources}}{dt}=-\frac{dTS_{sup}}{dt}=-\frac{dQ_{sup}}{dt} \qquad (75)$$

and, finally, that

$$-\frac{dE_{res}}{dt}=\frac{dTS_{sup}}{dt}=-\iiint\limits_V \left\{ \int\limits_{-\infty}^{+\infty}\int\limits_{-\infty}^{+\infty}\int\limits_{-\infty}^{+\infty} kT\frac{(\phi-1)}{\phi}\rho^{s}\left(\frac{d_s\phi}{dt}\right)d^3p \right\} d^3q \qquad (76)$$

that for a stationary state far from equilibrium is maximum with respect the variations of $<\dot{x}_s>$.

Therefore, for a classical phase of molecules undergoing elastic collisions and without chemical reactions at quasi-isothermal condition, the system finds the stationary condition by maximizing its free energy dissipation.

Under the same conditions of validity of equation (76), Sawada [9] has shown and experimentally measured in the electro-convective instability that when the steady state configuration is achieved the system reaches the maximum of free energy.

Moreover, for stationary states far from equilibrium where the energy dissipation $\frac{dE_{res}}{dt}$ cannot be controlled or known (76) simply reads

$$\frac{dTS_{sup}}{dt} \cong \frac{TdS_{sup}}{dt} = -\iiint_V \{ \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT\frac{(\phi-1)}{\phi}\rho^s(\frac{d_s\phi}{dt})d^3p\,\}\,d^3q \qquad (77)$$

that represents the principle of “maximum heat transfer” (i.e., $\frac{TdS_{sup}}{dt}$) given by of Malkus and Veronis [6] for fluid dynamics and showed holding in describing the atmosphere turbulence.

Finally, it is worth mentioning that a basic difference exists between the present enunciation and the Sawada and the Malkus and Veronis ones. Here, the analytical calculations show that (76) is not of general validity but it holds only in the case of quasi-isothermal conditions for an ordinary real gas (with its fluid phase) made of structureless molecules (e.g., classical rigid-spheres) sustaining elastic collisions and not undergoing to chemical reactions.

Actually, from the general form (69)

$$\frac{dTS_{sup}}{dt} + \frac{dT\Delta S_{sup}}{dt} - \Delta_0 - \Delta_1 = -\iiint_V \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT\frac{(\phi-1)}{\phi}\rho^s(\frac{d_s\phi}{dt})d^3p\;\;d^3q \qquad (78)$$

maximum with respect the variation of $< \dot{x}_s >$, we can see that the condition of maximum heat transfer $\frac{dTS_{sup}}{dt}$ is not as general as the right side of (78) since both the terms Δ_0, Δ_1 and $\frac{dT\Delta S_{sup}}{dt}$ are not every time null. As far as it concerns for the free energy dissipation we even have $\frac{dE_{res}}{dt} \neq -\frac{dTS_{sup}}{dt}$.

Minimum entropy production in stationary states at local-equilibrium

By introducing (101) in (73) we obtain

$$-\iiint_V \{ \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT\frac{(\phi-1)}{\phi}\rho^s(\frac{d_s\phi}{dt})d^3p\,\}\,d^3q = \frac{dTS_{sources}}{dt} \qquad (79)$$

that, since T is not function of time (in stationary states) leads to

$$-\iiint_V \{ \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} k\frac{(\phi-1)}{\phi}\rho^s(\frac{d_s\phi}{dt})d^3p\,\}\,d^3q = \frac{dS_{sources}}{dt} \qquad (80)$$

if we displace the system from equilibrium in a stationary condition by imposing an external constraint, we have $\nabla\phi \neq 0$. Moreover, given that in a near-equilibrium state the variation of $\nabla\phi$ happens on a distance much larger than the local statistical system, hence, we can consider $\nabla\phi$ a locally constant field.

Making reference to the locally constant field $\nabla\phi$, we can design $\nabla\phi_{//}$ as the component along this direction and $\nabla\phi_{\perp}$ the component perpendicular to it.

If we are in a stationary condition at local equilibrium, the fixed external constraint maintains $\nabla\phi_{//} \neq 0$ constant, while $\nabla\phi_{\perp}$ can fluctuate around zero such as $\nabla\phi_{\perp} = 0 + \nabla\phi_{fluct}$, where $\nabla\phi_{fluct}$ represents the statistical fluctuations.

Thence, being D definite positive, and being $\nabla\phi_{//}$ fix, from the SFED it follows that

$$| \frac{d_s\phi}{\delta t} | = D\nabla\phi \bullet \nabla\phi > 0 \qquad (81)$$

is minimum with respect the fluctuations of the system around $\nabla\phi_{\perp} = 0$. Thence, for states at local equilibrium (80) represents the Prigogine's principle of minimum entropy production.

DISCUSSION AND CONCLUSIONS

One important objection to the present work can come by asserting that equation (41) is equivalent to the introduction of the local equilibrium condition.

If the local equilibrium exists, then $\nabla\phi$ is small and (41) holds, but vice versa if the radiative coupling is null (i.e., Θ =constant and independent by $\nabla\phi$), then the condition $\nabla ln[D^*] = 0$ would apply whatever large is $\nabla\phi$ and the system far from equilibrium. Therefore, the hypothesis of weak radiative coupling allows that the approximation (41) can be retained even if the local equilibrium condition is not achieved.

The hydrodynamic free energy ϕ and the *hydrodynamic distribution function* ρ^s are well-defined in the far from equilibrium states. On this condition is hence possible to define a criterion that holds far from equilibrium. Once the evolution dynamics is defined by equations (37,41) then the principle of maximal dissipation (of the stochastic part of the hydrodynamic free energy) in far from equilibrium stationary states comes.

This principle is not in contradiction with the preceding principles due to: 1) Prigogine, 2) Sawada and 3) Malkus and Veronis, but agrees with them clarifying their controversial relationships. The present model shows that in the case of a real gas or Marcovian fluids, with no chemical reactions at quasi-isothermal conditions, the principle disembogues into the maximum free energy dissipation one, given by Sawada, or into the principle of maximum heat transfer given by Malkus and Veronis. Contemporarily, for stationary states near-equilibrium, the theory shows that the principle leads to the Prigogine's principle of minimum entropy production.

The SQHA theory shows that the minimum entropy production and the maximum statistical free energy dissipation are two different principia (two extremal criteria defined respect two different variations) but both descend by a unique coherent approach.

The proposed principle clearly shows that the energy (through dissipation) is the physical tool that can lead to the appearance of order. Far from equilibrium, any system, in order to dissipate as faster as possible its statistical free energy, follows a pathway where ordered configurations may exist as demonstrated by Sawada in the electro-convective experiments.

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[19] Ibid 18 pp. 465-474.

[20] Ibid 18 p. 496.

[21] Ibid 20, pp. 482,486; fig 5 and fig. 9.

APPENDIX A

From dynamics to statistics: the classic-stochastic and the quantum-deterministic aspects of the SQHA probability distribution

The existence of the quantum non-locality length λ_q and hence of a scale-transition between the quantum and the classic dynamics confers to the PTF of ρ (namely $P(\rho)$) both the quantum and the statistical character.

