# Tentative statistical interpretation of non-equilibrium entropy

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**Abstract**

We suggest a certain statistical interpretation for the entropy produced in driven thermodynamic processes. The exponential function of *half* irreversible entropy re-weights the probability of the standard Ornstein-Uhlenbeck-type thermodynamic fluctuations. (We add a proof of the standard Fluctuation Theorem which represents a more natural interpretation.)

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In 1910 Einstein [1], paraphrasing [2] Boltzmann's lapidary formula $S = \log W$, expressed the probability distribution of thermodynamic variables $x$ through the entropy function $S(x)$:

$$W(x) \sim e^{S(x)} \ . \tag{1}$$

This equation describes thermodynamic fluctuations in Gaussian approximation properly. Going beyond the stationary features, the time-dependence of fluctuations $x_t$ can be characterized by a certain probability functional $W[x]$ over complete paths $\{x_t;\ t \in (-\infty, \infty)\}$. It turns out that, in driven thermodynamic processes, this probability is related to the irreversible entropy $S_{irr}[x]$. Symbolically, we can write the following relationship:

$$W[x] \sim W_{OU}[x - \bar{x}] e^{S_{irr}[x]/2} \ , \tag{2}$$

where $\bar{x}_t$ is the 'driving' value of parameter $x_t$ and $W_{OU}[z]$ turns out to correspond to fluctuations $z_t$ of Ornstein-Uhlenbeck type. This relationship offers $S_{irr}$ a certain statistical interpretation, somehow resembling Einstein's suggestion (1) for the equilibrium entropy $S(x)$. In this short note, Einstein's approach to the thermodynamic fluctuations is outlined and standard equations of time-dependent fluctuations are invoked from irreversible thermodynamics. Then I give a precise form to the relationship (2) for driven thermodynamic processes.

The equilibrium conditions for isolated composite thermodynamic systems derive from the maximum entropy principle:

$$S(x) = max \ , \tag{3}$$

where $S(x)$ is the total entropy of the system in function of certain free thermodynamic parameters $x$ [3]. If the function $S(x)$ is maximum at $x = \bar{x}$ then $\bar{x}$ is the equilibrium state. For example, $x$ may be the temperature $T$ of a small (yet macroscopic) subsystem in the large isolated system of temperature $\overline{T} = \bar{x}$. Then, the function $S(x)$ must be the total entropy of the isolated system, depending on the variation of the subsystem's temperature around its equilibrium value. The equilibrium value $\bar{x}$ [as well as $S(x)$ itself] may vary with the deliberate alteration of the initial conditions. Surely, in our example the temperature $\overline{T}$ of the whole isolated system can always be controlled at will. For later convenience, especially in treating driven thermodynamic processes, we may prefer the explicit detailed notation $S(x|\bar{x})$ for $S(x)$. Though $S(\bar{x}) - S(x)$ might qualify the lack of equilibrium, nearby values $x \approx \bar{x}$ have no interpretation in phenomenological thermodynamics. They only have it in the broader context of statistical physics. In finite thermodynamic systems there are fluctuations around the equilibrium state $\bar{x}$ and their probability follows Eq. (1):

$$W(x|\bar{x})dx = \mathcal{N} e^{S(x|\bar{x}) - S(\bar{x}|\bar{x})} dx \ . \tag{4}$$

Assume, for simplicity, that there is a single free variable $x$. The Taylor expansion of the entropy function yields Gaussian fluctuations:

$$W(x|\bar{x}) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\Big(-\frac{1}{2\sigma^2}(x-\bar{x})^2\Big) \ , \tag{5}$$

where

$$\frac{1}{\sigma^2} = -S''(\bar{x}) \equiv -\frac{\partial^2 S(x|\bar{x})}{\partial x^2}\Big|_{x=\bar{x}} \ . \tag{6}$$

In our concrete example $\sigma^2 = T^2/C$ where $C$ is the specific heat of the subsystem.

