Exploring Quantized Entropy Production Strength in Mesoscopic Irreversible Thermodynamics

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Abstract

This letter aims to investigate thermodynamic processes in small systems in the Onsager region by showing that fundamental quantities such as total entropy production can be discretized on the mesoscopic scale. Even the thermodynamic variables conjugate to the thermodynamic forces and the Glansdorff-Prigogine's dissipative variable may be discretized. The Canonical Commutation Rules (CCRs) valid at the mesoscopic scale are postulated and the measurement process consists of determining the eigenvalues of the operators associated with the thermodynamic quantities. The nature of the quantized quantity β, entering the CCRs, is investigated by a heuristic model for nano-gas and analyzed through the tools of classical statistical physics. We conclude that according to our model, the constant β does not appear to be a new fundamental constant but corresponds to the minimum value.

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Mesoscopic structures have emerged as a dynamic and rapidly advancing research frontier, captivating scientists across disciplines from physics, chemistry, and mineralogy to the life sciences. The relentless push towards miniaturization, with devices now spanning mere nanometers, is not only revolutionizing the creation of new materials but also deepening our grasp of the fundamental laws that dictate the behavior of systems at the mesoscopic scale. Based on recent experimental results and previous theoretical research, we investigate thermodynamic processes in small systems in Onsager's region. To this end, we begin with a brief overview of the key aspects of Prigogine's formulation of thermodynamic processes within Onsager's regime. Let us consider a system characterized by n *degrees of advancement* $\xi_1, \cdots, \xi_n$. The deviations of ξ_i from the values $\xi_\mu^{eq.}$, assumed by the degrees of advance when the system is in local equilibrium, are denoted by $\bar{\alpha}_\mu$, that is $\bar{\alpha}_\mu \equiv \xi_\mu - \xi_i^{eq.}$. So, $\bar{\alpha}_\mu$ may represent the fluctuations of the various thermodynamic quantities such as temperature, pressure, etc. According to the principles of thermodynamics, one can introduce for any macroscopic system a state function S, the entropy of the system, which has the following properties. The entropy variation due to the fluctuations reads [1]

$$\Delta S = \Delta_e S + \Delta_I S \tag{1}$$

where

$$\Delta S = \int_{\xi^{eq.}}^{\xi} dS = S(\xi) - S(\xi^{eq.}) \quad ; \quad \Delta_e S = \int_{\xi^{eq.}}^{\xi} d_e S \quad ; \quad \Delta_I S = \int_{\xi^{eq.}}^{\xi} d_I S \tag{2}$$

$\Delta_e S$ denotes the entropy supplied to the system by its surroundings, and $\Delta_I S$ is the entropy produced inside the system, respectively. The second law of thermodynamics states that $d_I S$ must be zero for reversible (or equilibrium) transformations and positive for irreversible transformations of the system i.e., $\Delta_I S \geq 0$. The entropy supplied $\Delta_e S$, on the other hand, may be positive, zero, or negative, depending on the interaction of the system with its surroundings. We also have [2]

$$\bar{\sigma} = \frac{\delta}{\delta V}\Big(\frac{d\Delta_I S}{dt}\Big) = \frac{d}{dt}\Big(\frac{\delta \Delta_I S}{\delta V}\Big) = \frac{\partial \Delta_I s}{\partial \bar{\alpha}_\mu}\frac{d\bar{\alpha}_\mu}{dt} = x^\mu j_\mu \quad \text{with} \quad j_\mu \equiv \frac{d\bar{\alpha}_\mu}{dt} \tag{3}$$

with j_μ denoting the *thermodynamic fluxes* conjugate to the thermodynamic force x^μ, and δV denotes an infinitesimal spatial volume element occupied by the system. In Eq. (3) we have adopted the Einstein convention of repeated indices. Unless stated otherwise, this convention will also be adopted in the sequel of this manuscript. To work with entropy production strength, which has dimension [Energy]/([Temperature] × [time]), we adopt the following definition for the thermodynamic forces, the thermodynamic fluxes, and the thermodynamic variables, respectively:

$$X^{\mu}(\mathbf{r},t) \equiv \sqrt{V}x^{\mu} \quad ; \quad J_{\mu}(\mathbf{r},t) \equiv \sqrt{V}j_{\mu} \quad ; \quad \alpha_{\mu}(\mathbf{r},t) \equiv \sqrt{V}\bar{\alpha}_{\mu} \tag{4}$$

