Nonequilibrium nanothermodynamics

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Entropy production for a system outside the thermodynamic limit is formulated using Hill's nanothermodynamics, in which a macroscopic ensemble of such systems is considered. The external influence of the environment on the average nanosystem is connected to irreversible work with an explicit formula based on the Jarzynski equality. The entropy production retains its usual form as a sum of products of fluxes and forces and Onsager's symmetry principle is proven to hold for the average nanosystem, if it is assumed to be valid for the macroscopic ensemble, by two methods. The first one provides expressions that relate the coefficients of the two systems. The second gives a general condition for a system under an external force to preserve Onsager's symmetry.

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Nonequilibrium thermodynamics tries to understand macroscopic systems out of equilibrium, and particularly those in steady states, without having to resort to the (unattainable) dynamic description of all their microscopic degrees of freedom, using instead the same few macroscopic variables as in the thermostatic case but allowing for situations where they depend on time. Interest in this field can be traced back to the works of Boltzmann on Thomson's hypothesis about the division of a general process into a reversible and an irreversible part [1]. However, it was not until 1931 that a truly systematic derivation of the thermodynamics of irreversible processes near equilibrium was attained by Onsager [2,3] and later refined by Casimir [4].

Entropy production is perhaps the most important concept in nonequilibrium thermodynamics, totally absent from thermostatics. It is usual to look at it as a function of two sets of variables, the thermodynamic fluxes $\{\phi_i\}$ and forces $\{F_i\}$, defined in such a way that this production can be expressed as a sum of products of conjugates, $\dot{\Delta S} = \Sigma_i F_i \phi_i$, the fluxes being zero at equilibrium. This expression is supplemented by a set of phenomenological relations which gives the fluxes as functions of the forces, these relations being such that the forces cancel at equilibrium. It is an experimental fact that there exists a neighborhood of equilibrium where the relations between the two sets of variables are linear, that is, $\phi_i = \Sigma_j L_{ij} F_j$.

Onsager's main result [2,3] is the symmetry of the phenomenological coefficients $L_{ij} = L_{ji}$, proven on the basis of two general hypothesis: regression of fluctuations and microscopic dynamic reversibility. Systems under the effect of external magnetic fields or Coriolis forces are exceptions already known to Onsager and later treated by Casimir in Ref. [4]. More recently, it has been shown that the second hypothesis can be dropped for certain models [5].

In the last decades, interest in nanoscopic systems has led to placing them in the front line of science and technology. Important research from the point of view of statistical mechanics has been done during the last decade, leading to such notable results as the Jarzynski equality [6], the Evans [7], and Crooks [8] fluctuation theorems, which have been experimentally verified [9]. A good overview of these topics can be found in Ref. [10]. Nevertheless, since the seminal work of Hill [11] in the early 60s, not much theoretical efforts were dedicated to the strictly thermodynamic formalism in the nanoscale up to the first years of the twenty first century, when the same author revisited his own work and renamed it as "nanothermodynamics" [12,13]. Hill generalized the equations for open systems introducing a term associated to the number of small systems in a macroscopic ensemble of them that explicitly takes into account the energetic contribution of surface and edge effects, system rotation, and translation, etc., usually negligible for macroscopic systems.

In this context, it is of great importance to have a theoretical framework for describing the operation of nanomachines. Therefore, some thermodynamic results have been tentatively extended to systems far from the thermodynamic limit. Particularly, regarding the theory of nonequilibrium fluctuations (of interest for the development of nanomotors), the validity of Onsager's reciprocal relations is sometimes taken for granted [14]. It is thus desirable to put the nonequilibrium thermodynamics of small systems on firm theoretical foundations. The formulation of such a nonequilibrium nanothermodynamics is the main aim in this Brief Report. By analogy with Hill's equilibrium theory, the number of nanosystems in an ensemble, which can be modified by production, destruction, and transport, is introduced as a macroscopic variable that survives in the nanoscopic description.