We are going to regard the time-dependence of the parameter $x_t$ fluctuating around $\bar{x}$, according to the standard irreversible thermodynamics [3]. The time-dependent fluctuation $z_t \equiv x_t - \bar{x}$ is an Ornstein-Uhlenbeck (OU) stochastic process [4] of zero mean $\langle z_t \rangle \equiv 0$ and of correlation

$$\langle\ z_t\ z_{t'}\ \rangle_{OU} = \sigma^2 e^{-\lambda|t-t'|} \ . \tag{7}$$

The relaxation rate $\lambda$ of fluctuations is related to the corresponding Onsager kinetic constant $\gamma$ by $\lambda = \gamma/\sigma^2$. It can be shown that the probability distribution of $x_t = z_t + \bar{x}$ at any fixed time $t$ is the Gaussian distribution (5) as it must be. For the probability of the complete fluctuation path $z_t$, the zero mean and correlation (7) are equivalent with the following functional:

$$W_{OU}[z]\mathcal{D}z = \exp\Big(-\frac{1}{4\gamma}\int\ (\dot{z}_t^2 + \lambda^2 z_t^2)dt\Big)\mathcal{D}z \ , \tag{8}$$

where a possible constant of normalization has been absorbed into the functional measure $\mathcal{D}z$.

In order to construct and justify a relationship like (2) one needs to proceed to driven thermodynamic processes. In fact, we assume that we are varying the parameter $\bar{x}$ with small but finite velocity. Formally, the parameter $\bar{x}$ becomes time-dependent. For simplicity's sake we assume that the coefficients $\sigma, \gamma$ do not depend on $\bar{x}$ or, at least, that we can ignore their variation throughout the driven range of $\bar{x}_t$. We define the irreversible entropy production during the driven process as follows:

$$S_{irr}[x|\bar{x}] = \frac{1}{\sigma^2}\int (\bar{x}_t - x_t)dx_t \ . \tag{9}$$

In our concrete example $dS_{irr} = (C/T^2)(\overline{T} - T)dT \approx dQ(T^{-1} - \overline{T}^{-1})$ which is indeed the entropy produced randomly by the heat transfer $dQ$ from the surrounding to the subsystem. By partial integration, Eq. (9) leads to an alternative form:

$$S_{irr}[x|\bar{x}] = \frac{1}{\sigma^2}\int (\bar{x}_t - x_t)d\bar{x}_t + \frac{1}{\sigma^2}(x_{-\infty} - \bar{x}_{-\infty})^2 - \frac{1}{\sigma^2}(x_{\infty} - \bar{x}_{\infty})^2 \ . \tag{10}$$

In relevant driven processes the entropy production is macroscopic, i.e., $S_{irr} \gg 1$ in $k_B$-units, hence it is dominated by the integral term above. I exploit this fact to replace expression (9) by

$$S_{irr}[x|\bar{x}] = \frac{1}{\sigma^2}\int (\bar{x}_t - x_t)d\bar{x}_t \tag{11}$$

which vanishes for constant $\bar{x}$. In the sense of the guess (2), I suggest the following form for the probability distribution of the driven path:

$$W[x|\bar{x}] = \mathcal{N}[\bar{x}]W_{OU}[x - \bar{x}]e^{S_{irr}[x|\bar{x}]/2} \ . \tag{12}$$

The non-trivial normalizing pre-factor is a consequence of $\bar{x}$'s time-dependence and will be derived below. Since the above distribution is a Gaussian functional and $S_{irr}[x|\bar{x}]$ is a linear functional (11) of $x$, we can easily calculate the expectation value of the irreversible entropy:

$$S_{irr}[\bar{x}] \equiv \langle S_{irr}[x|\bar{x}]\rangle = \frac{1}{2\sigma^2}\int\int \dot{\bar{x}}_t\dot{\bar{x}}_{t'}e^{-\lambda|t-t'|}dtdt' \ . \tag{13}$$

In case of moderate accelerations $\ddot{\bar{x}} \ll \lambda\dot{\bar{x}}$, this expression reduces to the standard irreversible entropy $\gamma^{-1}\int \dot{\bar{x}}_t^2 dt$ of the phenomenological theory of driven processes [5]. Coming back to the normalizing factor in Eq. (12), we can relate it to the mean entropy production (13): $\mathcal{N}[\bar{x}] = exp(-S_{irr}[\bar{x}]/4)$. Hence, the ultimate form of Eq. (12) will be:

$$W[x|\bar{x}] = W_{OU}[x - \bar{x}]e^{S_{irr}[x|\bar{x}]/2 - S_{irr}[\bar{x}]/4} \ . \tag{14}$$

This result gives the precise meaning to our symbolic relationship (2). If the entropy production $S_{irr}$ were negligible then the thermodynamic fluctuations $x_t - \bar{x}_t$ would follow the OU statistics (7) like in case of a steady state $\bar{x}_t = const$. Even in slow irreversibly driven processes $S_{irr}$ may grow essential and $exp[S_{irr}/2]$ will re-weight the probability of OU fluctuations. The true stochastic expectation value of an arbitrary functional $F[x]$ can be expressed by the OU expectation values of the re-weighted functional:

$$\langle F[x] \rangle = \left\langle F[x]e^{S_{irr}[x|\bar{x}]/2 - S_{irr}[\bar{x}]/4} \right\rangle_{OU} \ . \tag{15}$$

