COMPETING STYLES OF STATISTICAL MECHANICS: II. Comparison of Theory and Experiment and Further Illustrations

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In the present follow-up article of a previous one [1] we illustrate the use of the Unconventional Statistical Mechanics described and discussed in the latter. This is done via the analysis, resorting to Renyi’s approach, of experimental results in the case of so-called ”anomalous” luminescence in nanometric quantum wells in semiconductor heterostructures, and the so-called ”anomalous” cyclic voltammetry in fractal-like electrodes in microbatteries. Also a purely theoretical analysis is done in the cases of an ideal gas and of radiation comparing the conventional and unconventional approaches. In all of these situations it is discussed which is the failure to satisfy Fisher’s Criteria of Efficiency and/or Sufficiency thus requiring to resort to the unconventional approach, and what determines the value of the infoentropic index in each case, and its dependence on the system characteristics. Moreover, on the basis of the results we obtain, it is conjectured that the infoentropic index may satisfy what we call a law defining a ”path to sufficiency”.

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1. INTRODUCTION

In a preceding article [1] (heretofore referred to as I) has been presented the construction of a so-called Unconventional Statistical Mechanics (USM), that is to say auxiliary forms for use instead of the conventional one – the latter based on the quite general and well established formalism of Boltzmann and Gibbs – when, as there noticed, the researcher is unable to satisfy Fisher’s Criteria of Efficiency and/or Sufficiency in Statistics, namely, a failure in the characterization of the system and its dynamics in what is relevant for the problem in hands. In the present paper we apply the theory to some particular cases, namely two experimental situations involving systems with fractal-like structures, and an analysis of ideal gases.

We consider in next section measurements of “anomalous” luminescence in nanometric quantum wells in semiconductor heterostructures. In section 3 we describe the case of experiments of cyclic voltammetry in microbatteries with thin-film fractal electrodes, where it is involved the so-called “anomalous” diffusion of charges. In section 4 is presented a study of ideal gases comparing the case when a proper characterization is used and the one when as incomplete characterization is used. In all cases we resort to the use of Renyi statistics [2, 3] described in I; as expected the infoentropic index $\alpha$ can only be 1 in the first situation (the criteria of efficiency and sufficiency are satisfied), but different from 1 in the incomplete description when the criteria of efficiency and/or sufficiency are faltering. As already noticed in I, the infoentropic index (when different from 1) depends on several characteristics of the system and its dynamics, viz. the fractal topography, the type and size of the system’s geometry, its equilibrium or nonequilibrium thermodynamic state, the experimental protocol, and so on. Furthermore, as we shall see below, it appears that the infoentropic index can be related to quantities characterizing the system and its description, through relations which can be considered as indicating a kind of “path to sufficiency”.

After the presentation of the five sections with the applications, in a last section we add some additional comments and a summary of the results.

2. “ANOMALOUS” LUMINESCENCE

There exists nowadays a large interest on the question of optical properties of quantum wells in semiconductor heterostructures, which have been extensively investigated in the last decades as they have large relevance for the high perfor-
formance of electronic and optoelectronic devices (see for example Ref. [4]). To deal with these kind of systems, because of the constrained geometry that they present (where phenomena develop in nanometer scales) the researcher has to face difficulties with the theoretical analysis. A most relevant question to be dealt with is the one related to the interface roughness, usually having a kind of fractal-like structure, that is, it is present a spatially varying confinement, which leads to energies and wavefunction depending on boundary conditions which need account for spatial correlations. As a consequence the different physical properties of these systems appear as, say, “anomalous” when the results are compared with those that are observed in bulk materials. A particular case is the one of photoluminescence which we briefly describe here. The conventional treatment via the well established Boltzmann-Gibbs formalism has its application impaired because of the spatial correlations resulting from the spatially varying confinement (as noticed above), relevant in the characterization of the system, on which one does not have access to (obviously the interface roughness varies from sample to sample and one does not have any easy possibility to determine the topography of the interface). This is then the reason why the criterion of sufficiency is not satisfied in this case.

Let us consider a system of carriers (electrons and holes) produced, in the quantum well of a heterostructure, by a laser pulse. They are out of equilibrium and their nonequilibrium macroscopic state can be described in terms of an informational-based statistical thermodynamics [5]. It is characterized by the time evolving quantities energy and density or alternatively by the intensive nonequilibrium variables (Lagrange multipliers in the variational approach to statistical mechanics) quasitemperature $T^*_c(t)$ and quasi-chemical potentials $\mu_e(t)$ and $\mu_h(t)$ ($e$ for electrons and $h$ for holes) [6]. Electrons and holes do recombine producing a luminescence spectrum which, we recall, is theoretically expressed as

$$I(\omega \mid t) \propto \sum_{n,n',k_{\perp}} f^n_{e k_{\perp}}(t) f^{n'}_{h k_{\perp}}(t) \delta (\hbar \Omega - \epsilon_n^{e k_{\perp}} - \epsilon_{n'}^{h k_{\perp}}) ,$$

(1)

where $f^n_e$ and $f^n_h$ are the populations of electrons and of holes, $\hbar \Omega = \hbar \omega - E_G$, with $\omega$ being the frequency of the emitted photon and $E_G$ the energy gap, and the $\epsilon_n^{e h}$ are the electron (hole) individual energy levels in the quantum well (index $n$ for the discrete levels and $k_{\perp}$ for the free movement in the $x - y$ plane).

The textbook expression for the energy levels corresponding to the use of
perfectly smooth bidimensional boundaries is given by

\[ \epsilon_{n\mathbf{k}_\perp} = n^2 \frac{\pi^2 \hbar^2}{2m^*_{e(h)}L_{QW}^2} + \frac{\hbar^2 k_{\perp}^2}{2m^*_{e(h)}} , \]

where \( L_{QW} \) is the quantum-well width and \( m^*_{e(h)} \) is the effective mass and the populations \( f \) take a form that resembles instantaneous in time Fermi-Dirac distributions \([5, 6]\). Using this expression in the calculation of \( I \) of Eq. (1) and comparing it with the experimental results \([7]\) one finds a disagreement, and then it is used the name of “anomalous” luminescence for these experimental results. This is a consequence that we are using an improper description of the carriers’ energy levels – we are not satisfying the criterion of sufficiency (as discussed in I) –, resulting of ignoring the roughness of the boundaries (with self-affine fractal structure \([8]\)) which needs be taken into account in these nanometric-scale geometries, and then the boundary conditions to be placed on the wavefunctions are space dependent. Hence complicated space correlations are to be introduced, but to which we do not have access (information), as already noticed. Hence, this limitation on the part of the researcher breaks the sufficiency criterion, and application of the Boltzmann-Gibbs-Shannon-Jaynes construction is impaired. As noticed in the preceding article, one can try to circumvent the difficulty (which, we stress once again, resides in the limitations the researcher has to possess a proper characterization of the system and its dynamics, and not in Boltzmann-Gibbs statistics) introducing unconventional statistics based on parameter-dependent structural informational entropies.

To deal with the “anomalous” luminescence in nanometric quantum wells in semiconductor heterostructures, we have used the unconventional statistics that is derived from Renyi structural entropy, which depends on a single parameter, namely, the infoentropic index \( \alpha \) (see I). Taking as basic variables, for describing the nonequilibrium thermodynamic state of the “hot” carrier system, the energy \( E_c (t) \) and electron and hole particle number (or density), \( N_e (t) \) and \( N_h (t) \) \([6]\) (the thermodynamically conjugated intensive variables are the quasitemperature \( T^*_c (t) \) and quasi-chemical potentials \( \mu_e (t) \) and \( \mu_e (t) \)), and using Renyi informational entropy, as shown in I \([\text{cf. Eq. (I-42)}]\), we do have for the carriers’ populations, to be used in Eq. (1), that

\[ \bar{f}_{n\mathbf{k}_\perp, \alpha} (t) = \left\{ 1 + (\alpha - 1) B_{\alpha}^{e(h)} (t) \left[ \epsilon_{n\mathbf{k}_\perp} - \mu_{\alpha}^{e(h)} (t) \right] \right\}^{\frac{\alpha - 1}{\alpha + 1}} \pm 1 . \]
a reciprocal of a pseudotemperature, and $\mu$ of a quasi-chemical potential (see I and [6]). Using these populations in the nondegenerate limit (cf. Eq. (53) in I), which depend on $\epsilon_{ek}^{(h)}$, that is, the ideal single-carrier energy level of Eq. (1), the luminescence spectrum is given by

$$I(\omega | t) \propto \left[ 1 + (\alpha - 1) \frac{m_x}{m_e^{*}} B^{e}_{\alpha} (t) \hbar \Omega \right]^{\frac{\alpha}{1-\alpha}} \left[ 1 + (\alpha - 1) \frac{m_x}{m_h^{*}} B^{h}_{\alpha} (t) \hbar \Omega \right]^{\frac{\alpha}{1-\alpha}} =$$

$$= \left[ 1 + (\alpha - 1) \beta_{eff,\alpha} (t) \hbar \Omega + (\alpha - 1)^{2} B^{e}_{\alpha} (t) B^{h}_{\alpha} (t) \frac{m_x^{2}}{m_e^{*} m_h^{*}} (\hbar \Omega)^{2} \right]^{\frac{\alpha}{1-\alpha}}, \quad (4)$$

where $\beta_{eff,\alpha} (t) = \frac{m_e^{*}}{M} B^{e}_{\alpha} (t) + \frac{m_h^{*}}{M} B^{h}_{\alpha} (t)$, $m_x^{-1} = [m_e^{*}]^{-1} + [m_h^{*}]^{-1}$, and $M = m_e^{*} + m_h^{*}$. The second contribution in the last term in Eq. (4) is much smaller than the first, as verified a posteriori, and then we approximately have that

$$I(\omega | t) \propto \left[ 1 + (\alpha - 1) \beta_{eff,\alpha} (t) (\hbar \omega - E_G) \right]^{\frac{\alpha}{1-\alpha}} \quad . \quad (5)$$

The experiments reported in [7] are time integrated, that is, the spectrum is given by

$$I(\omega) = \frac{1}{\Delta t} \int_{t}^{t+\Delta t} dt' I(\omega | t') \quad , \quad (6)$$

where $\Delta t$ is the resolution time of the spectrometer. Using Eq. (5) in Eq. (6), and in the spirit of the mean-value theorem of calculus we write

$$I(\omega) \propto \left[ 1 + (\alpha - 1) \beta_{eff,\alpha} (\hbar \omega - E_G) \right]^{\frac{\alpha}{1-\alpha}} \quad , \quad (7)$$

introducing the mean value $\beta_{eff,\alpha}$ (as an open parameter), which we rewrite as $[\beta_{eff,\alpha}]^{-1} = k_B \Theta_\alpha$, defining an average, over the resolution time $\Delta t$, effective temperature of the nonequilibrium carriers, that is, a measure of their average kinetic energy (see [9]).