with $(\mathbf{r},t)$ denoting the space-time. Eq. (3) links the entropy production strength with the thermodynamic forces and the conjugate fluxes. To obtain the expression for the entropy production strength solely in terms of the thermodynamic forces, it is necessary to relate the dissipative fluxes to the thermodynamic forces that produce them. These closure relations are called *transport flux-force relations.* For thermodynamic systems in Onsager's region, the most used transport relations are [2]

$$J_{\mu} = L_{\mu\nu}X^{\nu} \tag{5}$$

with $L_{\mu\nu} = L_{\nu\nu}$. $L_{\mu\nu}$ is called *Onsager's Matrix* where the entries are the transport coefficients, independent of the thermodynamic forces. Note that to perform calculations, the transport coefficients must be written in a dimensionless form. In terms of the transport coefficients, in Onsager's region, the local entropy production strength can be brought into the form

$$\sigma = L_{\mu\nu}X^{\mu}X^{\nu} = VL_{\mu\nu}x^{\mu}x^{\nu} = V\bar{\sigma} \tag{6}$$

So, as we wish, σ has dimension [Energy]/([Temperature]×[time]) while $\bar{\sigma}$ has dimension [Energy]/([Temperature]×[time]×[Volume]).

A. The Space of the Thermodynamic Forces

To continue with the formalism it is necessary to define the space where we can perform calculations. For this, we have to specify two quantities: the *metric tensor* and the *affine connection* [3], [4], [5], [6], [7], [8]. The metric tensor and the affine connection are determined by physics. More specifically, the metric tensor is identified with the symmetric piece of the transport coefficients, and the expression of the affine connection is determined by imposing the validity of the Glansdorff-Prigogine *Universal Criterion of Evolution* [5], [8]. For the second law of thermodynamics, the square distance between two infinitely close points in the space of the thermodynamic forces is always a nonnegative quantity. Additionally, in the thermodynamic space, the total entropy production σ_T in Onsager's region reads

$$\sigma_T(t) = \frac{1}{V}\int_V L_{\mu\nu} X^\mu X^\nu \sqrt{L} d^n X \tag{7}$$

with L denoting the determinant of Onsager's matrix and V the volume occupied by the system, respectively.

I. QUANTIZATION OF THE ENTROPY PRODUCTION STRENGTH

A. A Heuristic Approach

One of the main objectives of the Brussels School of Thermodynamics, founded by Théphile De Donder and Ilya Prigogine, was to investigate systems on a mesoscopic scale to discover the fundamental laws governing them. We start our analysis with the following (heuristic) observation. A *quasi-localized* disturbance of entropy production can be obtained using a linear superposition of modes with close mode numbers. So, if the system is subject to ”n” independent thermodynamic forces, a *local disturbance* of entropy production strength can be represented as a superposition of plane waves with the generic wave number $\mathbf{K}$ compatible with periodicity conditions:

$$\sigma(\mathbf{X}, t) = \frac{1}{(2\pi)^n}\int_{-\infty}^{+\infty}\left(\sigma_{\mathbf{K}} e^{i(\mathbf{K}\cdot\mathbf{X}-\omega_{\mathbf{K}} t)} + \sigma^\star_{\mathbf{K}} e^{-i(\mathbf{K}\cdot\mathbf{X}-\omega_{\mathbf{K}} t)}\right) d\mathbf{K} \tag{8}$$

Notice that the modes are in the space of thermodynamic forces (and not in the ordinary space). As known, Fourier's theorem requires:

$$\Delta t\Delta\omega \geq 1 \quad ; \quad \Delta K_\mu \Delta X^\mu \geq 1 \quad \text{(no summation convention on } \mu;\ \mu = 1, \cdots, n) \tag{9}$$

Recent experimental results lead to postulate the heuristic idea where, on mesoscopic scale, in the space of the thermodynamic forces the entropy production strength is proportional to the frequency and the thermodynamic variable α_μ, conjugate to the thermodynamic forces X^μ, is proportional to the wave-vector K_μ i.e.,

$$\sigma = \not{k}_B\omega \qquad ; \qquad \alpha_{\mu,\mathbf{K}} = \not{k}_B\mathbf{K}_\mu \qquad \text{with} \quad \not{k}_B \equiv \beta k_B \tag{10}$$

with $\not{k}_B$ denoting Boltzmann's constant k_B times a pure number, say β, undetermined at this stage. A combination of Eq. (9) with Eq. (10) yields

$$\begin{aligned} &\Delta t\Delta\sigma \geq \not{k}_B && (11)\\ &\Delta\alpha_\mu\Delta X^\mu \geq \not{k}_B \quad \forall\mu \qquad \text{(no summation convention on } \mu;\ \mu = 1, \cdots, n) \end{aligned}$$