Once the $P(\rho)$ of the SPDE (13) is defined, both the quantum wave equation on "microscopic" scale and the statistical distribution on huge-scale are defined.

When the quantum coherence length λ_c goes to infinity (with respect the scale of our system or description) $P(\rho)$ tends to the Dirac function $\delta(\rho - \rho_{(quantum)})$ so that ρ tends to $\rho_{(quantum)}$ and the SQHA converges to the quantum mechanics. In this case, the PDF ρ has the full quantum meaning given by (4-5) and actually is a "quantum mechanical " distribution.

On the other hand, when λ_q is very small compared to the physical length ΔL of the problem (e.g., mean particle distance or free molecular path), the classical stochastic dynamics (24-29) arises.

When we deal with a system of a huge number of (non-linearly interacting) particles with a finite interaction distance [41] (i.e, r_0 for L-J potentials), each coarse-graining cell with a side $\Delta\Omega_q{}^s >> \Delta L >> \lambda_q, r_0$ (containing a large number of molecules) can constitute a local system. This because in the thermodynamic limit (infinite system volume) the quantum correlations involve a small fraction of molecules in a thin layer at the $\Delta\Omega_q{}^s$-boundary.

Therefore, when superficial effects can be disregarded with respect to those of the bulk (i.e., thermodynamic limit) the overall system can be ideally subdivided into a large number of quantum uncorrelated randomly distributed $\Delta\Omega_q{}^s$-subsystems.

In this case it is possible to write the statistical distribution of those $\Delta\Omega_q{}^s$-copies in terms of operators applied to the "mother distribution" $P(\rho)$. This is warranted by the fact that once the evolution of the SQHA probability $P(\rho)$ is defined, it also defines the evolution of the corresponding (statistical) distribution on large-scale (regardless the establishment of the local thermodynamic equilibrium).

The coarse-grained SQHA statistical distribution

Here, we derive the statistical distribution from the SHQA dynamics distribution by subdividing the system in cells of side $\Delta\Omega_q{}^s$.

In order to have independent $\Delta\Omega_q{}^s$ subsystems, in addition to the conditions: (□ □ □$\Delta\Omega_q{}^s >> \Delta L$ (where ΔL is the physical length on molecular scale (e.g., the mean molecular distance)) and (2) $\lambda_q << \Delta\Omega_q{}^s$, we need that the molecules in $\Delta\Omega_q{}^s$ interact with the particles out of it, just through the border of $\Delta\Omega_q{}^s$ for a layer whose characteristic length is much smaller than $\Delta\Omega_q{}^s$ radius. This condition is satisfied for L-J intermolecular potentials where its range of interaction r_0 results $2r_0 < \Delta L$ or even in gas $2r_0 << \Delta L$.

Thence, assuming both $\lambda_q << \Delta\Omega_q{}^s$ and $\Delta L << \Delta\Omega_q{}^s$, the particles on $\Delta\Omega_q{}^s$ border are an infinitesimal fraction of those ones contained in its volume. Hence, in the limit of infinite (sufficiently large) $\Delta\Omega_q{}^s$ volume, the superficial effects (quantum ones included) can be disregarded so that the $\Delta\Omega_q{}^s$ domains tend to be de-coupled and quantum uncorrelated each other.

Under these conditions, since the $\Delta\Omega_q{}^s$ -systems are constituted by a sufficiently large number of non-linearly interacting particles and, hence, classically chaotic, they can be assumed to evolve with random initial conditions because the correlation with their initial state decays quickly.

Therefore, when the local equilibrium is set, the $\Delta\Omega_q{}^s$ -domains are random copies of each other and build up the grand canonical ensemble.

For sake of completeness, it must be said that the condition $\lambda_q < \infty$ needed for obtaining the classical description allows the domains $\Delta\Omega_q{}^s$ to own a finite side.

On the contrary, in the case of perfectly harmonic solids, the quantum potential range of interaction λ_q is infinite and the local means cannot be defined. Since we require the $\Delta\Omega_q{}^s$ -cell length much larger than λ_q , in this case it would comprehend the entire system and we cannot speak in term of local stochastic means but only in term of the quantum means of the entire system.

Actually, for a real solid the intermolecular potential is of L-J type. In this case, the harmonic interaction extends itself to the nearest molecules but not to infinity and λ_q is in the reality finite [16].

We can warrant the above prescriptions by restraining ourselves to the sufficiently general case, to be of interest, of finite-range potentials that have a rapid decreasing Mayers functions [18] as for gas and van der Waals fluids or, more generally for L-J potentials for which we have $\lambda_q \cong 0{,}23 r_0 < \Delta L << \Delta\Omega^s$ [16].

If ΔN_k is the number of the groups of k-molecules in $\Delta\Omega_q{}^s$ and Δn_{kjh} the number of the groups of k-molecules in the domains $\Delta\Omega_{jh} = ((j-1)\Delta q < q < j\Delta q,\ (h-1)\Delta p < p < h\Delta p)$ contained in $\Delta\Omega_q{}^s$, we obtain

$$\Delta N_k = \sum_{j \in \Delta\Omega_q{}^s} \sum_{h=-\infty}^{+\infty} \Delta n_{kjh} \qquad \text{(A.1)}$$

where

$$\Delta n_{kjh} = \sum_i \int_{((j-1)\Delta q)_1}^{(j\Delta q)_1} \dots \int_{((j-1)\Delta q)_{3k}}^{(j\Delta q)_{3k}} \left(\int_{((h-1)\Delta p)_1}^{(h\Delta p)_1} \dots \int_{((h-1)\Delta p)_{3k}}^{(h\Delta p)_{3k}} P_{i(k)}(\rho) d^{3k} p \right) d^{3k} q = \sum_i n_{ikjh} \qquad \text{(A.2)}$$

where V is the system volume, *i(k)* is the index of the i-th group of k-molecules in the entire system and ***P****i(k)* is the projector operator for the *i(k)*-th group that reads

$$P_{i(k)} = \int_{-\infty}^{+\infty} .... \int_{-\infty}^{+\infty} d^{3k} q_{j(k)=1} d^{3k} q_{j(k)\neq i(k)} d^{3k} q_{j(k)=t} \int_{-\infty}^{+\infty} .... \int_{-\infty}^{+\infty} d^{3k} p_{j(k)=1} d^{3k} p_{j(k)\neq i(k)} d^{3k} p_{j(k)=t}$$

(A3)

(A.3)

where $t = 3\frac{n!}{(n-k)!\,k!}$.

It must be said that being ρ the quantum probability (18), it implicitly accounts for the indistinguishability of particles.