In Fig.1 is shown the fitting of the experimental data with the theoretical curve as obtained from Eq. (7). It contains the results referring to four samples having different values of the quantum well width. The corresponding values of $\alpha$, and the kinetic temperature $\Theta_\alpha$ are given in Table I. The information-entropic index $\alpha$ depends, as expected, on the dimensions of the system: as the width of the quantum well increases the values of $\alpha$ keep increasing and tending to 1. This is a clear consequence that the fractal-like granulation of the boundary surface...
becomes less and less relevant, for influencing the outcome of the phenomenon, as the width of the quantum well falls outside the nanometer scale, and is approached the situation of a normal bulk sample. On the other hand the kinetic temperature of the carriers is smaller with increasing quantum well width, as also expected once the relaxation processes, mainly as a result of the interaction with the phonon system, become more effective and the cooling down of the hot carriers proceeds more rapidly.

Moreover, we can empirically derive what we term as a law of “path to sufficiency”, namely,

\[ \alpha (L) \simeq \frac{L + L_1}{L + L_2}, \]

where, by best fitting, \( L_1 \simeq 139 \pm 17 \) \( L_2 \simeq 204 \pm 24 \), all values given in Ångstrom. We do have here that as \( L \) largely increases, the entropic index tends to 1, when one recovers the expressions for the populations in the conventional situation (see I), but as \( L \) decreases \( \alpha \) tends to a finite value \( L_1/L_2 \), in this case \( \sim 0.7 \pm 0.06 \). This indicates that the insufficiency of description when using Eq. (2) in the calculations (the ideal energy levels) becomes less and less relevant as the size of the system increases as already commented.

It is relevant to notice that there exists computer-modelled experiments, in which a certain controlled roughness of the quantum-well boundaries is introduced, Schrödinger equation is solved and the corresponding energy levels are obtained [10]. The conventional statistics is applied, and the results, for this model, qualitatively agree with the experimental ones in real systems. Furthermore, the results of the computer modelled system, with the sufficiency criterion being satisfied, can be reproduced using the ideal eigenvalues of Eq.(2) but in the Renyi statistics we used adjusting the infoentropic index \( \alpha \) [7]. Another observation is that experiments in which are present quantum wells with the same width, but obtained with careful and improved methods of growing, show that as smoother and smoother the boundary surfaces the entropic index \( \alpha \) increases tending to 1, the value corresponding to the ideal situation of perfectly smooth surfaces [7]. Moreover, from the experimental data [7] it can be noticed that the linewidth \( \Gamma \), in each of the four samples of Fig. 1, appears to depend on temperature \( T \), for \( T > 20K \), through a power law, say, \( \Gamma \sim T^{\nu} \), with \( \nu \) approaching 1 (the conventional result) as the quantum-well width increases, as expected; study of the connection of \( \nu \) and the infoentropic index \( \alpha \) is under way.

As a consequence, it can be noticed that through measurements of luminescence it is possible to obtain an evaluation of the microroughness of the samples
being grown, what implies in a kind of method for quality control. On this we may comment that the interface structural properties in quantum wells (QW’s) have been extensively investigated, as they are extremely important for the high performance of electronic and optoelectronic QW-based devices[11–13]. Semiconductor heterostructures interfaces have been investigated by means of direct or indirect characterization techniques. Direct investigations of the interfacial quality have been obtained, for instance, by scanning tunneling microscopy, atomic force microscopy, and transmission electron microscopy [14]. However, interfaces are not easily accessible through these direct investigation methods, so optical techniques (which indirectly probe the interfaces) can constitute a useful approach in semiconductor-interface characterization in heterostructures, as shown above.

This first illustration of the theory clearly evidences the already stated fact that the infoentropic index $\alpha$ is not a universal one for a given system, but it depends on the knowledge of the correct dynamics, the geometry and size including the characteristics and influence of the boundary conditions (e.g. the fractality in the present case), the macroscopic (thermodynamic) state of the system of equilibrium or nonequilibrium conditions, and the experimental protocol.

The case we presented consisted of experiments in time-integrated optical spectroscopy. The phenomenon of “anomalous” luminescence in nanometric quantum wells in semiconductor heterostructures, is also present in the case of time-resolved experiments (nanosecond time resolution where the infoentropic index and the (nonequilibrium) kinetic temperature change in time accompanying the irreversible evolution of the system [15]). The use of USM in a completely analogous way as done above (note that Eq. (4) is valid for a time-resolved situation) allows to determine the evolution in time of the kinetic temperature $\Theta_\alpha (t)$, and the infoentropic index $\alpha (t)$, which is then changing in time as it proceeds the evolution of the irreversible processes in the nonequilibrium thermodynamic state of the carriers, which is a work under way.

3. “ANOMALOUS” DIFFUSION

As a second illustration we consider the question of behavior of fractal electrodes in microbatteries. As a consequence of the nowadays large interest associated to the development of microbatteries (see for example Ref. [16]), the study of growth, annealing, and surface morphology of thin-film depositions used in cathodes, has acquired particular relevance. These kind of systems are characterized by microroughnessed surface boundaries in a geometrically constrained region (nanometric
thin films), and then fractal characteristics can be expected to greatly influence the physical properties [8]. In other words the dynamics or hydrodynamics involved in the functioning of such devices can be expected to be governed by some type or other of scaling laws. Such characteristics have been experimentally evidenced and the scaling laws determined. Researchers have resorted to the use of several experimental techniques: atomic force microscopy allows to obtain the detailed topography of the surface – and then measuring the fractality of it –; cyclic voltammetry is an electrochemical technique used for the study of several phenomena, also allowing for the characterization of the fractal characteristics (scaling laws) of the system [17–19]. Particularly, through cyclic voltammetry it can be put into evidence the property of the so-called “anomalous” diffusion in these systems, what we consider here.

The difference of chemical potential between an anode and a cathode with a thin film (nanometric fractal surface) of, say, nickel oxides, produces a movement of charges in the electrolyte from the former to the latter. In a cyclic voltammetry experiment these charges circulate as a result of the application of an electric field, $e(t)$, with particular characteristics: It keeps increasing linearly in time as $e_0 + vt$, where $v$ is a scanning velocity, during an interval, say $\Delta t$, and next decreases with the same scanning velocity, i.e. $e_0 + v\Delta t - vt$, until recovering the value $e_0$. A current $i(t)$ is produced in the closed circuit, which following the field $e(t)$ keeps increasing up to a peak value $i_p$, and next decreases. This current is the result of the movement of the charges that keep arriving to the thin film fractal-like cathode.

It is found that there follows a power law relation between the peak value, $i_p$, of the current and the rate of change, $v$, of the electric field, namely $i_p \sim v^\xi$. Such current in the fractal electrode, generated by the application of the external potential, depends on the charges that are brought to the interface. Such density of charges $n(x,t)$ at the interface is the one accumulated as a result of a diffusive motion, generated by the difference of chemical potentials between both electrodes. Using the standard Fick’s law it follows that the power index $\xi$ must be $1/2$. Observation shows that it departs from that value and to account for the disparity it has been postulated an “anomalous” diffusion law of the type

$$\frac{\partial}{\partial t}n(\mathbf{r},t) - D_\gamma \nabla^2 n^\gamma(\mathbf{r},t) = 0$$

(9)

where when $\gamma = 1$ is recovered the standard result. Such kind of result can be derived using the USM of $I$, and we resort to the statistics based on Renyi
structural information-entropy, as done in the previous section. The question now is which is the source of the lack of sufficiency in the well established Boltzmann-Gibbs formalism, which forces us to resort to the unconventional approaches. The answer resides in that is being used a quite incomplete hydrodynamic approach to describe the motion of the fluid. Fick’s law is an approximation which gives good results under stringent conditions imposed on the movement (one being the limit of very large wavelengths, that is, the movement is characterized by being of smooth variation in space (near uniform), see Appendix A). Motion of the particles (charges) towards the thin film in the cathode proceeds through the microroughneessed fractal region, and then involves a description requiring to consider intermediate to short wavelengths. Hence, for its description one needs to remove the limitations that restrict the movement to be purely diffusive, that is, to introduce a higher-order generalized hydrodynamics [21, 22] (see also section 4). This means to introduce as basic hydrodynamic variables not only the density, \( n(\mathbf{r}, t) \), but its fluxes of all order, \( I_n(\mathbf{r}, t) \) and \( I_n^{[r]}(\mathbf{r}, t) \), where \( r \geq 2 \) indicates the order of the flux and its tensorial rank: see Eqs. (38) to (42) in Section 4. The motion is then determined by a complicated set of equations of evolutions of the type [5, 21, 23]

\[
\frac{\partial}{\partial t} I_n^{[r]}(\mathbf{r}, t) + \nabla \cdot I_n^{[r+1]}(\mathbf{r}, t) = \mathcal{J}_n^{[r]}(\mathbf{r}, t),
\]

where \( r = 0 \) for the density, \( r = 1 \) for the first (vectorial) flux, or current, and \( r \geq 2 \) for the all higher-order fluxes, \( \mathcal{J}_n^{[r]} \) are the collision operators, and \( \nabla \cdot \) is the operator indicating to take the divergence of the tensor. Solving this set of coupled equations of evolution is a formidable, almost unmanageable, task. As a rule one uses, depending on each experimental situation, a truncation in the set of equations (i.e. they are considered from \( r = 0 \) up to a certain value, say \( n \), of the order \( r \)). Furthermore, to build and solve the set of equations with the spatially quite complicated interface boundary conditions is practically not possible (at most can be attempted in a computer-modelled system). Hence, introducing such truncation produces a failure of the criterion of sufficiency when using the conventional, and universal, approach. Consequently, a way to circumvent the problem is, as done in the previous section, to make calculations in terms of unconventional statistical mechanics, what we do resorting to Renyi’s approach.