In order to study the thermostatics of a small system, Hill [11] started with a large number $\mathcal{N}$ of them, so that the ensemble itself was a system in the thermodynamic limit. The author developed a theory suitable for measurement devices that interact with many of the small systems in such a way that the relevant thermodynamic quantities are not those of an individual nanosystem, but their averages over a significant number of them, which in a homogeneous system will be equal to their average over all of the nanosystems. In other words, if each nanosystem is described by a set of extensive variables $\{X^{(\alpha)}\}_{\alpha=1}^{\nu}$, and the state of the total system is characterized by $\{X_t^{(\alpha)}\}_{\alpha=1}^{\nu} \cup \{\mathcal{N}\}$, the quantities accessible to measurement are $\left\{ \bar{X}^{(\alpha)} := \frac{X_t^{(\alpha)}}{\mathcal{N}} \right\}_{\alpha=1}^{\nu}$. The entropy of a nanosystem can likewise be defined as $S = \frac{S_t}{\mathcal{N}}$.

The total system obeys the usual set of thermostatic relations, particularly the Gibbs and Euler equations in entropic form, $dS_t = \sum_\alpha y^{(\alpha)} dX_t^{(\alpha)} - \frac{\varepsilon d\mathcal{N}}{T}$ and $S_t = \sum_\alpha y^{(\alpha)} X_t^{(\alpha)} - \frac{\varepsilon \mathcal{N}}{T}$, with $y^{(\alpha)} := \left(\frac{\partial S_t}{\partial X_t^{(\alpha)}} \right)_{X_t^{(\beta \neq \alpha)}, \mathcal{N}}$ and $\varepsilon := -T \left(\frac{\partial S_t}{\partial \mathcal{N}} \right)_{X_t^{(\alpha)}}$. Obviously, in the description of the overall system ε is simply the chemical potential associated with the number of nanosystems. However, in the thermodynamics of small systems it is called the *subdivision potential*, a variable with no analog in conventional macroscopic thermodynamics.

To formulate the Euler equation for the nanosystems it is enough to divide both terms in the Euler equation by $\mathcal{N}$. Taking into account that $dS = \frac{1}{\mathcal{N}}[dS_t - S d\mathcal{N}]$, the Gibbs equation can also be formulated and, subtracting the two equations for dS, an inhomogeneous pseudo-Gibbs-Duhem equation arises. Thus, the thermodynamic equations for the average small system are

$$ S = \sum_\alpha y^{(\alpha)} \bar{X}^{(\alpha)} - \frac{\varepsilon}{T}, \tag{1a} $$

$$ dS = \sum_\alpha y^{(\alpha)} d\bar{X}^{(\alpha)}, \tag{1b} $$

$$ -d\left(\frac{\varepsilon}{T} \right) = -\sum_\alpha \bar{X}^{(\alpha)} dy^{(\alpha)}. \tag{1c} $$

Comparing Eqs. (1b) and (1a), it becomes apparent that S does not satisfy Euler's theorem and thus it is not a homogeneous function of $\{\bar{X}^{(\alpha)}\}$ in the nanothermodynamic formalism. The thermostatics of a small system depends on its environment through ε. Thus, a small system has more degrees of freedom than its large counterpart. The additional contribution to the entropy (or, equivalently, to the internal energy) comes from the aforementioned interface, edge, rotation, and translation effects, which must become negligible as the size of the system is increased, if conventional thermodynamics is to be recovered.

Recently, Ben-Amotz and Honig [15] have used the Jarzynski equality to give a general expression $dS = \frac{\langle \mathdj W \rangle_{\chi(t)}}{T} + k_B \ln \langle \exp(\frac{-\mathdj W}{k_B T}) \rangle_{\chi(t)}$ for the entropy production of a system under a time-dependent constraint $\chi(t)$ in contact with a thermostat at the (possibly also time-dependent) temperature T, averaged over the processes compatible with that constrain ($\mathdj W$ is the elementary work associated to a particular process). If it is assumed that this kind of operation amounts to an average over the ensemble of nanosystems (a reasonable hypothesis since $\mathcal{N}$ is large) it is possible, using Eq. (1), to give an expression for the change in ε between times 0 and t_0 during the process determined by $\chi(t)$, suitable for measurement or simulation:

$$ \Delta\varepsilon_{\chi(t)} = T\sum_\alpha y^{(\alpha)} X^{(\alpha)} \big|_0^{t_0} $$
$$ - \int_{\chi(t)} \left[\mathdj W + k_B T \ln \left\langle \exp\left(\frac{-\mathdj W}{k_B T} \right) \right\rangle \right]. \tag{2} $$