These inequalities establish a fundamental limit on the precision with which certain pairs of physical quantities, such as entropy production rate and time or thermodynamic force and its corresponding thermodynamic variable, can be predicted from initial conditions. In other words, we cannot precisely determine both the entropy production rate of a system and time simultaneously; the more accurately we know the system's entropy production, the less accurately we know the time, and vice versa. Similarly, there is an uncertainty relationship between a thermodynamic force and its corresponding thermodynamic variable. The pairs of variables (t, σ) and (α_μ, X^μ) may be called *canonically conjugate* (in analogy with the quantum mechanics' terminology).

B. The Formalism of Second Quantization and the Thermodynamic Commutation Rules

We are now faced with two issues: i) The *heuristic intuitions* expressed in the previous subsection must be supported by a rigorous formalism, and ii) We are dealing with many entities with infinite degrees of freedom as these entities are continually being produced and absorbed. The appropriate mathematical tool to treat these problems is provided by the formalism of the *second quantization* (SQ) largely used in quantum field theory. The second quantization is a mathematical algorithm for dealing with a large assembly of identical entities [9]. This mathematical algorithm is based on introducing canonical commutation rules (CCRs) where the physical quantities are "promoted" to operators. Note that the introduction of the CCRs do not necessarily concern quantum mechanics. Still, they are an indispensable tool for treating a very large number of identical entities that can be produced and absorbed. Hence, by the SQ-formalism, we have to promote the single variables σ and t, and X^μ and α_μ to *operators*, which act on some state space of the system, separately, imposing a "bind" between them so that their products behave "as we wish" (see also [10]). At the mesoscopic scale, we have to write:

$$
\begin{aligned}
&[t, \sigma] = i\frac{\not{k}_B}{2} \qquad\qquad\qquad\qquad\qquad\qquad (12)\\
&[\alpha_{\mu,\mathbf{K}}, X^\nu_{\mathbf{K}'}] = i\frac{\not{k}_B}{2}\delta_{\mu\nu}\delta_{\mathbf{K}\mathbf{K}'} \qquad \text{with} \quad \not{k}_B = \beta k_B
\end{aligned}
$$

with $[\cdots]$ denoting the *commutator* between two operators: $[A, B] = AB - BA$ and $\delta_{\mu\nu}$ the Kronecker delta, respectively. In [11] we can find recent experiments where the entropy production in non-equilibrium systems has been measured. To the best of our knowledge, [11] provides the most accurate value of the lowest limit of this constant that appeared up to now in the literature. In [11] we find several examples of experimental traces for the tip position of different mechano-sensory hair bundles as a function of time. The authors estimated the local irreversibility measure obtained from single 30 *sec.* recordings of the oscillations shown in these examples. The sampling rate was $\omega = 2.5kHz$. From these experiments, we can estimate (albeit approximately) the numerical value of β. We find $\beta \sim 1.2 \times 10^{-8}$ so, $\not{k}_B \sim 1.6 \times 10^{-31}\ J/K$. In the forthcoming section, we shall provide a (rough) estimation of constant β for a quasi-ideal gas. We shall see that, in this case, β does not appear to be a new fundamental constant but corresponds to the minimum value.

II. DISCRETIZATION OF THE TOTAL ENTROPY PRODUCTION STRENGTH IN ONSAGER'S REGIME

The *total entropy production strength* reads

$$\sigma_T(t) = \frac{1}{V}\int_V \sigma(\mathbf{X},t)\sqrt{L}d^nX = \frac{1}{V}\int_V L_{\mu\nu}X^\mu X^\nu \sqrt{L}d^nX \tag{13}$$

The local entropy production strength can be split into two contributions

$$\sigma(\mathbf{X},t) = L_{\mu\nu}X^\mu X^\nu = \frac{1}{2}L_{\mu\nu}X^\mu X^\nu + \frac{1}{2}L^{\mu\nu}J_\mu J_\nu \tag{14}$$