The density of states of groups of k molecules on phase space domain $\Delta\Omega_{jh}$ reads

$$\rho^{s}{}_{k(q_j, p_h)} = \frac{\Delta n_{khj}}{\Delta q^{3k} \Delta p^{3k}}$$

$$= \Delta q^{-3k} \Delta p^{-3k} \sum_i \int_{(j-1)\Delta q_1}^{j\Delta q_1} .... \int_{(j-1)\Delta q_{3k}}^{j\Delta q_{3k}} \left(\int_{(h-1)\Delta p_1}^{h\Delta p_1} .... \int_{(h-1)\Delta p_{3k}}^{h\Delta p_{3k}} P_{i(k)}(\rho) d^{3k} p \right) d^{3k} q \qquad \text{(A.4)}$$

It is worth noting that the distribution (A.4) is not generally a statistical distribution. It acquires the statistical character when the $\Delta\Omega_q{}^s$-systems is constituted by a sufficiently large number of sub-systems $\Delta\Omega_q{}^s{}_j = \sum_{h=-\infty}^{h=+\infty} \Delta\Omega_{jh}$ not–correlated each other evolving with random initial conditions (this can happen in a system of non-linear classically chaotic particles where $\lambda_c \ and \ \lambda_q << \Delta q << \Delta\Omega_q{}^s$).

Given the energy function for a group of k molecules

$$E_k = \sum_i E_{i(k)} = \sum_i \frac{p_{n(i(k))} p_{n(i(k))}}{2m} + U_{k(i)} \qquad \text{(A.5)}$$

where $p_{n(i(k))}$ is the momentum of the n-th molecule of the i-th group of k molecules and $U_{k(i)}$ is the potential energy of the i-th group of k molecules. Therefore, the mean value in $\Delta\Omega_{jh}$ follows

$$< E_k >= \frac{\sum_i n_{ikhj} E_{i(k)}}{\sum_i n_{ikhj}} = \frac{\sum_i \frac{n_{ikhj}}{\Delta q^{3k} \Delta p^{3k}} E_{i(k)} \Delta q^{3k} \Delta p^{3k}}{\sum_i n_{ikhj}} \qquad \text{(A.6)}$$

$$= \frac{\int_{\Delta\Omega} .... \int \rho^{s}{}_{k} E_{i(k)} d^{3k} q \, d^{3k} p}{\Delta n_{khj}}$$

where

$$< E_k >_{(q,p)} = \frac{\sum_i \int_{(j-1)\Delta q_1}^{j\Delta q_1} \int_{(j-1)\Delta q_{3k}}^{j\Delta q_{3k}} \int_{(h-1)\Delta p_1}^{h\Delta p_1} \int_{(h-1)\Delta p_{3k}}^{h\Delta p_{3k}} P_{i(k)}(\rho) E_{i(k)} d^{3k}p \ d^{3k}q}{\sum_i \int_{(j-1)\Delta q_1}^{j\Delta q_1} \int_{(j-1)\Delta q_{3k}}^{j\Delta q_{3k}} \int_{(h-1)\Delta p_1}^{h\Delta p_1} \int_{(h-1)\Delta p_{3k}}^{h\Delta p_{3k}} P_{i(k)}(\rho) d^{3k}p \ d^{3k}q}$$

$$< E >_{(q,p)} = \frac{\sum_k \Delta n_{khj} < E_k >}{\sum_k \Delta n_{khj}} \tag{A.7}$$

Moreover, defining the operator $\mathrm{O}^{s}{}_{p_{i(k)}}$ such as

$$\mathrm{O}^{s}{}_{p_{i(k)}} = \Delta q^{-3k} \Delta p^{-3k} \sum_i \int_{(j-1)\Delta q_1}^{j\Delta q_1} \int_{(j-1)\Delta q_{3k}}^{j\Delta q_{3k}} \int_{(h-1)\Delta p_1}^{h\Delta p_1} \int_{(h-1)\Delta p_{3k}}^{h\Delta p_{3k}} P_{i(k)} d^{3k}p \ d^{3k}q \tag{A.8}$$

we can formally link the coarse-grained quantities to the “mother probability distribution” □ in a synthetic manner as follows

$$\mathrm{O}^{s}{}_{p_{i(k)(\rho)}} = \rho^{s}{}_{k(q,p)} \tag{A.9}$$

$$\mathrm{O}^{s}{}_{p_{i(k)(\rho)}}(E_k) = \rho^{s}{}_{k(q,p)} < E_k > \tag{A.10}$$

and, finally,

$$< E >_{(q,p)} = \frac{\sum_k \Delta n_{khj} < E_k >}{\sum_k \Delta n_{khj}} = \frac{\sum_k \mathrm{O}^{s}{}_{p_{i(k)(\rho)}}(E_k)}{\sum_k \mathrm{O}^{s}{}_{p_{i(k)(\rho)}}} \tag{A.11}$$

The summation over all the configurations ρ with probability $P(\rho,\rho')$ leads to the re-defined quantity

$$\rho^{s}{}_{k(q,p)} = \int \mathrm{O}^{s}{}_{p_{i(k)(\rho)}} P(\rho,\rho') d\rho' \tag{A.12}$$

$$< E >_{(q,p)} = \frac{\int \sum_k \mathrm{O}^s \, p_{i(k)(\rho)} (E_k) P(\rho,\rho') d\rho'}{\int \sum_k \mathrm{O}^s \, p_{i(k)(\rho)} P(\rho,\rho') d\rho'} \qquad \text{(A.13)}$$

In many macroscopic problems we can approximate the PTF $P(\rho)$ as a δ-peaked function such as $P(\rho) \cong \delta(\rho' - \rho)$ so that (A.12-13) leads to (A.9,A.11).

The local equilibrium limit

As far as it concerns the above distribution (A.12) as well as the mean energy (A21), it is worth noticing that no hypothesis on thermodynamic equilibrium has been introduced to obtain them so far.

If the characteristic length over which the thermodynamic gradients generate appreciable variations is much bigger than the system dimension, so that the equilibrium can be assumed, the $\Delta\Omega^s$-domains in absence of external fields (otherwise appropriate thermodynamic potentials can be defined) become (random) copies of each others giving rise to the canonical ensemble. In force of this “equalization process” (when it happens), the coarse-grained quantity (A20-A21) can refer to those of the canonical ensemble of the $\Delta\Omega^s$–random–copies, converging to the classical expressions of the statistics of equilibrium. By utilizing the definition of the partition function Z_k

$$Z_k = \frac{1}{V} \int_{-\infty}^{+\infty} .... \int_{-\infty}^{+\infty} \rho^{eq}{}_k \, d^{3k} q \, d^{3k} p \qquad \text{(A.14)}$$

we obtain that

$$lim_{TE} \int_{-\infty}^{+\infty} .... \int_{-\infty}^{+\infty} \rho^s{}_k \, d^{3k} q \, d^{3k} p = N_k = Z_k^{-1} \frac{N_k}{V} \int_{-\infty}^{+\infty} .... \int_{-\infty}^{+\infty} \rho^{eq}{}_k \, d^{3k} q \, d^{3k} p \qquad \text{(A.15)}$$

where $N_k = \sum_k \Delta N_k$ and hence that

$$lim_{TE} \, \rho^s{}_k = Z_k^{-1} \frac{N_k}{V} \rho^{eq}{}_k \qquad \text{(A.16)}$$

Ideal gas

For ideal gas (i.e., punctual particles with $r_0 \to 0$) the only relevant distribution is for k = 1 so that (A.16) reads

$$lim_{TE} \, \rho^s{}_1 = Z^{-1} \frac{N}{V} \rho^{eq} , \qquad \text{(A.17)}$$

Real gas

For a real gas the relevant values of k are k = 1, 2, while for condensed phases k > 1 (practically, for L-J potentials with strong repulsive core, it can be taken values of k about those of the coordination number of the elemental cell).