The central part of this report is devoted to the application of Hill's course of reasoning to a system out of equilibrium in the thermodynamic branch (linear regime). For simplicity, only the case with two homogeneous macroscopic subsystems (A and B) will be considered. The results can be readily generalized to an arbitrary number of partitions or even to a continuous distribution, as long as large enough macroscopic differential volumes are taken in order to assure that they contain sufficient numbers of nanosystems. The method used is valid as long as differential calculus can describe the changes in the variables of the nanosystems to a good approximation (i.e., they are not too small).

Suppose that the systems are separated by a diathermic, permeable, and deformable wall and slightly out of equilibrium with each other. With the total system $A \cup B$ completely isolated, the total deformation variables $\{X_t^{(\alpha)} = X_{At}^{(\alpha)} + X_{Bt}^{(\alpha)}\}_{\alpha=1}^\nu$ are conserved. $\mathcal{N} = \mathcal{N}_A + \mathcal{N}_B$, however, can vary since it is perfectly conceivable that the nanosystems (e.g. micelles) could split or merge even in a macroscopically isolated system. Conservation of $\mathcal{N}$ would be a reasonable assumption in two opposite limits: static nanosystems whose dissociation energy is so high that interactions with their environment cannot split them, and highly dynamic nanosystems which are continuously reorganizing, but in such a way that the fluctuations in the total number of systems are small compared to the average value. It is possible to choose the time derivatives of all extensive thermodynamic variables as fluxes. Expanding $\Delta S_t = S_t - S_{t,eq} = \Delta S_{At} + \Delta S_{Bt}$ to second order in these coordinates,

$$ \Delta S_t = \sum_{I \in \{A,B\}} \sum_\alpha \Delta X_{It}^{(\alpha)} \left(y_I^{(\alpha)} + \frac{1}{2} \sum_\beta \frac{\partial y_I^{(\alpha)}}{\partial X_{It}^{(\beta)}} \Delta X_{It}^{(\beta)} \right) $$
$$ + \sum_{I \in \{A,B\}} \Delta \mathcal{N}_I \left(-\frac{\varepsilon_I}{T} + \sum_\alpha \frac{\partial y_I^{(\alpha)}}{\partial \mathcal{N}_I} \Delta X_{It}^{(\alpha)} \right) $$
$$ + \frac{1}{2} \sum_{I \in \{A,B\}} \frac{\partial^2 S_{It}}{\partial \mathcal{N}_I^2} (\Delta \mathcal{N}_I)^2, \tag{3} $$

where ΔX denotes the deviation of X from its equilibrium value and all the derivatives are evaluated at equilibrium. Note that the bars have been dropped for notational simplicity. This implies that $y_A^{(\alpha)} = y_B^{(\alpha)}$ for all α and $\varepsilon_A \Delta \mathcal{N}_A = -\varepsilon_B \Delta \mathcal{N}_B$ and, given the conservation of $X^{(\alpha)}$, it follows that $\Delta X_A^{(\alpha)} = -\Delta X_B^{(\alpha)}$. Taking this into account and differentiating the previous expression with respect to time,