We take a truncated description introducing as basic variables the densities of energy and particles and the first (vectorial) particle flux, the corresponding
dynamical operators being
\[ \hat{H}_o = \int d^3r \, \hat{h}(\mathbf{r} | \Gamma) , \]  
with
\[ \hat{h}(\mathbf{r} | \Gamma) = \sum_{i=1}^{N} \frac{p_i^2}{2m} \delta(\mathbf{r} - \mathbf{r}_i) , \]
and
\[ \hat{n}(\mathbf{r} | \Gamma) = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) , \]
\[ \hat{I}_n(\mathbf{r} | \Gamma) = \sum_{i=1}^{N} \frac{p_i}{m} \delta(\mathbf{r} - \mathbf{r}_i) . \]

The unconventional statistical operator is in this case given by Eq. (I.21) using in it the auxiliary ("instantaneous frozen" or quasiequilibrium) statistical operator
\[ \bar{\rho}_\alpha(\Gamma | t, 0) = \frac{1}{\bar{\eta}_\alpha(t)} \left\{ 1 + (\alpha - 1) \left[ \beta \hat{H}_o + \int d^3r \, \tilde{F}_n(\mathbf{r}, t) \hat{n}(\mathbf{r} | \Gamma) + \int d^3r \, \tilde{F}_n(\mathbf{r}, t) \cdot \hat{I}_n(\mathbf{r} | \Gamma) \right] \right\}^{\frac{1}{1-\alpha}} , \]
where \( \tilde{F}_n(\mathbf{r}, t) \) and \( \tilde{F}(\mathbf{r}, t) \) are modified Lagrange multipliers that the variational method introduces, \( \beta = 1/k_B T \) with \( T \) being the temperature of the system, and then we are assuming that the material motion does not affect the thermal equilibrium, and \( \bar{\eta}_\alpha(t) \) ensures the normalization of the distribution, \( \Gamma \) is a point in phase space and we shall designate by \( d\Gamma \) the element of volume in phase space (taken adimensional).

The equations of evolution for the basic variables, derived in the context of the kinetic theory based on the Nonequilibrium Statistical Ensemble Formalism (NESEF) [1, 5, 24] are
\[ \frac{\partial}{\partial t} n(\mathbf{r}, t) = -\nabla \cdot \mathbf{I}_n(\mathbf{r}, t) , \]
\[ \frac{\partial}{\partial t} \mathbf{I}_n(\mathbf{r}, t) = -\nabla \cdot \mathbf{J}^{[2]}_{n\alpha}(\mathbf{r}, t) + \mathbf{J}_{n\alpha}(\mathbf{r}, t) . \]
where the second order flux is given in Eq. (A.18) of Appendix A and \( \nabla \cdot \) is the tensorial divergence operator. Equation (16) is the conservation equation for the density; the terms with the presence of the divergence operator arise out of the contribution resulting from performing the, in this classical case, Poisson bracket with the kinetic energy operator \( \hat{H}_o \); and

\[
J_{n\alpha}(r, t) = \int d\Gamma \left\{ \left\{ \hat{I}_n(r | \Gamma), \hat{H}'(\Gamma) \right\} \tilde{D}_\alpha \left\{ \tilde{\rho}_\alpha(\Gamma | t, 0) \right\} \right\}
\]

(18)
is a scattering operator in the Markovian approximation accounting for the effects of the collisions generated by the interactions with the surrounding media via an interaction Hamiltonian \( \hat{H}' \), and where [cf. Eq. (A.21)]

\[
\tilde{D}_\alpha \left\{ \tilde{\rho}_\alpha(\Gamma | t, 0) \right\} = [\tilde{\rho}_\alpha(\Gamma | t, 0)]^\alpha / Tr \left\{ [\tilde{\rho}_\alpha(\Gamma | t, 0)]^\alpha \right\}
\]

(19)
that is, the escort probability that the unconventional statistics requires to be used in the calculation of averages values (cf. Eq. (18) in I). To solve the system of Eqs. (16) and (17), we need in Eq. (18) to express the right-hand side in terms of the basic variables. The scattering operator takes in general the form of the kind that is present in the relaxation-time approach, as for example shown in Refs. [23–25], namely

\[
J_{n\alpha}(r, t) \equiv -I_n(r, t) / \tau_{I\alpha}
\]

(20)
where \( \tau_{I\alpha} \) is the momentum relaxation time (see Ref. [26], where it is presented an analysis of diffusion in the photoinjected plasma in semiconductors dealt with in the conventional statistical mechanics once the sufficiency condition is verified).

Transforming Fourier in time Eq. (17) we have, after using Eq. (20), that

\[
(1 + i\omega \tau_{I\alpha}) I_n(r, \omega) = -\tau_{I\alpha} \nabla \cdot I^{[2]}_{n\alpha}(r, \omega)
\]

(21)
which in the limit of small frequency, meaning \( \omega \tau_{I\alpha} \ll 1 \), becomes, after back transforming to the time coordinate,

\[
I_n(r, t) = -\tau_{I\alpha} \nabla \cdot I^{[2]}_{n\alpha}(r, t)
\]

(22)
and then, after using Eq. (22), Eq. (16) becomes

\[
\frac{\partial}{\partial t} n(r, t) = \tau_{I\alpha} \nabla \cdot I^{[2]}_{n\alpha}(r, t)
\]

(23)
In order to close Eq. (23) we need to express the second-order flux in terms of the basic variables, \( n \) and \( I_n \), and after some calculus we find that (cf. Eq. (A.20) in Appendix A where some additional comments and considerations are presented)

\[
\nabla \cdot I^{[2]}_n (r, t) = \xi_\alpha \nabla n^{\gamma_\alpha} (r, t),
\]

(24)

where power index \( \gamma_\alpha \) has the \( \alpha \)-dependent expression

\[
\gamma_\alpha = \frac{5 - 3\alpha}{3 - \alpha},
\]

(25)

where the values of \( \alpha \) are restricted to the interval \( 1 \leq \alpha < \frac{5}{3} \), (see Appendix A) and consequently it follows the “anomalous” diffusion equation as given by Eq. (9), where \( D = \xi_\alpha \tau_{I\alpha} \), once we take \( \xi_\alpha \) and \( \tau_{I\alpha} \) as varying slowly in space and time, neglecting then their dependence on \( (r, t) \).

Let us analyze this question of anomalous cyclic voltammetry in fractal electrodes in terms of the previous results. The solution of Eq. (9), for movement in one dimension, say, in \( x \)-direction normal to the electrode surface, is given, for \( 0 < \gamma \leq 1 \), by [27]

\[
n(x, t) = b_\alpha t^{-\mu_\alpha} \left[ a^2 + x^2 t^{-2\mu_\alpha} \right] \frac{1}{\gamma_\alpha - 1},
\]

(26)

where \( a \) and \( b_\alpha \) are constants and \( \mu_\alpha = (\gamma_\alpha + 1)^{-1} = \frac{1}{4} (3 - \alpha) / (2 - \alpha) \). Hence, taking into account that the current, as noticed, is proportional to the arriving charges, and, once \( \mu_\alpha > 0 \), admitting that \( x^2 t^{-2\mu_\alpha} \ll a^2 \), there follows that

\[
I(t) \approx \frac{b_\alpha}{\gamma_\alpha - 1} a^{\gamma_\alpha - 1} t^{-\frac{1}{\gamma_\alpha - 1}} = \frac{1}{2} \left[ \frac{3 - \alpha}{1 - \alpha} \right] b_\alpha a^{\frac{3 - \alpha}{2 - \alpha}} t^{-\frac{1}{\gamma_\alpha - 1}}. \]

(27)

Finally, taking into account that the applied field is \( e(t) = e_o + vt \) (where \( v \) is the scanning velocity), and then \( t = (e - e_o) / v \), Eq. (27) leads to the potential law

\[
I \sim v^\xi
\]

(28)

which stands for the peak value in the experiment and where \( \xi \) is \( \mu_\alpha \), that is

\[
\xi = (\gamma_\alpha + 1)^{-1} = \frac{1}{4} \left[ \frac{3 - \alpha}{2 - \alpha} \right],
\]

(29)

then it has been proved the empirical law, with the power \( \xi \) expressed in terms of the infoentropic index \( \alpha \); the latter is then determined from the experimental value of \( \xi \), which should be contained in the interval \( 0.5 \leq \xi < 1 \), once \( 1 \leq \alpha < 5/3 \).
In Fig. 2 are shown the experimental results linking the values of the peak current for varying values of the scanning velocity $v$, from which can be derived the values of $\xi$ for each $v$, and then those of $\alpha$ through Eq. (29). Hence, keeping all other characteristics of the experiment fixed, the entropic index is dependent on the experimental protocol, in this case on $v$. From Fig. 2 and Eq. (25), it can be derived (similarly to what was done in the previous section) a “path to sufficiency”, given in this case by

$$\alpha(v) \simeq \frac{v + v_1}{v + v_2},$$

(30)

where, by best fitting, $v_1 \simeq 235 \pm 20$ and $v_2 \simeq 145 \pm 15$, in mV/s. As we can see, as $v$ largely increases $\alpha$ goes to 1 – when one recovers the conventional result, that is, the standard Fick’s law, indicating that the Criterion of Sufficiency in the conventional Boltzmann-Gibbs formalism is satisfactorily verified – while for small values of $v$, $\alpha$ tends to the lower bound value $v_1/v_2 \simeq 1.6 \pm 0.15$ in the experiment considered above. We can interpret this as a consequence that a large rate of change of the electric field leads to a very rapid transit of the charge through the roughened layer at the boundary giving no time for the movement tending to get adapted to the morphology of the thin film boundary.