Let us now perform the following linear coordinate transformation:

$$X'^\lambda = A^\lambda_\kappa X^\kappa, \quad \text{with } \ A^\mu_\nu \text{ such that } \ A^\alpha_\lambda L^{\lambda\kappa} A^\beta_\kappa = \mathrm{I}^{\alpha\beta} \tag{15}$$

with $\mathrm{I}^{\alpha\beta}$ denoting the Identity matrix. So, after transformation, $\sqrt{L} \rightarrow 1$. Notice that, since the matrix $L_{\mu\nu}$ is a positive definite matrix, there exists always a matrix A^μ_ν, which satisfies condition (15). After transformation we get

$$\sigma_T(t) = \frac{1}{V'}\int_{V'} \sigma(\mathbf{X}',t)d^nX' \qquad \text{with} \qquad \sigma(\mathbf{X}',t) = \frac{1}{2}\sum_{\mu=1}^{n}\Big(\mid X'^\mu \mid^2 + \mid J'_\mu \mid^2\Big) \tag{16}$$

In the space of the thermodynamic forces, the Fourier expansion in a finite box of volume V of the thermodynamic fluxes reads

$$J'_\mu(\mathbf{X}',t) = \sum_{\mathbf{K}}\Big(J_{\mu,\mathbf{K}}(t)e^{i(\mathbf{K}\cdot\mathbf{X}')} + J^\star_{\mu,\mathbf{K}}(t)e^{-i(\mathbf{K}\cdot\mathbf{X}')}\Big) \tag{17}$$

where

$$J_{\mu,\mathbf{K}}(t) = i\omega_{\mathbf{K}}\alpha_{\mu,\mathbf{K}}(t) \qquad \text{and} \qquad J^{\star}_{\mu,\mathbf{K}}(t) = -i\omega_{\mathbf{K}}\alpha^{\star}_{\mu,\mathbf{K}}(t) \tag{18}$$

By plugging Eq. (17) and the expression for $X^{\mu}_{\mathbf{K}}(t)$ (in this case, $X^{\mu}_{\mathbf{K}} = X^{\mu\star}_{-\mathbf{K}'}$) into Eq. (16) yields

$$\sigma_T(t) = 2\sum_{\mu=1}^{n}\sum_{\mathbf{K}}\left(\mid X^{\mu}_{\mathbf{K}}(t)\mid^2 + \mid J_{\mu,\mathbf{K}}(t)\mid^2\right) = 2\sum_{\mu=1}^{n}\sum_{\mathbf{K}}\left(\mid X^{\mu}_{\mathbf{K}}(t)\mid^2 + \omega^2_{\mathbf{K}}\mid \alpha_{\mu,\mathbf{K}}(t)\mid^2\right) \tag{19}$$

where the orthogonality relation

$$\frac{1}{V}\int_V e^{i\mathbf{K}\cdot\mathbf{X}}e^{-i\mathbf{K}'\cdot\mathbf{X}}d^nX = \delta_{\mathbf{K}\mathbf{K}'} \tag{20}$$

has been taken into account. This expression is identical to the Hamiltonian of a harmonic oscillator if we set the value of the *mass* = 4 and we identify the following terms: *position*→ $\alpha_{\mu,K}$, *momemtum*→ $2X^{\mu}_{K}$, and *frequency*→ ω_K (see, for example, [12]). So, we first define two new dimensionless operators $\tilde{X}^{\mu}_{K}$ and $\tilde{\alpha}_{\mu,K}$, as follows:

$$\tilde{X}^{\mu}_{\mathbf{K}} = \sqrt{\frac{2}{\not{k}_B\omega_{\mathbf{K}}}}X^{\mu}_{\mathbf{K}} \qquad ; \qquad \tilde{\alpha}_{\mu,\mathbf{K}} = \sqrt{\frac{2\omega_{\mathbf{K}}}{\not{k}_B}}\alpha_{\mu,\mathbf{K}} \tag{21}$$

In terms of these new variables, the expression for $\sigma_T(t)$ reads

$$\sigma_T(t) = \sum_{\mu=1}^{n}\sum_{\mathbf{K}}\not{k}_B\omega_{\mathbf{K}}\left(\mid \tilde{X}^{\mu}_{\mathbf{K}}\mid^2 + \mid \tilde{\alpha}_{\mu,\mathbf{K}}\mid^2\right) \tag{22}$$