$$ \Delta \dot{S}_t = \sum_\alpha \left[\frac{\partial y_A^{(\alpha)}}{\partial \mathcal{N}_A} \Delta \mathcal{N}_A - \frac{\partial y_B^{(\alpha)}}{\partial \mathcal{N}_B} \Delta \mathcal{N}_B \right. $$
$$ + \sum_\beta \left(\frac{\partial y_A^{(\alpha)}}{\partial X_{At}^{(\beta)}} + \frac{\partial y_B^{(\alpha)}}{\partial X_{Bt}^{(\beta)}} \right) \Delta X_{At}^{(\beta)} \bigg] \Delta \dot{X}_{At}^{(\alpha)} $$
$$ + \left(\sum_\alpha \frac{\partial y_A^{(\alpha)}}{\partial \mathcal{N}_A} \Delta X_{At}^{(\alpha)} + \frac{\partial^2 S_{At}}{\partial \mathcal{N}_A^2} \Delta \mathcal{N}_A \right) \Delta \dot{\mathcal{N}}_A $$
$$ + \left(-\sum_\alpha \frac{\partial y_B^{(\alpha)}}{\partial \mathcal{N}_B} \Delta X_{At}^{(\alpha)} + \frac{\partial^2 S_{Bt}}{\partial \mathcal{N}_B^2} \Delta \mathcal{N}_A \right) \Delta \dot{\mathcal{N}}_B. \tag{4} $$

This expression has the form of a sum of products of fluxes and forces, the terms inside square brackets being the forces $\{F^{(\alpha)}\}_{\alpha=1}^{\nu}$ and $F^{(\mathcal{N})}$. To translate this expression into the nanoscopic language, the following equalities must be used:

$$\Delta \dot{X}_{It}^{(\alpha)} = \frac{d\Delta(\mathcal{N}_I X_I^{(\alpha)})}{dt} = \mathcal{N}_I \Delta \dot{X}_{It}^{(\alpha)} + \Delta \dot{\mathcal{N}}_I X_{It}^{(\alpha)}, \quad (5\text{a})$$

$$\Delta \dot{S} = \frac{\Delta \dot{S}_t}{\mathcal{N}} - S_t \frac{\Delta \dot{\mathcal{N}}_A + \Delta \dot{\mathcal{N}}_B}{\mathcal{N}^2}, \quad (5\text{b})$$

$$\Delta X_{It}^{(\alpha)} = \mathcal{N}_I \Delta X_I^{(\alpha)} + X_I^{(\alpha)} \Delta \mathcal{N}_I - \Delta X_I^{(\alpha)} \Delta \mathcal{N}_I, \quad (5\text{c})$$

giving the result

$$\Delta \dot{S} = \sum_\alpha F^{(\alpha)} \Delta \dot{X}_A^{(\alpha)} + F_{\mathcal{N}_A} \Delta \dot{\mathcal{N}}_A + F_{\mathcal{N}_B} \Delta \dot{\mathcal{N}}_B, \quad (6\text{a})$$

with

$$F^{(\alpha)} := F_t^{(\alpha)} \frac{\mathcal{N}_A}{\mathcal{N}}, \quad (6\text{b})$$

$$F_{\mathcal{N}_A} := \frac{F_{\mathcal{N}_A t} + \sum_\alpha F_t^{(\alpha)} X_A^{(\alpha)}}{\mathcal{N}} - \frac{S_t}{\mathcal{N}^2}, \quad (6\text{c})$$

$$F_{\mathcal{N}_B} := \frac{F_{\mathcal{N}_B t}}{\mathcal{N}} - \frac{S_t}{\mathcal{N}^2}, \quad (6\text{d})$$

which means that the entropy production of the average small system can also be written as a sum of products of fluxes and forces. As mentioned previously, there exists a neighborhood of equilibrium in which a set of linear phenomenological relations between these variables holds. By means of Eqs. (5) and (6), the macroscopic and nanoscopic linear coefficients can be related,

$$L_t^{(\alpha\beta)} = \frac{\mathcal{N}_A}{\mathcal{N}}(\mathcal{N}_A L^{(\alpha\beta)} + X_A^{(\alpha)} L^{(\mathcal{N}_A\beta)}) + \frac{X_A^{(\beta)}}{\mathcal{N}}(\mathcal{N}_A L^{(\alpha\mathcal{N}_A)} + X_A^{(\alpha)} L^{(\mathcal{N}_A N_A)}), \quad (7\text{a})$$

$$L_t^{(\alpha\mathcal{N}_I)} = \frac{1}{\mathcal{N}}(\mathcal{N}_A L^{(\alpha\mathcal{N}_I)} + X_A^{(\alpha)} L^{(\mathcal{N}_A\mathcal{N}_I)}), \quad (7\text{b})$$