In the present type of experiments in electrochemistry we can derive the same conclusion as the one of the previous section in the experiments in semiconductor physics: the infoentropic index $\alpha$ is not an universal one for a given system but depends on the correct dynamics, geometry and size as well as the characteristics and influence of the boundary conditions, the macroscopic (thermodynamic) state of the system, and the experimental protocol.

Two other interesting problems belong to this question of an “anomalous” diffusion-advection in polymer solutions and “anomalous” current in ionic-conducting glasses [28]. In the first case, macromolecules under flow, one faces the difficulty in the description resulting from the self-similarity in a type of average fractal structure (what we have called “Jackson Pollock Effect”, in view of the analogy with his painting with the dripping method, leading to fractal structures [29]). Without entering into details, given elsewhere [28], the “anomalous” diffusion-advection equation has the form

$$\frac{\partial}{\partial t} n(r,t) = D_\alpha \nabla^2 n^\gamma (r,t) = -\tau_\alpha \nabla \cdot \nabla \cdot (n(r,t) v(r,t) \nabla (r,t)))$$

(31)

where $\gamma_\alpha$ is the one of Eq. (25), $D_\alpha$ of Eq. (9).
In the second case, ionic-conducting glasses, the difficulty in dealing with them consists into the presence of long-range correlations in space, mediated by Coulomb interaction, having scaling characteristics. It leads to the so-called Curie-von Schwaitler current

\[ J(t) \sim t^{-\nu} \]  

that is, following a power law in time. Again, resorting to USM (in Renyi approach) while ignoring the scaling characteristic, we arrive at such power law, with power \( \nu \) related to the information index by the expression

\[ \nu = \frac{3 - \alpha}{(\alpha - 1)^2} \]

(33)

4. IDEAL GAS IN INSUFFICIENT DESCRIPTION

As additional illustrations we consider, first, an ideal gas of \( N \) particles in a volume \( V \), but in the thermodynamic limit and we call \( r_j \) and \( p_j \) the position and velocity of the \( j \)-th particle, with \( \hat{H}(\Gamma) = \sum_j p_j^2 / 2m \) being the Hamiltonian. The most general description of this system in any circumstances is in terms of all the observables of the system, that is from the knowledge of the single-particle dynamical function [5], which in classical mechanics is given by

\[ \hat{n}_1(r, p | \Gamma) = \sum_{j=1}^{N} \delta(r - r_j) \delta(p - p_j) \]

(34)

The statistical operator depends on it and, in NESEF (see I), on the associated Lagrange multiplier which we call \( \varphi_1(r, p; t) \), determined by the informational constraints consisting in the average values

\[ n_1(r, p; t) = \int d\Gamma \hat{n}_1(r, p | \Gamma) \bar{\varrho}(\Gamma | t, 0) \]

(35)

and we do have in the conventional formalism

\[ \bar{\varrho}(\Gamma | t, 0) = Z^{-1}(t) \exp \left\{ -\int d^3r \int d^3p \varphi_1(r, p; t) \hat{n}_1(r, p | \Gamma) \right\} \]

(36)

for the auxiliary (“instantaneous frozen quasiequilibrium”) statistical operator, with the nonequilibrium statistical operator given in terms of it by Eqs (I.14) to (I.17) in I.
As shown elsewhere [5, 22] we can alternatively write the statistical operator in the form of a generalized grand-canonical one, the associated auxiliary operator being

$$\bar{\rho}_{GC}(\Gamma | t, 0) = Z_{GC}^{-1}(t) \exp \left\{ - \int d^3r \int d^3p [\beta (r, t) \hat{h} (r) + A (r, t) \hat{n} (r) + \nu_h (r, t) \cdot \hat{I}_h (r) + \nu_n (r, t) \cdot \hat{I}_n (r) + \sum_{r \geq 2} \left[ F_h^{[r]} (r, t) \otimes \hat{I}_h^{[r]} (r) + F_n^{[r]} (r, t) \otimes \hat{I}_n^{[r]} (r) \right] \right\}$$

(37)

In this Eq. (37) are present the quantities (generalized fluxes)

$$\hat{I}_\gamma^{[r]} (r | \Gamma) = \int d^3p \ u_h^{[r]} (p) \ \hat{n}_1 (r, p | \Gamma) = \sum_{j=1}^{N} \int d^3p \ u_n^{[r]} (p) \ \hat{n}_{1j} (r, p | \Gamma_j)$$

(38)

with $r = 0, 1, 2, ...$ and $\gamma = h$ or $n$, and where

$$\hat{n}_{1j} (r, p | \Gamma_j) = \delta (r - r_j) \delta (p - p_j)$$

(39)

is the individual one-particle dynamical operator and $\Gamma_j$ indicates the one-particle phase point $(r_j, p_j)$, and

$$u_h^{[r]} (p) = [u (p) ... (r - times) ... u (p)]$$

(40)

$$u_n^{[r]} (p) = (p^2/2m) \ u_n^{[1]} (p)$$

(41)

Moreover, in Eq. (40) $[u (p) ... (r - times) ... u (p)]$ indicates the tensorial product of $r$-times the generating velocity

$$u (p) = p/m$$

(42)

where $r = 0$ stands for the densities of energy, $\hat{h} (\gamma = h)$, and particles, $\hat{n} (\gamma = n)$, and their fluxes of all orders, i.e. the vectorial ones (currents) for $r = 1$, and the higher order (tensorial) ones for $r \geq 2$; moreover, we have designated the Lagrange multipliers by $\beta, A, \nu_h, F_h^{[r]}$, and we recall that $\otimes$ stands for fully contracted product of tensors. For an alternative derivation of the auxiliary operator of Eq. (37), through the use of the auxiliary one of Eq. (36), see Appendix B.
The average of the quantities of Eq. (38) over the nonequilibrium ensemble provides the macroscopic variables that are the basic ones for the construction of a nonlinear higher-order hydrodynamics (for example, in a linear approximation, see [24]). The single-particles are independent and then the statistical operator of Eq. (36) can be written as a product of distributions for each particle, namely

\[
\bar{\varrho} (\Gamma | t, 0) = \prod_{j=1}^{N} \bar{\varrho}_j (\Gamma_j | t, 0)
\]

(43)

with

\[
\bar{\varrho}_j (\Gamma_j | t, 0) = Z_j^{-1} (t) \exp \left\{ - \int d^3r \ d^3p \ \varphi_1 (r, p; t) \ \hat{n}_{1j} (r, p | \Gamma_j) \right\}
\]

(44)

where \( \hat{n}_{1j} \) is the one-particle dynamical operator of Eq. (39), \( Z_j \) ensures the normalization, \( \varphi_1 \) is the corresponding Lagrange multiplier. In the grand-canonical description we have that

\[
\bar{\varrho}_{1GC} (\Gamma_j | t, 0) = Z_j^{-1} (t) \exp \left\{ - \int d^3r \ \left[ \beta (r, t) \Delta \hat{h}_1 (r) + A (r, t) \Delta \hat{n}_1 (r) + \right. \right.
\]

\[
+ \nu_h (r, t) \cdot \Delta \hat{I}_{h1} (r) + \nu_n (r, t) \cdot \Delta \hat{I}_{n1} (r) + \left. \right. \right.
\]

\[
\left. \left. \sum_{r \geq 2} \left[ F_{h}^{[r]} (r, t) \otimes \Delta \hat{j}_{h1}^{[r]} (r) + F_{n}^{[r]} (r, t) \otimes \Delta \hat{j}_{n1}^{[r]} (r) \right] \right\} \right)
\]

(45)

where

\[
\Delta \hat{h}_1 (r) = \hat{h}_1 (r) - Tr \left\{ \hat{h}_1 (r) \ \bar{\varrho}_1 (\Gamma_j | t, 0) \right\}
\]

(46)

\[
\hat{h}_1 (r) = \int d^3p \ \frac{p^2}{2m} \hat{n}_{11} (r, p | \Gamma_j)
\]

(47)

and similarly for \( \Delta \hat{n}_1 (r) \), etc.

But let us now consider – as it was in the case of the preceding Section 3 – the situation in which we are forced to resort to a truncated description using, say, a finite small number \( s \) of fluxes (that is \( r = 0, 1, 2, \ldots, s; \ s = 1 \) in Section 3). Therefore Fisher’s criterion of sufficiency is then violated if we proceed with the conventional statistics. Hence, if we want to analyze an experiment where these \( s \) fluxes are accessible, calculating expected values and response function depending on them, we should introduce USM. We proceed next to analyze such
incomplete description of the hydrodynamics of the ideal gas in USM, resorting again to Renyi approach [2, 3].

Consequently, for obtaining the one-particle statistical operator, \( \hat{\rho}_1 (\Gamma_j \mid t, 0) \) one proceeds to maximize Renyi generating functional in terms of escort probabilities as discussed in I, that is [cf. Eq. (I20)]

\[
n_{11} (r, p; t) = \int d\Gamma_j \hat{\rho}_1 (r, p \mid \Gamma_j) \ D_\alpha \{ \hat{\rho}_1 (\Gamma_j \mid t, 0) \} ,
\]

which for \( \alpha = 1 \), i.e. when the condition of sufficiency is satisfied, goes over the conventional expression, as given by Eq. (I.5).