As for the case of the harmonic oscillator, we have to assume the validity of the following *Canonical Commutation Rules* (CCRs):

$$[\tilde{\alpha}_{\mu,\mathbf{K}}, \tilde{X}^{\nu}_{\mathbf{K}'}] = i\delta_{\mu\nu}\delta_{\mathbf{K}\mathbf{K}'} \qquad \text{so} \quad [\alpha_{\mu,\mathbf{K}}, X^{\nu}_{\mathbf{K}'}] = i\frac{\not{k}_B}{2}\delta_{\mu\nu}\delta_{\mathbf{K}\mathbf{K}'} \tag{23}$$

The two operators of *creation* "$\mathrm{a}^{(\mu)+}_{\mathbf{K}}$" and *destruction* "$\mathrm{a}^{(\mu)}_{\mathbf{K}}$" can be introduced and defined as usual (see, for example, [13]):

$$\mathrm{a}^{(\mu)}_{\mathbf{K}} = \frac{1}{\sqrt{2}}\left(\tilde{\alpha}_{\mu,\mathbf{K}} + i\tilde{X}^{\mu}_{\mathbf{K}}\right) \quad ; \quad \mathrm{a}^{(\mu)+}_{\mathbf{K}} = \frac{1}{\sqrt{2}}\left(\tilde{\alpha}_{\mu,\mathbf{K}} - i\tilde{X}^{\mu}_{\mathbf{K}}\right) \quad ; \quad [\mathrm{a}^{(\mu)}_{\mathbf{K}}, \mathrm{a}^{(\mu')+}_{\mathbf{K}'}] = \delta_{\mu\mu'}\delta_{\mathbf{K}\mathbf{K}'} \tag{24}$$

We finally get the discretization of the total entropy production strength in Onsager's region

$$\boldsymbol{\sigma}_T(t) = \sum_{\mu=1}^{n}\sum_{\mathbf{K}}\not{k}_B\omega_{\mathbf{K}}\left(\mathbf{n}^{(\mu)}_{\mathbf{K}} + \frac{1}{2}\right) \tag{25}$$

where the *number operator* $\mathbf{n}^{(\mu)}_{\mathbf{K}} \equiv \mathrm{a}^{(\mu)+}_{\mathbf{K}}\mathrm{a}^{(\mu)}_{\mathbf{K}}$ has been introduced. To sum up, *in the space of the thermodynamic forces the total entropy production strength behaves as the sum of "$\mathbf{K}$" (discretized) independent one-dimensional harmonic oscillators, each oscillating with frequency $\omega_{\mathbf{K}}$*.

III. THE CORRESPONDENCE PRINCIPLE WITH THE EINSTEIN-PRIGOGINE THEORY OF FLUCTUATIONS

In principle, the constant contribution

$$\sigma_0 = \frac{1}{2}\sum_{\mu=1}^{n}\sum_{\mathbf{K}} \not{k}_B \omega_{\mathbf{K}} \tag{26}$$

diverges. This expression is the total entropy production for a macroscopic system generated by very small fluctuations around the thermodynamic equilibrium. To analyze this term we consider the Einstein-Prigogine theory of equilibrium fluctuations. In this theory, the probability P of finding a state in which the values of α_μ lie between α_μ and $d\alpha_\mu$ is

$$P d\alpha_1 \cdots d\alpha_n = P_0 \exp(-\Delta_I S/k_B) d\alpha_1 \cdots d\alpha_n \tag{27}$$

where P_0 ensures normalization to unity. Expression (27) is only valid for small spontaneous fluctuations around the thermodynamic equilibrium and not for systematic deviations from equilibrium. Prigogine showed the validity of the following important result: whatever the thermodynamic system (hydrodynamic, chemical, etc.), due to spontaneous equilibrium fluctuations, the average entropic production is [1]

$$\overline{\overline{\Delta_I S}} = \int \cdots \int \Delta_I S P d\alpha_1 \cdots d\alpha_n = \frac{n}{2} k_B \tag{28}$$

with n denoting the number of the independent thermodynamic forces. Now we have to calculate the eigenvalues of the $\mathbf{\Delta_I S}$ operator by using the canonical commutation rules. Detailed calculations for getting the expression for the $\mathbf{\Delta_I S}$ operator can be found in [10]. We have:

$$\mathbf{\Delta_I S} = \frac{1}{4V}\int \left(\hat{q}_{\mu\nu} X^\mu X^\nu + q^{\mu\nu}\alpha_\mu\alpha_\nu\right)\sqrt{L}\ d^n X \tag{29}$$

where $\hat{q}_{\mu\nu}$ is a definite positive matrix. Hence, there exists a linear coordinates transformation such that

$$\alpha'_\lambda = A^\kappa_\lambda \alpha_\kappa, \quad \text{with } \ A^\mu_\nu \text{ such that } \ A^\alpha_\lambda q^{\lambda\kappa} A^\beta_\kappa = \mathrm{I}^{\alpha\beta} \tag{30}$$