$$L_t^{(\mathcal{N}_I\alpha)} = \frac{1}{\mathcal{N}}(\mathcal{N}_A L^{(\mathcal{N}_I\alpha)} + X_A^{(\alpha)} L^{(\mathcal{N}_I\mathcal{N}_A)}), \quad (7\text{c})$$

$$L_t^{(\mathcal{N}_I\mathcal{N}_J)} = \frac{L^{(\mathcal{N}_I\mathcal{N}_J)}}{\mathcal{N}}; I, J \in \{A, B\}. \quad (7\text{d})$$

The macroscopic system satisfies Onsager's reciprocity by hypothesis, i.e., $L_t^{(\alpha\mathcal{N}_A)} = L_t^{(\mathcal{N}_A\alpha)}$. It is easy to see, starting with the last equations of the previous block and progressively back-substituting, that the nanoscopic coefficients are also symmetric in this situation. These proportionality relations ensure that the second law of thermodynamics is obeyed by

the average systems (although it can be transitorily violated by a small system), a topic also discussed in Ref. [15].

The quantity S_t is indeterminate in one additive constant; therefore, the component of the fluxes proportional to it, arising from the terms in Eqs. (6c) and (6d), must be zero. This last condition is equivalent to

$$L^{(\alpha\mathcal{N}_A)} = -L^{(\alpha\mathcal{N}_B)}, \quad (8\text{a})$$

$$L^{(\mathcal{N}_A\mathcal{N}_A)} = L^{(\mathcal{N}_B\mathcal{N}_B)} = -L^{(\mathcal{N}_A\mathcal{N}_B)}. \quad (8\text{b})$$

These equalities allow for further interpretation of Eq. (7) using the change of variables $(\mathcal{N}_A, \mathcal{N}_B) \to (\mathcal{N}, D)$, with $D := \mathcal{N}_A - \mathcal{N}_B$. The time derivative of $\mathcal{N}$ represents the creation of nanosystems per unit time, while at fixed $\mathcal{N}$ the time derivative of D corresponds to the transport of small systems. The two possible causes of variation of $(\mathcal{N}_A, \mathcal{N}_B)$ are thus decoupled by this change. Furthermore, application of the Curie principle shows that variation of D can only be coupled to vectorial fluxes such as those treated in this Brief Report, while variation of $\mathcal{N}$ can be coupled with chemical (scalar) processes. In particular, they cannot be coupled with each other because of the different tensor rank of the forces involved.

Equations (8) are equivalent to stating that $L^{(\alpha\mathcal{N})} = L^{(\alpha\mathcal{N}_A)}$, $L^{(DD)} = L^{(\mathcal{N}_A\mathcal{N}_A)}$ and the rest of the phenomenological coefficients involving $\mathcal{N}$ or D are zero. $L_t^{(DD)}$ is proportional, with a factor $\frac{1}{\mathcal{N}}$, to its nanometric equivalent. The remaining coefficients are

$$L_t^{(\mathcal{N}\alpha)} = \frac{L_t^{(\mathcal{N}_A\alpha)} + L_t^{(\mathcal{N}_B\alpha)}}{2} = \frac{2\mathcal{N}}{\mathcal{N}+D} L^{(\mathcal{N}\alpha)}, \quad (9\text{a})$$

$$L_t^{(\alpha D)} = \frac{L_t^{(\mathcal{N}\mathcal{N})} X_A^{(\alpha)}}{\mathcal{N}}. \quad (9\text{b})$$

The last equation can be used as a definition of $L^{(\mathcal{N}\mathcal{N})}$ in the particular case in which $\mathcal{N}$ is fixed. This result means that the contribution of a flux of nanosystems to that of an extensive variable $X_{At}^{(\alpha)}$ is proportional to the amount $X_A^{(\alpha)}$ of that variable that each nanosystem carries with it in its transit from A to B, as expected.