Given that the interaction distance for the Hamiltonian L-J potential is of order of r_0 as well as for the quantum pseudo-potential (of order of $r_0 + \lambda q$) [16], in a sufficiently rarefied gas phase (i.e., $\Delta L >> r_0 + \lambda q$), particles can be assumed independent and the SQHA-WFM distribution can be factorized as $\rho = \prod_i \rho_i$ and the one-particle group projector $P_{i(1)}$ reads

$$P_{i(1)} = \int_{-\infty}^{+\infty} .... \int_{-\infty}^{+\infty} d^3 q_1 d^3 q_{j \neq i} d^3 q_{3n} \int_{-\infty}^{+\infty} .... \int_{-\infty}^{+\infty} d^3 p_1 d^3 p_{j \neq i} d^3 p_{3n} \qquad \text{(A.18)}$$

leading to

$$P_{i(1)}(\rho) = \rho_i \qquad \text{(A.19)}$$

and

$$\rho^s(q_j, p_h) = \frac{\sum\limits_i \int_{(j-1)\Delta q_1}^{j\Delta q_1} .... \int_{(j-1)\Delta q_3}^{j\Delta q_3} \left(\int_{(h-1)\Delta p_1}^{h\Delta p_1} .... \int_{(h-1)\Delta p_3}^{h\Delta p_{3k}} \rho_i d^3 p \right) d^3 q}{\Delta q^3 \Delta p^3} = \frac{\sum\limits_i \int ... \int_{\Delta\Omega} \rho_i d^3 p \; d^3 q}{\Delta\Omega} \qquad \text{(A.20)}$$

$$\mathrm{O}^s{}_{P_{i(1)(\rho)}} = \rho^s(q, p) \qquad \text{(A.21)}$$

$$\mathrm{O}^s{}_{P_{i(1)(\rho)}}(E) = \rho^s(q, p) < E > \qquad \text{(A.22)}$$

Using the definition of the projector operator $P_{i(1)}$, the number of particles Δn_{1jh} in $\Delta\Omega_{jh}$ can be expressed as

$$\Delta n_{1jh} = \sum_i \int_{(j-1)\Delta q_1}^{j\Delta q_1} \int_{(j-1)\Delta q_{3k}}^{j\Delta q_{3k}} \int_{(h-1)\Delta p_1}^{h\Delta p_1} \int_{(h-1)\Delta p_{3k}}^{h\Delta p_{3k}} \rho_i d^3 p \; d^3 q \qquad \text{(A.23)}$$

with the normalization condition $\iiint d^3 q \iiint d^3 p \rho_i = 1 \; \forall$ i.

The summation over all the configurations ρ with probability $P(\rho, \rho')$ leads to the re-defined quantities

$$\rho^s_{(q,p)} = \int O^s p_{i(1)(\rho)} P(\rho,\rho')d\rho' \qquad \text{(A.24)}$$

$$< E >_{(q,p)} = \frac{\int O^s p_{i(1)(\rho)}(E_k)P(\rho,\rho')d\rho'}{\int O^s p_{i(1)(\rho)}P(\rho,\rho')d\rho'} \qquad \text{(A.25)}$$

APPENDIX B

The SQHA single-particle distribution

In the independent molecule description (that in the case of Lennard Jones potentials is possible when the range of quantum potential interaction (of order of r_0 [16]) is smaller than the mean intermolecular distance) between two consecutive molecular collisions, we consider the SQHA equation (1,5) for the single molecule with the noise $\eta_{(q_\alpha,t)}$

$$\partial_t\rho_{(q,p,t)} = -\nabla\bullet(\rho_{(q,p,t)}\dot{x}_H) + \eta_{(q,t,\Theta)}\delta(p-\nabla_q S) \qquad \text{(B.1)}$$

$$\partial_t n_{(q,t)} = -\nabla_q\bullet(n_{(q,t)}\dot{q}_{cl}) + \eta_{(q_\alpha,t,\Theta)} \qquad \text{(B.2)}$$

$$<\eta_{(q_\alpha,t)},\eta_{(q_\alpha+\lambda,t+\tau)}> = \underline{\mu}\,\delta_{\alpha\beta}\frac{2k\Theta}{\lambda_c}\delta(\lambda)\delta(\tau) \qquad \text{(B.3)}$$

that can be re-cast in the form

$$\partial_t n_{(q,t)} = -\nabla_q\bullet(n_{(q,t)}\dot{q}_{cl} + \delta N_{(q,t,\Theta)}) \qquad \text{(B.4)}$$

$$\partial_t\rho_{(q,p,t)} = -\nabla\bullet(\rho_{(q,p,t)}(\dot{x}_H + \Delta\dot{x})) \qquad \text{(B.5)}$$

$$\Delta\dot{x} = \rho^{-1}\begin{pmatrix}\delta N\delta(p-\nabla_q S)\\ 0\end{pmatrix} \qquad \text{(B.6)}$$

where [17]

$$\begin{aligned}&<\nabla_q\bullet\delta N_{(q_\alpha,t)},\nabla_\lambda\bullet\delta N_{(q_\beta+\lambda,t+\tau)}> = \nabla_q\bullet\nabla_\lambda<\delta N_{(q_\alpha,t)},\delta N_{(q_\beta+\lambda,t+\tau)}>\\ &=<\eta_{(q_\alpha,t)},\eta_{(q_\beta+\lambda,t+\tau)}> = \underline{\mu}\,\delta_{\alpha\beta}\frac{2k\Theta}{\lambda_c}\delta(\lambda)\delta(\tau)\end{aligned} \qquad \text{(B.7)}$$

Discretizing the spatial coordinates by a cell of side δL , with $\delta L > \lambda_c$, for the Markov process (B.3) we can write [17]

$$<\delta N_{(q_\alpha,t)},\delta N_{(q_\beta+\lambda,t+\tau)}> = n_{(q,t)}2D_{(q)}\,\delta_{\alpha\beta}\delta(\lambda)\delta(\tau). \qquad \text{(B.8)}$$

where $D_{(q)}$ is defined positive as well as $n_{(q,t)}$. By comparing (B.7) with (B.8) we obtain

$$2\nabla_q n_{(q,t)}D_{(q)}\,\nabla_\lambda\,ln[\,\delta(\lambda)] = \underline{\mu}\frac{2k\Theta}{\lambda_c} \qquad \text{(B.9)}$$

that after standard calculations [17] leads to

$$\lim_{(\lambda_c/\lambda)\to 0} <\delta N_{(q_\alpha,t)},\delta N_{(q_\beta+\lambda,t+\tau)}> = D_{(\Theta)}\,|q|\,\delta_{\alpha\beta}\delta(\lambda)\delta(\tau) \qquad \text{(B.10)}$$

where $D_{(\Theta)} = 2\underline{\mu}k\Theta$.