The heterotypical probability distribution is built in terms of the resulting auxiliary one, the latter, in the grand-canonical description, given in this case by

\[
\hat{\rho}_{1\alpha} (\Gamma_j \mid t, 0) = \frac{1}{\eta_{1\alpha} (t)} \left[ 1 + (\alpha - 1) \int d^3r \ d^3p [ \beta_\alpha (r, t) \Delta \hat{h}_1 (r) + A_\alpha (r, t) \Delta \hat{n}_1 (r) + \right.
\]

\[
+ \nu_{\alpha} (r, t) \cdot \Delta \hat{I}_{h1} (r) + \nu_{\alpha} (r, t) \cdot \Delta \hat{I}_{n1} (r)
\]

\[
+ \sum_{r=2}^{s} \left[ F_{h\alpha}^{[r]} (r, t) \otimes \Delta \hat{I}_{h1}^{[r]} (r) + F_{n\alpha}^{[r]} (r, t) \otimes \Delta \hat{I}_{n1}^{[r]} (r) \right] \right] \frac{1}{\tilde{G}_\alpha (t)} ,
\]

where \( \Delta \hat{h}_1, \Delta \hat{n}_1 \), etc., are those defined after Eq. (47). The distribution of Eq. (49) can be written in an alternative form using the redefinitions of the Lagrange multipliers given by

\[
\tilde{\beta}_\alpha (r, t) = \beta_\alpha (r, t) / G_\alpha (t) ,
\]

\[
\tilde{A}_\alpha (r, t) = A_\alpha (r, t) / G_\alpha (t) ,
\]

\[
\tilde{\nu}_{\alpha} = \nu_{\alpha} / G_\alpha (t) ,
\]

\[
\tilde{\nu}_{\alpha} = \nu_{\alpha} / G_\alpha (t)
\]

and

\[
\tilde{F}_{h\alpha}^{[r]} (r, t) = F_{h\alpha}^{[r]} (r, t) / G_\alpha (t)
\]

where

\[
G_\alpha (t) = 1 - (\alpha - 1) \int d^3r \ d^3p [ \beta_\alpha (r, t) h (r, t) + A_\alpha (r, t) n (r, t) + \nu_{\alpha} (r, t) \cdot \mathbf{I}_h (r, t) + \nu_{\alpha} (r, t) \cdot \mathbf{I}_n (r, t) +
\]

\[
+ \nu_{\alpha} (r, t) \cdot \mathbf{I}_h (r, t) + \nu_{\alpha} (r, t) \cdot \mathbf{I}_n (r, t) +
\]

\[
\right]
\]

\[
\]
to obtain that
\[ \bar{\varrho}_{1\alpha} (\Gamma_j | t, 0) = \frac{1}{\tilde{\eta}_{1\alpha} (t)} \left[ 1 + (\alpha - 1) \int d^3r \ d^3p \ \xi_{\alpha} (r, p; \Gamma_j | t) \right]^{1/(1-\alpha)}, \quad (56) \]
where
\[ \int d^3r \ d^3p \ \xi_{\alpha} (r, p; \Gamma_j | t) = \Omega_{j\alpha} (r_j, p_j | t) \quad , \quad (57) \]
with
\[ \Omega_{j\alpha} (r_j, p_j | t) = \tilde{A}_{\alpha} (r_j, t) + \tilde{\beta}_{\alpha} (r_j, t) \frac{p_j^2}{2m} + \tilde{\nu}_{n\alpha} (r_j, t) \cdot \frac{p_j}{m} + \]
\[ + \tilde{\nu}_{h\alpha} (r_j, t) \cdot \frac{p_j^2}{2m^2} \sum_{r=2}^{s} \sum_{\gamma=n \ or \ h} \tilde{F}_{\gamma\alpha} (r_j, t) \otimes u_{\gamma}^{[r]} (p_j) \quad (58) \]
after using the definitions of the densities and fluxes of order \( r = 1 \) to \( s \) in terms of the individual single-particle dynamical function of Eq. (34), and the integrations in \( r \) and \( p \) are performed.

Consequently, the auxiliary probability density of Eq. (43) becomes the product of factors involving each particle individually, given in the Renyi’s approach we used by

\[ \bar{\varrho}_{\alpha} (\Gamma | t, 0) \simeq \frac{1}{\tilde{\eta}_{\alpha} (t)} \prod_{j=1}^{N} [1 + (\alpha - 1) \Omega_{j\alpha} (\Gamma | t)]^{1/(1-\alpha)} \quad . \quad (59) \]

In section 3 we have applied these results, for \( s = 1 \), to derive an “anomalous” diffusion equation (for fitting the experimental data) in voltammetry measurements in microbatteries with fractal electrodes, and in continuation we present an additional application consisting in a study of hydrodynamic properties of an ideal gas of photons in black-body radiation, extending these results to deal now with a quantum system.

5. RADIATION IN INSUFFICIENT DESCRIPTION

Let us consider an ideal gas of photons in the presence of a uniform flux of energy (generated, for example, having different temperatures at both ends of
We look for the determination of the energy, what is done, on the one side using the conventional approach in a description that includes the energy and the energy flux as basic variables and, on the other side, using a quite incomplete description which includes only energy, but dealt with in USM. We indicated by \( \omega_k = c k \) the photon frequency-dispersion relation, and by \( a_k (a_k^\dagger) \) the annihilation (creation) operators in states \( |k\rangle \). The energy and flux of energy dynamical operators are given by

\[
\hat{H} = \sum_k \hbar \omega_k a_k^\dagger a_k ,
\]

\[
\hat{I}_h = \sum_k \hbar \omega_k \nabla_k \omega_k a_k^\dagger a_k .
\]

The auxiliary ("instantaneous frozen quasiequilibrium") statistical operator including both dynamical variables in the conventional formalism is

\[
\bar{\rho} (t, 0) = Z^{-1} (t) \exp \left\{ - F_h (t) \hat{H} - \nu_h (t) \cdot \hat{I}_h \right\} ,
\]

where \( F_h \) and \( \nu_h \) are the associated Lagrange multipliers (intensive nonequilibrium thermodynamical variable), with the nonequilibrium statistical operator given, in terms of this \( \bar{\rho} \), by Eq. (A.14) to (A.17). The averages of the basic dynamical variables can be calculated to obtain respectively that

\[
E (t) = \sum_k \hbar \omega_k \nu_k (t) ,
\]

\[
I_h (t) = \sum_k \hbar \omega_k \nabla_k \omega_k \nu_k (t) ,
\]

where

\[
\nu_k (t) = [\exp \{ F_h (t) \hbar \omega_k + \nu_h (t) \cdot \hbar \omega_k \nabla_k \omega_k \} - 1]^{-1}
\]

Considering the presence of a weak flux, introducing an expansion in \( F_h (t) \) keeping only the first nonnull contribution, we obtain the equations of state (i.e. relation between the basic nonequilibrium thermodynamic variables and the intensive one) given by

\[
\frac{1}{V} E (t) = a \ F_h^{-4} (t) + a_s (t) \ |\nu_h (t)|^2 ,
\]
\[
\frac{1}{V} \mathbf{I}_h(t) = b(t) \nu_h(t),
\]
where
\[
a = \frac{\pi^2}{15\hbar^3 c^3},
\]
\[
a_s(t) = \frac{2\pi^2}{9\hbar^3 c F_h^6(t)},
\]
\[
b(t) = -\frac{4\pi^2}{45\hbar^3 c F_h^5(t)}
\]
as shown in Appendix C. It has been used the relation \(\omega_k = c k\), and we notice that in equilibrium \(\nu_h = 0\) and \(F_h = \beta = [k_B T]^{-1}\), and then Eq. (66) becomes Stefan-Boltzmann law.

Using Eq. (67) in Eq. (66) we can write for the energy that
\[
\frac{1}{V} E(t) = \frac{a}{F_h^4(t)} + \frac{15}{8a c^2 F_h^4(t)} \left| \frac{\mathbf{I}_h(t)}{V} \right|^2.
\]

Let us next consider the most insufficient description, done in terms of only the energy, but using USM in Renyi’s approach, when the auxiliary statistical operator is given by
\[
\bar{\varrho}_\alpha(t,0) = \frac{1}{\bar{\eta}_\alpha(t)} \left[ 1 + (\alpha - 1) \varphi_h(t) \Delta \hat{H} \right]^{\frac{1}{1-\alpha}},
\]
with \(\Delta \hat{H} = \hat{H} - E(t)\), and we recall that in the calculation of average values is used the escort probability expressed in terms of \(\bar{\varrho}_\alpha\) [cf. Eq. (19)]. On the given assumption that the flux is weak, one should expect that \(\alpha\) is close to 1, we write \(\alpha = 1 + \epsilon\) (or \(\epsilon = \alpha - 1\)) and we perform the calculations retaining only terms up to first order in \(\epsilon\). As shown in Appendix C, after some calculation we find that
\[
E(t) = E_o(t) - (\alpha - 1) \varphi_h(t) \sigma_E^2(t),
\]
where
\[
E_o(t) = \sum_k \hbar \omega_k \nu_k(t) = V \Gamma(4) \zeta(4)/2\pi^2 (hc)^3 \varphi_h^4(t) = \frac{a}{F_h^4(t)},
\]
with \(a\) given in Eq. (68), \(\Gamma\) and \(\zeta\) being Gamma and Riemann functions respectively, which follow after using that
\[
N_k(t) = \left( \exp \{ \varphi_h(t) \hbar \omega_k \} - 1 \right)^{-1}.
\]
and $\sigma^2_E(t)$ is the fluctuation of energy

$$
\sigma^2_E(t) = \sum_k (\hbar \omega_k)^2 N_k(t) \left[ 1 + N_k(t) \right] - \left[ \sum_k \hbar \omega_k N_k(t) \right]^2 = 4 (\alpha - 1) \left[ V \Gamma (4) \zeta (4) / 2\pi^2 (\hbar c)^3 \varphi_h^4 (t) \right],
$$

(76)

and then

$$
\frac{1}{V} E(t) = a \varphi_h^{-4} \left[ 1 - 4 (\alpha - 1) \right].
$$

(77)

Equating Eqs. (71) and (77) there follows an equation for the infoentropic index $\alpha$ in terms of the variables which characterize the macroscopic state of the system, namely

$$
\frac{a}{\varphi_h^4} \left[ 1 - 4 (\alpha - 1) \right] = \frac{a}{\varphi_h^4} + \frac{15}{8} \frac{\varphi_h^4}{ac^2} \left[ \frac{I}{V} \right]^2.
$$

(78)

But in the noted condition of weak flux we admit that $F_h \simeq \beta_o$ and $\varphi_h \simeq \beta_o$ with, we recall, $\epsilon = \alpha - 1$, and where $\beta_o$ is the reciprocal of the average temperature of the gas (its gradient being small). Hence, using these results in Eq. (78) we arrive at the expression for $\alpha$ given approximately by

$$
\alpha \simeq 1 - C \left[ \frac{I}{V} \right]^2,
$$

(79)

where

$$
C = \frac{15}{8} \frac{\beta_o^8}{a^2 c^2}.
$$

(80)

It can be noticed that $C^{-1} \sim (a \beta_o^{-4} c)^2$ is something like the square of a flux of energy composed of the energy density of the radiation, $a \beta_o^{-4}$, traversing at the speed of light, while we should expect $I$ to be composed of something like the density of energy traversing at a speed determined by the gradient of temperature, and then, in fact, we do have that for the ideal gas of photons (black-body radiation) works quite well meaning that the insufficiency of characterization can be ignored.