The above results can be reproduced by an alternate method closer to the well-known macroscopic proof. This method rests on the hypothesis of regression of fluctuations, which states that the reaction of the system to a small deviation from equilibrium caused by an external force is the same as if it was caused by a spontaneous fluctuation. Moreover, if $\{Z^{(\alpha)}\}_{\alpha=1}^{\nu+1} := \{X_t^{(\alpha)}\}_{\alpha=1}^{\nu} \cup \{\mathcal{N}\}$, dynamic reversibility can be expressed as $\langle \Delta Z^{(\alpha)}(t)\Delta Z^{(\gamma)}(t+\tau)\rangle = \langle \Delta Z^{(\alpha)}(t+\tau)\Delta Z^{(\gamma)}(t)\rangle$, which straightforwardly gives $\langle \dot{\Delta Z}^{(\alpha)}\Delta Z^{(\gamma)}\rangle = \langle \Delta Z^{(\alpha)}\dot{\Delta Z}^{(\gamma)}\rangle$. Substituting here a linear development for a system in the thermodynamic limit, analogous to that of previous sections, $\dot{\Delta Z}^{(\alpha)} = \sum_\beta L_t^{(\alpha\beta)} z^{(\beta)}$, with $z^{(\beta)} := \frac{\partial S_t}{\partial Z^{(\beta)}}$, and using the fact that $\langle Z^{(\alpha)} z^{(\beta)}\rangle = -k_B \delta^{(\alpha\beta)}$ (easy to prove for a macroscopic system, see, for instance, Ref. [1]), the symmetry of the phenomenological matrix follows immediately. However, for the nano-

system, the temporal evolution of the internal variables cannot be related only to their deviations from equilibrium, adopting instead the more general form [16]

$$\Delta \dot{X}^{(\alpha)} = \sum_{\beta} L^{(\alpha\beta)} \frac{\partial S}{\partial X^{(\beta)}} + f^{(\alpha)}(t), \qquad (10)$$

where $f^{(\alpha)}(t)$ represents a general force acting on the system. From Eq. (5c), $\Delta X^{(\alpha)} = \frac{\Delta X_t^{(\alpha)} - X_{t,eq}^{(\alpha)} \Delta \mathcal{N}}{\mathcal{N}}$. Approximating $\frac{1}{\mathcal{N}} \simeq \frac{1}{\mathcal{N}_{eq}}$ and taking into account that derivatives at constant $\mathcal{N}$ are equal for the macroscopic and average system, it follows directly that $\left\langle \Delta X^{(\alpha)} \frac{\partial S}{\partial X^{(\beta)}} \right\rangle = -\frac{k_B \delta^{(\alpha\beta)}}{\mathcal{N}}$. Thus, temporal reversibility implies that

$$L^{(\alpha\beta)} - L^{(\beta\alpha)} = \langle f^{(\alpha)} \Delta X^{(\beta)} - f^{(\beta)} \Delta X^{(\alpha)} \rangle. \qquad (11)$$

This result represents a general condition for Onsager's symmetry to hold when evolution of the system is conditioned by a general external force. In this particular case, as it has previously been shown, the external forces $f^{(\alpha)}$ are proportional to $\Delta \mathcal{N}$ through constants $L^{(\alpha\mathcal{N})}$, which makes the right-hand side of the previous equation trivially equal to zero, thus proving the symmetry of the phenomenological submatrix involving only the internal coordinates. This second method cannot prove anything about the coefficients involving $\mathcal{N}$, an external variable. To show their symmetry it is still necessary to relate them to their macroscopical counterparts. This formulation, however, connects more easily with the language of the fluctuation theorems.

New cross-transport phenomena associated with the new degrees of freedom must appear in the nanosystems. As predicted by Eqs. (9), if the number of small systems is kept constant, these phenomena will consist simply in the exchange of extensive variables transported along with the nanosystems. Dynamic nanosystems, such as micelles, could be thus worthier of study. Since Hill's equilibrium formalism has already been applied (and successfully compared to experimental data) to nanostructures such as nanosolids and nanowires [17], they could also be good candidates to find these cross phenomena, for instance, in electric or thermal measurements.

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