Moreover, given that the single molecule is submitted to the field of other ones $\Delta\dot{p}_{mol} = \Delta\dot{p}_{mf} + \Delta\dot{p}_{coll}$ where $\Delta\dot{p}_{mf}$ concerns the mean field of the far away molecules and $\Delta\dot{p}_{coll}$ concerns the field of the colliding molecule that comes out of the cloud and arrives at the interaction distance (for van der Waals fluids it is enough to consider just the interaction between couples of molecules [18] being three molecular collisions unlikely) we can write the SDE for the velocity as

$$\rho_{(q,t)}\dot{x} = \rho_{(q,t)}\dot{x}_H + \delta N_{(q,t,\Theta)}\delta(p-\nabla_q S) + \rho_{(q,t)}\Delta\dot{x}_{coll} + \rho_{(q,t)}\Delta\dot{x}_{mf} \qquad \text{(B.11)}$$

where

$$\Delta\dot{x}_{coll} = (0,\Delta\dot{p}_{coll}). \qquad \text{(B.12)}$$

$$\Delta\dot{x}_{mf} = (0,-\frac{\partial\overline{V}}{\partial q}) = (0,\Delta\dot{p}_{mf}). \qquad \text{(B.13)}$$

where $\overline{V}$ is the mean-field potential of the cloud of molecules leading to the “mean field Hamiltonian”

$$\overline{H} = H + \overline{V} \qquad \text{(B.14)}$$

Moreover, given that $\delta N_{(q,t,\Theta)}$ and $\Delta\dot{p}_{coll}$ are independent (de-coupled) owing very a different time scale (the zero correlation time for the Θ–fluctuations and the molecular collision time τ for $\Delta\dot{p}_{coll}$) the SDE (B.11) mediated over the zero mean Θ–fluctuations reads

$$<\dot{x}> = <\dot{x}_{\overline{H}}> + <\Delta\dot{x}_{coll}> \qquad \text{(B.15)}$$

where

$$\dot{x}_{\overline{H}} = (\frac{\partial\overline{H}}{\partial p},-\frac{\partial\overline{H}}{\partial q}) \qquad \text{(B.16)}$$

owing the Θ-driven noise $\delta N_{(q,t,\Theta)}$ a zero-mean.

Moreover, since the molecular dynamics in a L-J gas phase is highly chaotic, it is possible to assume that molecular collisions are not correlated and hence $<\Delta\dot{x}_{coll}>$ can be approximated as a white noise

$$<\Delta\dot{x}_{coll}> = D^{\frac{1}{2}}\xi_{(t)} \qquad \text{(B.17)}$$

leading to the Fokker-Plank equation that written in a phase space conservation equation that reads

$$\partial_t\rho^* + \nabla\bullet(\rho^*(<\dot{x}_{\overline{H}}> + <\dot{x}_s>)) = 0 \qquad \text{(B.18)}$$

$$< \overset{\bullet}{x}_s >= -(\nabla \bullet \underline{\underline{D}} + \underline{\underline{D}} \bullet \nabla ln[\rho^*]) \qquad \text{(B.19)}$$

where

$$\underline{\underline{D}} \equiv D_{ij} = \frac{1}{2}\tau^{-2}\int_{t}^{t+\tau} < \Delta \overset{\bullet}{x}_{coll} >_i < \Delta \overset{\bullet}{x}_{coll} >_j dt \qquad \text{(B.20)}$$

Here, we derive the statistical probability density distribution ρ^* in term of the single-particle SQHA equation of motion instead that by the particle point density distribution (derived by the classical motion of molecules).

Given a non-linear classic system (no quantum correlations on the scale of molecular mean distance) [16] and hence ergodic, the phase space means $\rho^* = \frac{\Delta N_\Omega}{\Delta\Omega}$, where ΔN_Ω is the number of molecules in the phase space domain $\Delta\Omega_{(q,p)}$, coincides with the time-means.

In Appendix A is detailed how the SQHA "dynamical distribution" ρ leads to the statistical distribution ρ^s.

By using the definition ρ^s (see Appendix A) for the single molecule statistical distribution, we have

$$\begin{aligned}\rho^s{}_{1(q_j,p_h)} &= \frac{\Delta n_{1hj}}{\Delta q^{3k}\Delta p^{3k}} \\ &= \Delta q^{-3}\Delta p^{-3}\sum_i \int_{(j-1)\Delta q_1}^{j\Delta q_1} \ldots\ldots \int_{(j-1)\Delta q_3}^{j\Delta q_3} \left(\int_{(h-1)\Delta p_1}^{h\Delta p_1} \ldots\ldots \int_{(h-1)\Delta p_3}^{h\Delta p_3} P_{i(1)}(\rho) d^3p \right) d^3q\end{aligned} \qquad \text{(B.21)}$$

where the operator $P_{i(1)}$ reads

$$P_{i(1)} = \int_{-\infty}^{+\infty} \ldots\ldots \int_{-\infty}^{+\infty} d^3q_1 d^3q_{j\neq i} d^3q_{3n} \int_{-\infty}^{+\infty} \ldots\ldots \int_{-\infty}^{+\infty} d^3p_1 d^3p_{j\neq i} d^3p_{3n} \qquad \text{(B.22)}$$

Equation (B.22) for real gas (and Markovian van der Waals fluids), using the independent particle description with $\rho \cong \prod_i \rho_{(i)}$, leads to the explicit the connection with □*that reads

$$\begin{aligned}\rho^s{}_{1(q_j,p_h)} &= \Delta q^{-3}\Delta p^{-3}\sum_i \int_{(j-1)\Delta q_1}^{j\Delta q_1} \ldots\ldots \int_{(j-1)\Delta q_3}^{j\Delta q_3} \left(\int_{(h-1)\Delta p_1}^{h\Delta p_1} \ldots\ldots \int_{(h-1)\Delta p_3}^{h\Delta p_3} P_{i(1)}(\rho) d^3p \right) d^3q \\ &= \frac{\sum_i \int_{\Delta\Omega_{(q,p)}} \rho_{(i)} d^3q d^3p}{\Delta\Omega} = \frac{\Delta N_\Omega}{\Delta\Omega} = \rho^*\end{aligned} \qquad \text{(B.23)}$$

Thence, (B.18-B.19) read

$$\lim_{\Delta L >> \lambda_c, \lambda q} \partial_t \rho^s + \nabla \bullet (\rho^s (< \overset{\bullet}{x}_{\overline{H}} > + < \overset{\bullet}{x}_s >)) = 0 \qquad \text{(B.24)}$$

$$\lim_{\Delta L >> \lambda_c ,\lambda q} \rho^s < \dot{x}_s > = -\nabla \bullet (\underline{\underline{D}} \rho^s) \qquad \text{(B.25)}$$

The equality $\rho * = \rho^s$ follows by the absence of quantum correlation between particles and by the ergodicity, that for systems of a huge number of particle in the SQHA model is warranted by the non-linearity that is necessary to the establishing of the classical behavior [15-16]□ □