6. IDEAL GAS IN A FINITE BOX

We consider in this section other observation concerning the ideal gas, namely, that as a rule work in the thermodynamic limit is usually taken, what implies an infinite
volume, but real systems are finite [30]. Then in the case of an ideal quantum
gas in a finite box of volume $V$ and area $A$, summation over the states $k \equiv [n_x (\pi/L_x) ; n_y (\pi/L_y) ; n_z (\pi/L_z)]$ (where $n_x, n_y, n_z$ are 1, 2, etc. and $L_x, L_y, L_z$ are the size of the sides of the box) can be exactly replaced by an integral only in the thermodynamic limit. Otherwise we do have corrections depending on the area of the surface, and in the calculation of the partition function, internal energy, etc., there appears nonextensive terms.

According to Pathria’s textbook [31], and see also [32], the density of states of the ideal gas in the finite box is given by

$$g(\epsilon) = V \left[ 2\pi \left( \frac{m}{2\pi^2 \hbar^2} \right)^{3/2} \epsilon^{1/2} - \frac{1}{8V} \left( \frac{m}{\pi \hbar^2} \right) + \ldots \right], \quad (81)$$

where $V$ is the volume and $A$ the area, and dots stand for contributions quadratic and of higher powers in $(A/V)$; once we consider a finite but large box it is kept in what follows only the first-order contribution in $(A/V)$.

Taking the equilibrium grand-canonical ensemble with temperature $T$ and chemical potential $\mu$, using the density of states of Eq. (81) and taking for simplicity the statistically nondegenerate condition, it follows that (see Appendix D)

$$\frac{E}{N} \simeq \frac{3}{2} k_B T \left[ 1 - \frac{1}{6} \frac{A\lambda_T}{V} \right] \lambda_T^{-3} \exp \left\{ \frac{\mu}{k_B T} \right\}, \quad (82)$$

for the density of energy, and

$$\frac{N}{V} \simeq \left[ 1 - \frac{1}{4} \frac{A\lambda_T}{V} \right] \lambda_T^{-3} \exp \left\{ \frac{\mu}{k_B T} \right\}, \quad (83)$$

for the density of particles; $\lambda_T$ is the mean thermal de Broglie wavelength, namely, $\lambda_T^2 = \hbar^2/mk_B T$. Hence, the energy per particle is given by

$$\frac{E}{N} \simeq \frac{3}{2} k_B T \left[ 1 + \frac{1}{12} \frac{A\lambda_T}{V} \right]. \quad (84)$$

Evidently, in the thermodynamic limit (infinite box) it follows the standard result $E = (3/2) N k_B T$ (we recall that we took the nondegenerate condition).

Next we admit to be in the condition of insufficiency consisting in ignoring the finite size of the box, and we proceed with the calculations in the thermodynamics limit but resorting – to patch the limitation thus introduced – to Unconventional Statistical Mechanics.
Using USM in Renyi’s approach, in the insufficient condition, namely, using the thermodynamic limit (infinite-size box), that is using in the calculations the escort probability [cf. Eq. (19)] in terms of the auxiliary Renyi’s heterotypical distribution

$$\bar{\theta}_\alpha = \frac{1}{\eta_\alpha} \left\{ 1 + (\alpha - 1) \left[ F_h \left( \hat{H} - \langle \hat{H} \rangle \right) + F_n \left( \hat{N} - \langle \hat{N} \rangle \right) \right] \right\}^{\frac{1}{1-\alpha}} ,$$

and under the expected condition of \(\alpha\) near 1 (i.e. \(|\alpha - 1| \ll 1\) for a very large box it follows that

$$E \simeq E_o - (\alpha - 1) \left[ F_h \sigma_E^2 + F_n \sigma_{EN}^2 \right] ,$$

$$N = N_o - (\alpha - 1) \left[ F_n \sigma_N^2 + F_h \sigma_{NE}^2 \right] ,$$

where \(\sigma_E^2\) and \(\sigma_N^2\) are the energy and particle-number correlation functions, and \(\sigma_{EN}^2\) and \(\sigma_{NE}^2\) the cross-correlation functions (see Appendix D, for details) and where \(E_o = (3N_o/2F_h)\) and \(N_o\) are the first contribution in the expansion around \(\alpha = 1\).

Finally, we can write (see Appendix D)

$$\frac{E}{N} \simeq \frac{3}{2} F_h^{-1} \left[ 1 + \frac{1}{4} (\alpha - 1) \right] ,$$

where, evidently, in the thermodynamic limit \(\alpha\) approaches 1 as it should. Moreover, from Eq. (88) we can clearly see that the infoentropic index \(\alpha\) depends on the system dynamics, its geometry and size, and the thermodynamic state.

Further applications of USM are available in the literature on the subject, and we can mention the interesting cases of its use on dealing with hydrodynamic turbulence and collider physics in [33] and [34] respectively.

7. FINAL REMARKS

We have illustrated in this paper the use of what we have called Unconventional Statistical Mechanics, an auxiliary formalism which can provide a theoretical approach to situations when the conventional, and well established Boltzmann-Gibbs statistical mechanics has its use impaired because of a lack of a proper knowledge (for the problem in hands) of the characterization of the system and its dynamics on the part of the researcher (the Fisher’s criterion of sufficiency is not satisfied as discussed in [1]).
We have here dealt with “anomalous” luminescence from quantum wells in semiconductor heterostructures, where the failure of sufficiency resides at a microscopic level, in that one does not know the proper quantum mechanical states in the thin (nanometric scale) quantum well. This is the result that we cannot precisely solve Schrödinger equation for the carriers because a failure to impose boundary conditions on the fractal-like morphological structure of the boundaries, to which we do not have easy access; evidently the wave function is largely affected by the roughness of the frontiers in the nanometric structure. As shown, as the width of the quantum well increases, the “anomaly” tends to disappear. This is an example in the realm of semiconductor physics.

A second illustration, the one in section 3, is in the area of electro-physico-chemistry, namely the behavior of thin electrodes with a fractal-like morphology in microbatteries. An analysis of experiments of the so-called cyclic voltammetry has been performed, whose results are a consequence of the occurrence of an “anomalous” diffusion of charges from the electrolyte. In this case the failure of sufficiency resides at a macroscopic, or, better to say, mesoscopic level, when classical Onsagerian hydrodynamics is used instead of the higher-order hydrodynamics that the problem requires. As described the “anomaly” depends on the experimental protocol, and tends to disappear as the rate of charge transfer is increased.

The third illustration, see section 4, is a purely theoretical analysis concerning “anomalous” statistics of an ideal gas. As shown, once the ideal gas is perfectly and completely characterized in terms of the one-particle density function (Dirac-Landau-Wigner single-particle dynamical operator in the quantum case), the only possible description is the conventional one. But, if instead we work with truncated sets of linear combinations of the one-particle density, viz. the densities of particles and energy and the set of their fluxes up to a certain order, in a partial generalized grand-canonical description (and then we do have insufficiency of description), to overcome the fact that we are not complying with the criterion of sufficiency (i.e. to calculate properties) unconventional statistics can be introduced, at the price of having undetermined parameter(s). In terms of them one obtains “anomalous” hydrodynamic laws, for example, in the lowest order approximation, “anomalous” diffusion, with a power law, in the subsequent order an “anomalous” Maxwell-Cattaneo equation (damped waves), and so on. As the order used in the higher-order hydrodynamics increases the “anomaly” tends to disappear because one is approaching a description equivalent to the one in terms of the single-particle density matrix.
It can be noticed that we have always written the word anomalous within quotation marks: This is so because there is nothing anomalous in the physical laws governing the system; what is “anomalous” is the result obtained using the unconventional approach when, as noticed, we are unable to comply with the criterion of sufficiency in the use of the proper Boltzmann-Gibbs statistics. Moreover, concerning the, what we have called, “path to sufficiency” evidenced in the three cases we presented, it is tempting to conjecture that it may be a general characteristic of unconventional statistical mechanics, in any of the cases when different infoentropic-index-dependent structured informational entropies are used.

Finally, we add a couple of comments concerning other possible situations that can be analyzed in terms of USM, and its connection with the criteria of efficiency and sufficiency.

Application of a USM resorting to Havrda-Charvat structural infoentropy to the question of the evolution of a nonequilibrium temperature-like variable, say $T^* (t)$, in the case of a system with long-range spatial correlations [35] shows that in the approach to equilibrium is present a long and near-stationary plateaux above the reservoir temperature which is to be attained in the long range once final thermal equilibrium follows. The calculations are not related (compared) to experimental results, and so we do not know if they have any meaning, except to leave a suggestion of theoretical results in search of an experiment. If the experiment shall show in fact that there are differences in relation to the conventional calculation (“anomalous” results) one should look where Fisher’s criteria of efficiency and sufficiency is not satisfied (if it is the case, as already noticed should be related to improper handling of the long-range correlations; see below the case of the one-electron transistor). There exists a situation in the physics of semiconductors where is also present a near stationary state in the way to equilibrium associated to a slowing-down of the relaxation processes. In the case of the out of equilibrium photoinjected double plasma in semiconductors (see for example Chapter 6 in [5]) what is called the carriers’ quasitemperature $T^* (t)$ follows a path to equilibrium which strongly depends on the experimental protocol [36]. Thermal equilibrium with the reservoir follows very rapidly (tens to a hundred picoseconds) when the exciting laser pulse is short (pico- to subpico-second scale), but is slow and presenting a long near plateaux when the exciting laser pulse is long (tens of picoseconds duration). Such behavior in the latter case is not properly described by theory in the conventional formalism but could, we think, as in [35] be obtained resorting to USM with an appropriate adjustment of the infoentropic
index involved in, for example, Havrda-Charvat or Renyi approaches. The original failure in this case consisted that in the treatment that was applied one does not comply with the criterion of sufficiency by not considering the facts responsible for the phenomenon to occur, namely, “phonon bottleneck” and ambipolar diffusion (the latter keeps decreasing the density of particles), which once incorporated in the description produces an excellent agreement of (conventional) theory and experiment, and we have sufficiency at work [36].