With a suitable definition of a new set of dimensionless variables, we have

$$\mathbf{\Delta_I S} = \sum_{\mu=1}^{n}\sum_{\mathbf{K}} \not{k}_B \left(\mid \tilde{X}^\mu_{\mathbf{K}} \mid^2 + \mid \tilde{\alpha}_{\mu,\mathbf{K}} \mid^2\right) \tag{31}$$

and introducing the operators of creation and destruction $\mathrm{a}_{\mathbf{K}}^{(\mu)+}$ and $\mathrm{a}_{\mathbf{K}}^{(\mu)}$, and the number operator $\mathbf{n}_{\mathbf{K}}^{(\mu)}$, we get

$$\mathbf{\Delta_I S} = \sum_{\mu=1}^{n} \sum_{\mathbf{K}} \not{k}_B \mathbf{n}_{\mathbf{K}}^{(\mu)} + \frac{n}{2} \sum_{\mathbf{K}} \not{k}_B \tag{32}$$

where the canonical commutation rules have been taken into account. Eq. (32) coincides with the ground state calculated by the Einstein-Prigogine fluctuations theory by setting (the *Corresponding Principle*) [10]:

$$\frac{n}{2} \sum_{\mathbf{K}} \not{k}_B \equiv \frac{n}{2} k_B \tag{33}$$

This yields the following expression for the entropy production operator

$$\mathbf{\Delta_I S} = \sum_{\mu=1}^{n} \sum_{\mathbf{K}} \not{k}_B \mathbf{n}_{\mathbf{K}}^{(\mu)} + \frac{n}{2} k_B \tag{34}$$

having discrete eigenvalues

$$\Delta_I S = \sum_{\mu=1}^{n} \sum_{\mathbf{K}} \not{k}_B n_{\mathbf{K}}^{(\mu)} + \frac{n}{2} k_B \geq 0 \tag{35}$$

IV. A HEURISTIC MODEL FOR DETERMINING β FOR A QUASI-IDEAL GAS

We aim to investigate the physical origin of constant β entering the CCRs. We start with the simplest assumption: *by a statistical model for nano-gases we can derive the expression for* β. To this end, we adopt a (very) simple heuristic model for nano-gas with the following assumptions

1) The limit case is reached when the distance between the molecules of the nano-gas is (approximately) twice the Bohr radius (r_B).
2) The spherical-molecule model is adopted. Beyond the Heisenberg principle, classical statistical physics applies.
Note that these simplifications are frequently employed in classical scattering theory. Indeed, as a first approximation, choosing $\sigma_{cs} = 4\pi r_B^2$ is reasonable for representing the effective interaction area of a molecule [14] (for a more detailed explanation see [15]). Fig. 1 shows the classical spherical model to represent molecules in nano-gases. In our heuristic model, the impact parameter b is twice Bohr's radius and all the molecules of the nano-gas are equal (so, $r'_M = r_M$ with r_M denoting the molecular radius). The volume occupied by a

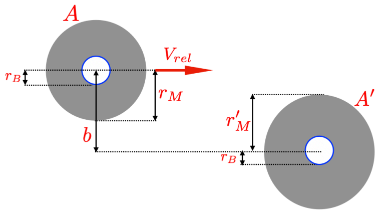

FIG. 1: **Collision between two molecules of a quasi-ideal nano-gas**. *The impact parameter b is the distance between the two centers of the molecules. In our heuristic model, the molecules are spherical and identical. The model assumes that if $b \leq 2r_B$ the two molecules collide, they "feel" the Heisenberg principle. The limit case is reached when the distance between the two molecules is $b = 2r_B$ and the perfect packing is reached (i.e., $n = V_M^{-1}$).*

molecule is $V_M = 4/3\pi r_M^3$. At thermal equilibrium, the (classical) uncertainty related to the measurement of the entropy production strength σ reads [15]:

$$\Delta\sigma \sim \frac{\Delta E}{T\tau} \tag{36}$$

with τ denoting the collision time, T the temperature of the system, and ΔE the energy uncertainty of the classical system, respectively. In classical statistical mechanics, the equipartition theorem relates the temperature of a system to its average energies:

$$\frac{1}{2}m_M\bar{v^2} = \frac{3}{2}k_BT \tag{37}$$

with $\bar{v^2}$ and m_M denoting the mean square speed and the molecule mass, respectively. The statistical theory of gases provides us with the expression of the collision time [16]:

$$\tau = \frac{1}{n\sigma_{cs}\bar{V}_{rel}} \tag{38}$$

where $\sigma_{cs} = \pi b^2 = 4\pi r_B^2$ is the cross section. n and $\bar{V}_{rel}$ are the number of molecules for unit volume and the mean relative velocity, respectively. $\bar{V}_{rel}$ is linked to the root mean square speed by the relation $\overline{V_{rel}^2} = 2\bar{v^2}$ [16]. If we do not make a distinction between the mean of the square and the square of the mean, we have $\bar{V}_{rel} \simeq \sqrt{2\bar{v^2}}$ [16]. By combining all these expressions we get

$$\Delta t\Delta\sigma = (\Delta t\Delta E)\frac{3n\sigma_{cs}}{\sqrt{2}m_M\sqrt{\bar{v^2}}}k_B \geq \frac{\hbar}{2}\frac{3n\sigma_{cs}}{\sqrt{2}m_M\sqrt{\bar{v^2}}|_{Max.}}k_B \tag{39}$$

In Eq. (39) we have taken into account the Heisenberg uncertainty principle:

$$\Delta t\Delta E \geq \frac{\hbar}{2} \tag{40}$$

with $\hbar$ denoting the reduced Planck constant ($\hbar = h/(2\pi)$). Here, Δt and ΔE are the uncertainties related to time and energy measurements of the system, respectively. According to our (raw) model, molecules collide with each other with a minimal impact factor when

$$n\sigma_{cs} = 3\eta \frac{r_B^2}{r_M^3} \tag{41}$$

with η denoting the *packing fraction* and r_M the radius of the average molecule of the nanomaterial, respectively. A perfect packing corresponds to $\eta = 1$. The product $\Delta t \Delta\sigma$ decreases as the average distance between molecules becomes smaller. In the ideal case of perfect packing ($\eta = 1$), minimizing the average distance between molecules reduces the uncertainty in entropy production strength ($\Delta\sigma$), resulting in more predictable and consistent entropy production behavior due to the dense packing of molecules. Finally, we get a rough estimation of β. Indeed,

$$\Delta t \Delta\sigma \geq \frac{9}{2\sqrt{2}} \frac{\hbar}{m_e c r_B} \left(\frac{r_B}{r_M}\right)^3 \left(\frac{m_e}{m_M}\right) k_B = \frac{9}{2\sqrt{2}} \alpha \left(\frac{r_B}{r_M}\right)^3 \left(\frac{m_e}{m_M}\right) k_B = \beta k_B \tag{42}$$

with m_e denoting the electron mass, c the speed of light, and α the fine-structure constant, respectively. Note that although the mass of the electron appears in Eq. (42) it plays no role since the product αm_e is independent of the mass of the electron. However, it is important from the physical point of view to put this quantity in evidence. From Eq. (42) we get,

$$\beta = \frac{9}{2\sqrt{2}} \alpha \left(\frac{V_B}{V_M}\right) \left(\frac{m_e}{m_M}\right) = \frac{9}{2\sqrt{2}} \alpha\chi \tag{43}$$

where V_B/V_M represents the relative size of the Bohr volume (volume of an atom based on the Bohr radius) to the volume occupied by a single molecule and the ratio m_e/m_M compares the mass of an electron to the mass of a molecule composing the material, respectively. Parameter $\chi \equiv (V_B m_e)/(V_M m_M)$ denotes the *Bohr-Molecular Ratio* (BMR). By plugging the values $\alpha = 1/137$, and typical values for $V_B/V_M \sim 10^{-3}$, and $m_e/m_M = 1/3000$ into Eq. (43) we get $\beta_{Theor.} \sim 10^{-8}$ which aligns with the experimental value found in [11]: $\beta_{Exp.} \sim 1.2 \times 10^{-8}$.

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