For a (classical) gas phase made up of structureless point-like particles interacting by central symmetric potential that do not undergo to chemical reactions (particles do not have bounded states (e.g., Lennard-Jones potential with small well, compared do the mean energy of particles) so that molecules with internal structure are not created) (B.25) can be further simplified by excluding the cross-correlations concerning different co-ordinates components, namely

$$D_{ij} = D_{(i)} \delta_{ij} = \begin{pmatrix} 3D_q & 0 \\ 0 & 3D_p \end{pmatrix} = D \begin{pmatrix} 3I_q & 0 \\ 0 & 3I_p \end{pmatrix} \qquad \text{(B.26)}$$

Disregarding the out of diagonal terms of the diffusion matrix D_{ij} , (B.25) reads

$$\lim_{\Delta L >> \lambda_c ,\lambda_q} \rho^s < \dot{x}_s > = -\nabla D_{(i)} \rho^s \qquad \text{(B.27)}$$

APPENDIX C

Thermodynamic equilibrium

Let' find now the equilibrium quantities ρ^s and $\lim_{TE} D = D_{TE}$.

In order to obtain that, we firstly observe that for structureless particles undergoing elastic collisions (e.g., no chemical reactions) in absence of external field H is conserved quantity and hence it holds $\nabla \bullet < \dot{x}_{\overline{H}} > = 0$ (the average "< >" is done on the Θ-fluctuation of each single molecule). By introducing this information in equation (43) for stationary states we obtain

$$\partial_t \rho^s + (< \dot{x}_{\overline{H}} > + < \dot{x}_s >) \bullet \nabla \rho^s = \rho^s \nabla \bullet D \nabla \phi (1 + A + O(\nabla \phi^2)) = \frac{d\rho^s}{dt} \qquad \text{(C.1)}$$

From (C.1) it immediately follows that the thermodynamic equilibrium (i.e., $\frac{d\rho^s}{dt} = 0$) is obtained for $\nabla \phi = 0$.

Being the thermodynamic equilibrium the stationary state with null dissipation (i.e., $\frac{\partial \rho^s}{\partial t} = 0$, $\frac{d\rho^s}{dt} = 0$ and $\nabla \phi = 0$) by (53-54) it follows that

$$\lim_{TE} < \dot{x}_s > = -D \nabla \phi (1 + A + O(\nabla \phi^2)) = 0 \qquad \text{(C.2)}$$

and, being $D > 0$, therefore, in absence of external field (for isotropic condition) that

$$\lim_{TE} \phi = \phi_{TE} = Cons\tan t \qquad \text{(C.3)}$$

where lim $_{TE}$ indicates the establishing of local thermodynamic equilibrium.

Moreover, given from (38) that

$$\rho^{s} = h^{-3}\frac{D^{*}}{D} exp[\,\phi\,] \tag{C.4}$$

it follows that

$$D = h^{-3}D^{*}\, exp[\,\phi + \frac{S^{s}}{k}\,] \tag{C.5}$$

and hence

$$\lim_{TE} D = D_{TE} = h^{-3}D^{*}\, exp[\,\phi_{TE} + \frac{S^{eq}}{k}\,] \tag{C.6}$$

where

$$\lim_{TE} S^{s} = S^{eq} \tag{C.7}$$

$$\phi_{TE} = ln[\,h^{-3}D^{*}\,] + ln[\,D_{TE}\,] - \frac{S^{eq}}{k} \tag{C.8}$$

that by posing

$$ln[\,h^{-3}D^{*}\,] = \phi_{0} \tag{C.9}$$

reads

$$\phi_{TE} - \phi_{0} = ln[\,D_{TE}\,] - \frac{S^{eq}}{k} \tag{C.10}$$

leading to

$$D_{TE} = exp[\,\phi_{TE} - \phi_{0} + \frac{S^{eq}}{k}\,] \tag{C.11}$$

Finally, as well known [ ], to derive the Maxwell-Boltzmann equilibrium distribution from the Fokker –Plank one additional information has necessarily to be introduced (i.e., the linear empirical relations between gradients and fluxes (i.e., null fluxes for null gradients).

In the present approach, we deduce the equilibrium condition by using a similar but less stringent condition (i.e., a sort of “equalization condition ” on the phase space WFM volume ϕ) assuming that at equilibrium there is translation invariance of ϕ and zero fluxes of it.

Given the thermodynamic equilibrium is the stationary state with null dissipation (constant free energy) and null net fluxes of free energy at the boundary (i.e., $\frac{d\Phi_{sup}}{dt} = 0$), by

(58) it follows that

$$\lim_{TE} k\frac{dT\phi}{dt} - \frac{d(E_{cin} + E_{int})}{dt} + \frac{dTS^{s}{}_{vol}}{dt} =$$

$$-\iiint_{V} \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT\frac{(\phi-1)}{\phi}\rho^{s}\left(\frac{d_{s}\phi}{dt}\right)d^{3}p\ d^{3}q = 0 \qquad \text{(C.12)}$$

and that

$$\lim_{TE} k\frac{dT\phi}{dt} = \lim_{TE}\left(\frac{dE}{dt} - \frac{dTS^{s}{}_{vol}}{dt}\right). \qquad \text{(C.13)}$$

That, integrating (C.13) and by using (C.10), finally leads to

$$\phi_{TE} - const = \frac{E_{TE}}{kT} - \frac{S^{s}{}_{vol\,TE}}{k} = ln[D_{TE}] - \frac{S^{eq}}{k} \qquad \text{(C.14)}$$

and, hence, to

$$D_{TE} = exp\left[\frac{E_{TE}}{kT}\right] \qquad \text{(C.15)}$$

and to

$$\phi_{TE} - \phi_{0} = \frac{E_{TE}}{kT} - \frac{S^{eq}}{k} \qquad \text{(C.16)}$$

where ϕ_{TE} represents the thermodynamic free energy.

Moreover, by using (C.1) the above relations lead to

$$\lim_{TE}\ \lim_{\Delta L >> \lambda_{c},\lambda_{q}} \rho^{s} = \rho^{eq} = \lim_{TE} h^{-3}\frac{D^{*}}{D}exp[\phi]$$

$$= \lim_{TE} exp[\phi - \phi_{0}]\,exp\left[-\frac{E}{kT}\right] = exp[\phi_{TE} - \phi_{0}]\,exp\left[-\frac{E_{TE}}{kT}\right] \qquad \text{(C.17)}$$

that is the Maxwell-Boltzmann equilibrium distribution.