Another interesting case to be considered is the one of single-electron transistors [37], when long-range and strong (because not screened) Coulomb interaction leads to difficulties when dealt with in a simple way in the conventional approach. Again, the point is a failure of sufficiency: in this case is the proper characterization of the states of the system as a result of long-range interconnected correlations. When renormalization of the carrier states is introduced, sufficiency is restored and there follows an excellent agreement between (conventional) theory and experimental data [37]. We conjecture that instead of application of the renormalization group for, as said, restore sufficiency (i.e. a good mimical description of the carriers’ states), one could use the unrenormalized description in terms of USM (a point to be considered in the future).

In the last two cases above it is also conjecturable that there may be present a kind of “path to sufficiency”, of the like of those presented in the three other former examples.

In a concluding remark, we can say, in summary, that the illustrations here presented of the application of the theory of the preceding article, allows for gaining a better perspective of USM, which appears as a useful and practical formalism for the macroscopic description of systems when the research cannot comply with criteria of efficiency and/or sufficiency in the conventional, well established, and physically and logically sound Boltzmann-Gibbs theory. Basically it is a sophisticated fitting formalism to be used in the referred conditions, namely, when one does not have a proper access to the characteristics of the system that are relevant to determine the property of the system we are studying.

It is worth noticing that in the illustrations we presented there appears a quite interesting connection between theory, experiment, and front-line technology.

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Appendix A. “Anomalous” Diffusion

Let us consider first the conventional case of diffusion, when the criterion of sufficiency is satisfied, meaning the several stringent restrictions its validity requires are met, namely, when are satisfied the conditions of local equilibrium, linear Onsager relations and symmetry laws, condition such that the motion is dominated by long wavelengths and very low frequencies contributions, and weak fluctuations. A specific criterion for validity is given in Ref. [38], where it is considered a Brownian-like system composed of two ideal fluids in interaction between them. The continuity equation for the flux $I_n$ (Eq. (17) in [38]) after transforming Fourier in time, takes the form

$$ (1 + i \omega \tau_{n1}) I_n(r, \omega) + \tau_{n1} \nabla \cdot I_n^{[2]}(r, \omega) = 0, \quad (A.1) $$

that is Eq. (10) for $r = 1$, and using Eq. (20) for the collision integral and then $\tau_{n1}$ is the momentum relaxation time. But, at sufficiently low frequencies, meaning that $\omega \tau_{n1}$ can be neglected, we have the appropriate expression

$$ I_n(r, \omega) \simeq -\tau_{n1} \nabla \cdot I_n^{[2]}(r, \omega), \quad (A.2) $$

and a direct calculation tells us that

$$ \nabla \cdot I_n^{[2]}(r, \omega) \simeq (k_B T/m) \nabla n(r, \omega). \quad (A.3) $$

Replacing Eq. (A.3) in Eq. (A.2), and the latter in the conservation equation for the density (Eq. (16) in [38]), we obtain the usual Fick’s diffusion equation

$$ \frac{\partial}{\partial t} n(r, t) + D \nabla^2 n(r, t) = 0, \quad (A.4) $$

where $D = \frac{1}{3} v^2_{th} \tau_{n1}$, with $\frac{1}{2}m v^2_{th} = \frac{3}{2} k_B T$; $v_{th}$ is the thermal velocity and $D$ the diffusion coefficient, with dimension $cm^2/ sec$.

Let us now go over the unconventional treatment, which is required once one is looking forward for an adjustment of data on the basis of a description in terms of a diffusive movement, when this is not possible, as a consequence that diffusion in the microroughness region is governed by not too long wavelengths.
(up to the nanometric ones, i.e. $10^{-7}$ cm, while the limitation of the diffusive domain [38] is the order of $D/v_{th}$, say, typically $10^{-2}$ to $10^{-4}$ cm). A higher-order hydrodynamics [24] needs to be introduced, but if the lower order description including only the density and its flux is kept, then we are not complying with the criterion of sufficiency and we need to introduce Unconventional Statistical Mechanics. Let us consider the auxiliary statistical operator which for this system of free particles can be approximated by a product of the statistical operator of the individual particles, namely (cf. Section 4)

$$\bar{\varrho} (\Gamma | t, 0) = \prod_{j=1}^{N} \bar{\varrho}_{1\alpha} (\Gamma_1 | t, 0), \quad (A.5)$$

where $\Gamma_1$ stands for the one-particle phase point $(r_j, p_j)$ and in Renyi statistics we do have that

$$\bar{\varrho}_{1\alpha} (\Gamma_1 | t, 0) = \frac{1}{z_{\alpha} (t)} \left[ 1 + (\alpha - 1) \int d^3r \int d^3p \varphi_{1\alpha} (r, p, t) \Delta n_{11} (r, p, t) \right]^{-\frac{1}{\alpha - 1}}, \quad (A.6)$$

where

$$\Delta n_{11} (r, p, t) = n_{11} (r, p | \Gamma_1) - \langle n_{11} (r, p | \Gamma_1) \rangle_{\alpha}, \quad (A.7)$$

with

$$\langle n_{11} (r, p | \Gamma_1) \rangle_{\alpha} = \int d\Gamma n_{11} (r, p | \Gamma_1) \tilde{D}_{1\alpha} \{ \varrho_{1\alpha} (\Gamma_1 | t, 0) \}, \quad (A.8)$$

and

$$\varphi_{1\alpha} (r, p, t) = F_{n\alpha} (r, t) + F_{h\alpha} (r, t) \frac{p^2}{2m} + F_{n\alpha} (r, t) \cdot \frac{P}{m}, \quad (A.9)$$

are modified forms of the associated Lagrange multiplier which appear in Eq. (I.16) in I, where in the latter the change in space of the energy density has been desconsidered (i.e. we took $F_{h\alpha} (r, t) = \beta$), $z$ ensures its normalization, and

$$\tilde{D}_{1\alpha} \{ \varrho_{1\alpha} (\Gamma_1 | t, 0) \} = [\varrho_{1\alpha} (\Gamma_1 | t, 0)]^{\alpha} / \int d\Gamma_1 [\varrho_{1\alpha} (\Gamma_1 | t, 0)]^{\alpha}, \quad (A.10)$$

is the accompanying escort probability (see I; [2]).
Introducing the modified Lagrange multiplier
\[ \tilde{\varphi}_{1\alpha}(\mathbf{r}, \mathbf{p}, t) = \varphi_{1\alpha}(\mathbf{r}, \mathbf{p}, t) / \left[ 1 - (\alpha - 1) \int d^3r \int d^3p \varphi_{1\alpha}(\mathbf{r}, \mathbf{p}, t) \langle \hat{n}_{11}(\mathbf{r}, \mathbf{p} | \Gamma_1) \rangle_{\alpha} \right], \]
\[
\text{(A.11)}
\]
we find that
\[ \tilde{\varrho}_{1\alpha}(\Gamma | t, 0) = \frac{1}{\bar{Z}(t)} \left[ 1 + (\alpha - 1) \int d^3r \int d^3p \varphi_{1\alpha}(\mathbf{r}, \mathbf{p}, t) \hat{n}_{11}(\mathbf{r}, \mathbf{p} | \Gamma_1) \right]^{\frac{1}{\alpha - 1}}, \]
\[
\text{(A.12)}
\]
with \( \bar{Z}(t) \) ensuring the normalization condition.

Using Eq. (A.5) to Eq. (A.12), after some lengthy but straightforward calculations, it follows for the energy density that
\[ h(\mathbf{r}, t) = u(\mathbf{r}, t) + n(\mathbf{r}, t) \frac{1}{2} m v_\alpha^2(\mathbf{r}, t), \]
\[
\text{(A.13)}
\]
i.e., composed of the energy associated to the drift movement (the last term) and the internal energy density
\[ u(\mathbf{r}, t) = \frac{3}{5 - 3\alpha} \frac{C_\alpha(\mathbf{r}, t)}{\beta_\alpha(\mathbf{r}, t)} n^{\gamma_\alpha}(\mathbf{r}, t), \]
\[
\text{(A.14)}
\]
where
\[ C_\alpha(\mathbf{r}, t) = \left\{ \frac{2\pi N}{(\alpha - 1) \frac{1}{2} \bar{Z}(t)} \left[ \frac{2m}{\beta_\alpha(\mathbf{r}, t)} B \left( \frac{3}{2}, \frac{\alpha}{\alpha - 1} - \frac{3}{2} \right) \right]^{\frac{2(\alpha - 1)}{\alpha - 3}} \right\}, \]
\[
\text{(A.15)}
\]
\( B(\nu, x) \) is the Beta function, we have written \( F_{\alpha}(\mathbf{r}, t) = \beta_\alpha(\mathbf{r}, t) \); \( F_{\alpha}(\mathbf{r}, t) = m \beta_\alpha(\mathbf{r}, t) v_\alpha(\mathbf{r}, t) \) introducing a “drift velocity” field \( v_\alpha(\mathbf{r}, t) \); moreover
\[ \gamma_\alpha = \frac{3\alpha - 5}{\alpha - 3}, \]
\[
\text{(A.16)}
\]
and the values of \( \alpha \) are restricted to the interval
\[ 1 \leq \alpha < \frac{5}{3}, \]
\[
\text{(A.17)}
\]
Finally, the second order flux is given by
\[ I^{[2]}_n(\mathbf{r}, t) = \int d^3p \left[ \frac{\mathbf{P} \cdot \mathbf{P}}{m^2 m} \right] \langle \hat{n}_{11}(\mathbf{r}, \mathbf{p} | \Gamma_1) \rangle_{\alpha}, \]
\[ n(r, t) \mathbf{v}(r, t) \mathbf{v}(r, t) + \frac{2}{3m} u(r, t) \mathbf{1}^{[2]} , \quad (A.18) \]

where \( \mathbf{1}^{[2]} \) is the unit second order tensor, \([..]\) stands for the tensorial product of vectors, and it can be noticed that

\[ P^{[2]}(r, t) = m I_n^{[2]}(r, t) - m n(r, t) \mathbf{v}(r, t) \mathbf{v}(r, t) \quad (A.19) \]

is the pressure tensor of classical hydrodynamics. Neglecting the terms quadratic in the drift velocity, combining the above equations we obtain that

\[ I_n^{[2]}(r, t) = \xi_{n\alpha} n^\alpha(r, t) , \quad (A.20) \]

where

\[ \xi_{n\alpha} = \frac{2}{3m} \frac{5}{5 - 3\alpha} \frac{c_\alpha(r, t)}{\beta_\alpha(r, t)} , \quad (A.21) \]

is the quantity present in Eq. (24).