Finally, it is interesting to see that the variation of the proportionality constant α in (34) brings to the change of the equilibrium free energy by a constant. In fact, given that

$$\rho^{eq} = h^{-3}\alpha\, exp[\phi_{TE}] = h^{-3}\alpha'\, exp[\phi'_{TE}] \qquad \text{(C.18)}$$

it follows that

$$ln[\frac{\alpha}{\alpha'}] = \phi' - \phi \qquad (C.19)$$

Out of local thermodynamic equilibrium

Out of equilibrium we can set

$$\begin{aligned}\rho^s &= exp[\,\phi - \phi_0\,]\,exp[-\frac{E}{kT}] \\ &= exp[\,\phi - \phi_{TE}\,]\,exp[-\frac{E - E_{TE}}{kT}]\,exp[\,\phi_{TE} - \phi_0\,]\,exp[-\frac{E_{TE}}{kT}] \\ &= exp[\,\Delta\phi\,]\,exp[-\frac{\Delta E}{kT}]\,exp[\,\phi_{TE} - \phi_0\,]\,exp[-\frac{E_{TE}}{kT}] = \rho^{eq}\,exp[-\frac{\Delta S}{k}]\end{aligned} \qquad (C.20)$$

with

$$\begin{aligned}\Delta\phi &= \phi - \phi_{TE} \\ \Delta E &= E - E_{TE}\end{aligned} \qquad (C.21)$$

$$\frac{\Delta S}{k} = -ln[\frac{\rho^s}{\rho^{eq}}] = -\Delta\phi + \frac{\Delta E}{kT} \qquad (C.22)$$

$$\phi = \phi_{TE} + \frac{\Delta E}{kT} - \frac{\Delta S}{k} \qquad (C.23)$$

APPENDIX D

Spatial kinetic equations

By posing

$$\Upsilon = \Upsilon^{eq} + \Delta\Upsilon = E - TS + \Delta\Upsilon \qquad (D.1)$$

it follows that equation (55) reads

$$\begin{aligned}\partial_t n\underline{\Upsilon} + \nabla \bullet n\underline{\Upsilon\,\dot{q}} - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\,\partial_t \Upsilon_{TE} + <\dot{x}_{\overline{H}}> \bullet\nabla\Upsilon_{TE}\,\}d^3p \\ - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\,\partial_t \Delta\Upsilon + <\dot{x}_{\overline{H}}> \bullet\nabla(\,\Delta\Upsilon\,)\}d^3p \\ = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \Upsilon\{\,\nabla \bullet \rho^s D\nabla\phi(1 + A + O(\nabla\phi^2\,))\}d^3p\end{aligned} \qquad (D.2)$$

From which we obtain that

$$\partial_t n\underline{\Upsilon} + \nabla \bullet n\Upsilon\,\underline{\dot{q}} - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\partial_t E + <\dot{x}_{\overline{H}}> \bullet \nabla E\}d^3p - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\partial_t \Delta\Upsilon + <\dot{x}_{\overline{H}}> \bullet \nabla(\Delta\Upsilon)\}d^3p$$
$$= -\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\partial_t TS + <\dot{x}_{\overline{H}}> \bullet \nabla TS\}d^3p + \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \Upsilon\{\nabla \bullet \rho^s D\nabla\phi(1 + A + O(\nabla\phi^2))\}d^3p \tag{D.3}$$

that

$$\partial_t n\underline{\Upsilon} + \nabla \bullet n\Upsilon\,\underline{\dot{q}} - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\frac{dE}{dt}\}d^3p - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\partial_t \Delta\Upsilon + <\dot{x}_{\overline{H}}> \bullet \nabla(\Delta\Upsilon)\}d^3p$$
$$= -\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\partial_t TS + <\dot{x}_{\overline{H}}> \bullet \nabla TS\}d^3p + \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \Upsilon\{\nabla \bullet \rho^s D\nabla\phi(1 + A + O(\nabla\phi^2))\}d^3p \tag{D.4}$$

that

$$\partial_t n\underline{\Upsilon} + \nabla \bullet n\Upsilon\,\underline{\dot{q}} - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{<\dot{p}> \bullet <\dot{q}>\}d^3p - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\partial_t \Delta\Upsilon + <\dot{x}_{\overline{H}}> \bullet \nabla(\Delta\Upsilon)\}d^3p$$
$$= -\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\partial_t TS + <\dot{x}_{\overline{H}}> \bullet \nabla TS\}d^3p + \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \Upsilon\{\nabla \bullet \rho^s D\nabla\phi(1 + A + O(\nabla\phi^2))\}d^3p \tag{D.5}$$

that

$$\partial_t n\underline{\Upsilon} + \nabla \bullet n\Upsilon\,\underline{\dot{q}} - F \bullet \underline{\dot{q}} - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\partial_t \Delta\Upsilon + <\dot{x}_{\overline{H}}> \bullet \nabla(\Delta\Upsilon)\}d^3p$$
$$= -\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s\{\partial_t TS + <\dot{x}_{\overline{H}}> \bullet \nabla TS\}d^3p + \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \Upsilon\{\nabla \bullet \rho^s D\nabla\phi(1 + A + O(\nabla\phi^2))\}d^3p \tag{D.6}$$

and that

$$\partial_t n\underline{\mathrm{Y}} + \nabla \bullet \underline{n\mathrm{Y}\dot{q}} - F \bullet \dot{\underline{q}} - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ \partial_t \Delta\mathrm{Y} + < \dot{x}_{\overline{H}} > \bullet \nabla(\Delta\mathrm{Y})\} d^3 p$$

$$= -\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ T\partial_t S + < \dot{x}_{\overline{H}} > \bullet T\nabla S \} d^3 p - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ S\partial_t T + < \dot{x}_{\overline{H}} > \bullet S\nabla T \} d^3 p$$

$$+ \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \mathrm{Y}\{ \nabla \bullet \rho^s D\nabla\phi(1 + A + O(\nabla\phi^2))\} d^3 p$$

(D.7)

Where the force on unit volume F reads $F = < \dot{p} >_{(q)}$ and for Hamiltonian potentials that are not function of momenta can be brought out of the integral, and where $\dot{\underline{q}} = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s < \dot{q} > d^3 p$.

Moreover, given that for elastic molecular collisions (e.g., no chemical reactions) $\overline{H}$ (41) is conserved so that

$$\nabla \bullet < \dot{x}_{\overline{H}} > = \frac{\partial^2 \overline{H}}{\partial p_i \partial q_i} - \frac{\partial^2 \overline{H}}{\partial q_i \partial p_i} = 0 , \qquad \text{(D.8)}$$

with the help of (48,52), it follows that

$$\partial_t \rho^s + \nabla \bullet \rho^s (< \dot{x}_{\overline{H}} > + < \dot{x}_s >) = 0$$

$$\partial_t \rho^s + < \dot{x}_{\overline{H}} > \nabla \rho^s = -\nabla \bullet (\rho^s < \dot{x}_s >) \qquad \text{(D.9)}$$

$$\partial_t \rho^s + < \dot{x}_{\overline{H}} > \nabla \rho^s = \nabla \bullet (\rho^s D\nabla\phi(1 + A + O(\nabla\phi^2)))$$

we obtain that the first term of the right side reads

$$\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ T\partial_t S + < \dot{x}_{\overline{H}} > \bullet T\nabla S \} d^3 p$$

$$= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ T\partial_t S^s + < \dot{x}_{\overline{H}} > \bullet T\nabla S^s \} d^3 p - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ T\partial_t \Delta S + < \dot{x}_{\overline{H}} > \bullet T\nabla \Delta S \} d^3 p$$

$$= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT\{ \partial_t \rho^s + < \dot{x}_{\overline{H}} > \bullet \nabla \rho^s \} d^3 p - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ T\partial_t \Delta S + < \dot{x}_{\overline{H}} > \bullet T\nabla \Delta S \} d^3 p$$

$$= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT\nabla \bullet (\rho^s D\nabla\phi(1 + A + O(\nabla\phi^2))) d^3 p - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ T\partial_t \Delta S + < \dot{x}_{\overline{H}} > \bullet T\nabla \Delta S \} d^3 p$$

(D.10)

where it has been used the relation

$$S^s = S + \Delta S$$

and hence that

$$\partial_t n\underline{Y} + \nabla \bullet n\underline{Y\dot{q}} - F \bullet \underline{\dot{q}} - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ \partial_t \Delta Y + < \dot{x}_{\bar{H}} > \bullet \nabla(\Delta Y)\} d^3 p$$

$$- \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ T\partial_t \Delta S + < \dot{x}_{\bar{H}} > \bullet T\nabla \Delta S\} d^3 p$$

$$= - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ S\partial_t T + < \dot{x}_{\bar{H}} > \bullet S\nabla T\} d^3 p + \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT(\phi - 1)\{\nabla \bullet \rho^s D\nabla\phi(1 + A + O(\nabla\phi^2))\} d^3 p$$

(D.11)

and that

$$\partial_t n\underline{Y} + \nabla \bullet n\underline{Y\dot{q}} - F \bullet \underline{\dot{q}} + \Delta_1$$

$$= - \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s S\{\frac{dT}{dt}\} d^3 p + \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT(\phi - 1)\{\nabla \bullet \rho^s D\nabla\phi(1 + A + O(\nabla\phi^2))\} d^3 p$$

(D.12)

providing that

$$\Delta_1 = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ \partial_t \Delta Y + < \dot{x}_{\bar{H}} > \bullet \nabla(\Delta Y)\} d^3 p + \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s \{ T\partial_t \Delta S + < \dot{x}_{\bar{H}} > \bullet T\nabla \Delta S\} d^3 p$$

(D.13)

Moreover, by using (57) it follows that

$$\partial_t n\underline{Y} + \nabla \bullet n\underline{Y\dot{q}} - F \bullet \underline{\dot{q}} - \Delta_1$$

$$= - \frac{\gamma}{k}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s S\{\frac{d < E >}{dt}\} d^3 p + \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT(\phi - 1)\{\nabla \bullet \rho^s D\nabla\phi(1 + A + O(\nabla\phi^2))\} d^3 p$$

(D.14)

that ordered gives

$$\partial_t n\underline{Y} + \nabla \bullet n\underline{Y\dot{q}} - F \bullet \underline{\dot{q}} + \frac{\gamma}{k}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} \rho^s S\{\frac{d < E >}{dt}\} d^3 p$$

(D.15)

$$= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT(\phi - 1)\{\nabla \bullet \rho^s D\nabla\phi(1 + A + O(\nabla\phi^2))\} d^3 p + \Delta_1$$

$$\partial_t n\underline{Y} + \nabla\bullet n\underline{Y\dot{q}} - F\bullet\underline{\dot{q}} + \frac{\gamma}{k}F\bullet\underline{S\dot{q}} + \frac{\gamma}{k}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\rho^s S\{m<\dot{q},\ddot{q}>\}d^3p$$
$$= \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT(\phi-1)\{\nabla\bullet\rho^s D\nabla\phi(1+A+O(\nabla\phi^2))\}d^3p+\Delta_1 \qquad \text{(D.16)}$$

where

$$n\underline{S\dot{q}} = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\rho^s S<\dot{q}>d^3p \qquad \text{(D.17)}$$

$$<\dot{q},\ddot{q}>\equiv\sum_i<\dot{q}_{\mathrm{i}},\ddot{q}_i> \qquad \text{(D.18)}$$

that finally reads

$$\partial_t n\underline{Y} + \nabla\bullet n\underline{Y\dot{q}} - F\bullet\underline{\dot{q}} + \frac{\gamma}{k}F\bullet\underline{S\dot{q}}$$
$$= -\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT\frac{(\phi-1)}{\phi}\rho^s(\frac{d_s\phi}{dt})d^3p+\Delta_0+\Delta_1 \qquad \text{(D.19)}$$

where

$$\Delta_0 =\{\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\phi^2(\nabla\bullet\nabla\phi)(1+A+O(\nabla\phi^2))d^3p\} \qquad \text{(D.20)}$$

Given that for independence of molecular velocity and acceleration we can set the variance

$$<\dot{q},\ddot{q}>=\sum_i<\dot{q}_{\mathrm{i}},\ddot{q}_i>\cong 0 \qquad \text{(D.21)}$$

Integrating (D.19) over a volume V and using the Gauss theorem, we find:

$$\iiint_V \partial_t n\underline{Y}\,d^3q + \oiint_\Sigma \nabla\bullet n\underline{Y\dot{q}}\,d\sigma - \iiint_V F\bullet(\underline{\dot{q}} - \frac{\gamma}{k}\underline{S\dot{q}})d^3q$$
$$= -\iiint_V\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT\rho^s(\frac{d_s\phi}{dt})d^3p\ d^3q + \iiint_V \Delta_0\ d^3q + \iiint_V \Delta_1\ d^3q \qquad \text{(D.22)}$$

If the integration is done on the volume of the system the first term is the total time derivative of the SQHA- free energy Φ such as:

$$\iiint_V \partial_t n\underline{\Upsilon}\, d^3q = \frac{d\Phi}{dt} \tag{D.23}$$

the second term represents that one that leaves the system due to the molecular flow through the boundary (positive outgoing) that, it results

$$\oint\!\!\oint_\Sigma \nabla \bullet n\underline{\Upsilon\,\dot{q}}\, d\sigma = -\frac{d\Phi_{sup}}{dt} \tag{D.24}$$

The third term represents the Φ-variation due to the volume force of the external reservoirs due to the flux of particles and entropy that respectively read

$$\iiint_V F \bullet \underline{\dot{q}}\, d^3q = \frac{dL_{ext(vol)}}{dt} = \frac{dE_{vol}}{dt} = \frac{dE_{cin}(\mathrm{vol})}{dt} + \frac{dE_{int}(\mathrm{vol})}{dt} \tag{D.25}$$

$$\frac{\gamma}{k}\iiint_V F \bullet \underline{S\,\dot{q}}\, d^3q = \frac{dTS^s{}_{vol}}{dt} \tag{D.26}$$

Hence, at constant volume we obtain

$$\frac{d\Phi}{dt} - \frac{d\Phi_{sup}}{dt} - \frac{d(E_{cin} + E_{int})}{dt} + \frac{dTS^s{}_{vol}}{dt} = -\iiint_V \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} kT\frac{(\phi-1)}{\phi}\rho^s\left(\frac{d_s\phi}{dt}\right)d^3p\; d^3q + \Delta_0 + \Delta_1 \tag{D.27}$$