**Appendix B. The Grand-Canonical Probability Distribution**

We introduce now the Taylor series expansion in \( p \) in the Lagrange multiplier of Eq. (36), namely

\[ \varphi_1(r, p; t) = \mathcal{F}(r, t) + \mathbf{F}(r, t) \cdot p + \mathcal{F}^{[2]}(r, t) \otimes [pp] + ... , \quad (B.1) \]

where \( \mathcal{F} = \varphi_1 \) with \( p = 0 \), \([F]_i = \partial \varphi_1 / \partial p_i \) \((i = x, y, z)\) with \( p = 0 \), \( \mathcal{F}^{[2]} \) is the tensor of components \( \mathcal{F}_{ij} = \partial^2 \varphi_1 / \partial p_i \partial p_j \) with \( p = 0 \), and \([pp] \) is the tensorial product of the vectors \( p \) and \( \otimes \) stands for fully contracted tensorial product, etc. Hence, for the quantity \( Z_{GC}(t) \) which ensures the normalization of the distribution we do have that

\[ \hat{\varrho}(\Gamma \mid t) = \frac{1}{Z_{GC}(t)} \exp \left\{ - \int d^3r \ d^3p \left[ \mathcal{F}_a(r, t) + \mathbf{F}_a(r, t) \cdot p + \mathcal{F}_a^{[2]}(r, t) \otimes [pp] + ... \right] \hat{n}_1(r, p \mid \Gamma) \right\} . \quad (B.2) \]

Rewriting the Lagrange multipliers \( \mathcal{F} \) as

\[ \mathcal{F}(r, t) = A(r, t) , \quad (B.3) \]

\[ \mathbf{F}(r, t) \cdot p = \nu_n(r, t) \cdot \frac{p}{m} + \frac{p^2}{2m} \nu_h(r, t) \cdot \frac{p}{m} , \quad (B.4) \]
\( \mathcal{F}^{[r]}(\mathbf{r}, t) \otimes [\mathbf{p}\ldots (r - \text{times}) \ldots \mathbf{p}] = F^{[r]}_n(\mathbf{r}, t) \otimes u_n^{[r]}(\mathbf{p}) + F^{[r]}_h(\mathbf{r}, t) \otimes u_n^{[r]}(\mathbf{p}) \), \hspace{1cm} (B.5)

we recover Eq. (37) [we recall that the Lagrange multipliers for energy and density are not independent but related by the law as shown in Ref. [39].

**Appendix C. Radiation Under Flow**

Using the auxiliary distribution of Eq. (62) – which, we recall produces for the basic variables and only the basic variables, in this case \( \hat{H} \) and \( \hat{I}_h \), the same average value as the proper nonequilibrium distribution, cf. preceding article –, it follows that

\[
E(t) = Tr \left\{ \sum_k \hbar \omega_k a_k^\dagger a_k \phi(t, 0) \right\} = \sum_k \hbar \omega_k Tr \left\{ a_k^\dagger a_k \phi(t, 0) \right\}, \quad (C.1)
\]

\[
N(t) = Tr \left\{ \sum_k a_k^\dagger a_k \phi(t, 0) \right\} = \sum_k Tr \left\{ a_k^\dagger a_k \phi(t, 0) \right\}, \quad (C.2)
\]

and after calculation

\[
Tr \left\{ a_k^\dagger a_k \phi(t, 0) \right\} = \nu_k(t), \quad (C.3)
\]

with \( \nu_k(t) \) given by Eq. (65) [a shifted-Planck population]. Considering the case of a weak flux, we can write

\[
\nu_k(t) = [\exp \{ F_h(t) \hbar \omega_k \} - 1]^{-1} + \ldots \quad (C.4)
\]

where \( \ldots \) stands for an expansion of Eq. (65) up to second order in \( \nu_h \). Using Eq. (C.4) in Eq. (C.1) and (C.2) one obtains the expression of Eqs. (66) and (67).

Let us now consider the insufficient condition in which the flux is ignored, and we resort to USM in Renyi's approach, introducing the heterotypical distribution of Eq. (72), is the one of Eq. (73) where

\[
E_o(t) = \left\langle \hat{H} \right\rangle_o = Tr \left\{ \hat{H} \phi_o(t, 0) \right\}, \quad (C.5)
\]

\[
\sigma^2_e(t) = \left\langle \hat{H} \hat{H} \right\rangle_o - \left\langle \hat{H} \right\rangle_o^2 = Tr \left\{ \left( \hat{H} - \left\langle \hat{H} \right\rangle_o \right)^2 \phi_o(t, 0) \right\}, \quad (C.6)
\]

after performing an expansion around \( \alpha = 1 \) in the exponent of the escort probability (cf. Appendix A in I) and retaining the first contribution assuming \( \alpha \) near
it can be noticed that these average values are dependent on the infoentropic index $\alpha$. Moreover,

$$E_o(t) = Tr \left\{ \sum_k \hbar \omega_k a_k^\dagger a_k \rho(t,0) \right\} = \sum_k \hbar \omega_k Tr \left\{ a_k^\dagger a_k \rho(t,0) \right\} = \sum_k \hbar \omega_k N_k(t),$$

where $N_k(t)$ is given in Eq. (75).

### Appendix D. Ideal Gas in a Finite Box

In the conventional approach using the grand-canonical ensemble we do have the well known results that the average energy is given by

$$E = \sum_{k\sigma} \epsilon_{k\sigma} f_{k\sigma} = \int_0^\infty d\epsilon \ g(\epsilon) \ \epsilon \ f(\epsilon),$$

and the average number of particles by

$$N = \sum_{k\sigma} f_{k\sigma} = \int_0^\infty d\epsilon \ g(\epsilon) \ f(\epsilon),$$

where

$$f(\epsilon) = \left[ \exp \left\{ \beta (\epsilon - \mu) \right\} + 1 \right]^{-1},$$

with $\beta = 1/k_B T$ and $\mu$ is the chemical potential, and $\epsilon_{k\sigma} = \hbar^2 k^2 / 2m$.

Using for density of states $g(\epsilon)$ the expression of Eq. (81) in Eqs. (D.1) and (D.2), after taking the statistically nondegenerate limit, i.e. neglecting in Eq. (D.3) 1 in comparison with the exponential, there follow the expressions of Eqs. (82) and (83) in the text.

We consider now the unconventional approach, introducing the insufficiency in Fisher’s sense of taking for $g(\epsilon)$ only the first term on the right of Eq. (81) – meaning the expression corresponding to the thermodynamic limit –, and resorting to Renyi’s approach, that is, using the statistical operator of Eq. (85) and in the calculation of averages the escort probability in term of it, it follows that the average value of energy is given by

$$E \simeq \langle \hat{H} \rangle_o - (\alpha - 1) \ F_h \left[ \langle \hat{H} \hat{H} \rangle_o - \langle \hat{H} \rangle_o^2 \right] - (\alpha - 1) F_n \left[ \langle \hat{H} \hat{N} \rangle_o - \langle \hat{H} \rangle_o \langle \hat{N} \rangle_o \right].$$
and for the average value of the particle number

\[ N \simeq \langle \hat{N} \rangle_o - (\alpha - 1) F_n \left[ \langle \hat{N} \hat{N} \rangle_o - \langle \hat{N} \rangle_o^2 \right] - (\alpha - 1) F_h \left[ \langle \hat{H} \hat{N} \rangle_o - \langle \hat{H} \rangle_o \langle \hat{N} \rangle_o \right], \]

(D.5)

where

\[ \langle \ldots \rangle = Tr \{ ... \hat{\varrho}_\alpha \} , \]

(D.6)

and it has been taken \( \alpha \) is near 1, i.e. the case of a finite but long box.

Performing the calculations, a lengthy but straightforward task, it follows that

\[ E = \frac{3}{2} N_o F_h^{-1} - (\alpha - 1) \left( \frac{15}{8} N_o F_h^{-1} + \frac{3}{2} N_o F_n F_h^{-1} \right) , \]

(D.7)

\[ N = N_o - (\alpha - 1) N_o \left( \frac{3}{2} + F_n \right) . \]

(D.8)

It should be noticed that the averages of the kind of Eq. (D.5) present in these expression are dependent on \( \alpha \). If, in a first approximation we approximate these average by taking \( \alpha \simeq 1 \), from Eq. (D.7) and (D.8) there follows Eq. (87) and consequently the expression for the infoentropic index \( \alpha \) as given by Eq. (88).
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Values of the infoentropic index $\alpha$ and kinetic temperature $\Theta$ fitting the luminescence spectrum as shown in Figure 1.

| $L_{QW} (\text{Å})$ | $\alpha$ | $\Theta (K)$ |
|---------------------|----------|--------------|
| 15                  | 0.698    | 48           |
| 30                  | 0.714    | 26           |
| 50                  | 0.745    | 17           |
| 80                  | 0.764    | 10           |
Figure 1: Comparison of theory (full line) and experimental results (filled geometric figures) in the luminescence spectra (high frequency side or Shockley-Roosbroecke domain purely dependent on the carriers’ dynamics), for several samples under identical processes of growth, but with different length of the quantum well. The corresponding values of the infoentropic parameter $\alpha$ and the kinetic temperature $\Theta$ are given in Table I.
Figure 2: Logarithmic plot of the current peak value with the scanning velocity $v$ of the applied electric field, in experiments of cyclic voltammetry in microbatteries with nanometric thin film fractal-like electrodes. The tangent at each point gives the value of the index $\xi$ of Eq. (29); the lower and upper straight lines are approximate fittings in regions where $\xi$ varies smoothly [cf. Eq. (31)].