I can verify the plausibility of Eq. (14) for the special case of small accelerations. Let us insert Eqs. (8,11) and also Eq. (13) while ignore $\ddot{\bar{x}}$ in comparison with $\lambda\dot{\bar{x}}$. We obtain:

$$W[x|\bar{x}] = W_{OU}[x - \bar{x} + \lambda^{-1}\dot{\bar{x}}] \ . \tag{16}$$

Obviously, the fluctuations of the driven system are governed by the OU process $z_t$ (7) in the equilibrium case when $\dot{\bar{x}} \equiv 0$. In driven process, when $\dot{\bar{x}} \neq 0$, there is only a simple change: The OU fluctuations happen around the retarded value $\bar{x}_t - \tau\dot{\bar{x}} \approx \bar{x}_{t-\tau}$ of the driven parameter. The lag $\tau$ is equal to the thermodynamic relaxation time $1/\lambda$. Consequently, the driven random path takes the following form:

$$x_t = \bar{x}_{t-\tau} + z_t \ , \tag{17}$$

where $z_t$ is the equilibrium OU process (7). This result implies, in particular, the equation $\langle x_t \rangle = \bar{x}_{t-\tau}$ which is just the retardation effect well-known in the thermodynamic theory of slightly irreversible driven processes. For example, in case of an irreversible heating process the subsystem's average temperature will always be retarded by $\tau\dot{\overline{T}}$ with respect to the controlling temperature $\overline{T}$ [5].

Finally, let us summarize the basic features of Einstein's formula (1) and of the present proposal (2). They characterize the quality of equilibrium in static and in driven steady states, respectively. They do it in terms of thermodynamic entropies while they refer to a statistical context lying outside both reversible and irreversible thermodynamics. Both formulae are only valid in the lowest non-trivial order and their correctness in higher orders is questionable [6]. Contrary to their limited validity, they can no doubt give an insight into the role of thermodynamic entropy in statistical fluctuations around both equilibrium or non-equilibrium states.

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*Note added.* The first version of this work proposed the relationship

$$W \sim W_{OU} e^{S_{irr}} \ ,$$

the exponent was free from the funny factor 1/2. The proof was wrong, of course. With the factor 1/2, my statistical interpretation for $S_{irr}$ has become less attractive. I also realized that a more natural statistical interpretation [8] was already discovered before. The present formalism offers the following convenient proof of the Fluctuation Theorem.

The true probability distribution of the slowly driven process is the Onsager–Machlup functional [7]:

$$W_{OM}[x|\bar{x}]\mathcal{D}x = \exp\Bigl(-\frac{1}{4\gamma}\int\ [\dot{x}_t + \lambda(x_t - \bar{x}_t)]^2 dt\Bigr)\mathcal{D}x \ ,$$

at fixed $x_{-\infty}$. Let us imagine the probability distribution of the time-reversed process $x^r_t = x_{-t}$ driven by the time-reversed surrounding $\bar{x}^r_t = \bar{x}_{-t}$. Formally, we only have to change the sign of $\dot{x}_t$, yielding:

$$W_{OM}[x^r|\bar{x}^r]\mathcal{D}x = \exp\Bigl(-\frac{1}{4\gamma}\int\ [\dot{x}_t - \lambda(x_t - \bar{x}_t)]^2 dt\Bigr)\mathcal{D}x \ ,$$

at fixed $x^r_{-\infty}$. We can inspect that the above distributions of the true and the time-reversed processes, respectively, satisfy the following relationship:

$$\log W_{OM}[x|\bar{x}] - \log W_{OM}[x^r|\bar{x}^r] = \frac{\lambda}{\gamma}\int(\bar{x}_t - x_t)dx_t \ .$$

Observe that the r.h.s. is the irreversible entropy production $S_{irr}[x|\bar{x}]$ of the driven process. This leads to the so-called Fluctuation Theorem:

$$W_{OM}[x^r|\bar{x}^r] = e^{-S_{irr}[x|\bar{x}]}W_{OM}[x|\bar{x}] \ .$$

The irreversible entropy turns out to be a concrete statistical measure of the time-reversal asymmetry.

# References


[1] A. Einstein, Ann.Phys.(Leipzig) **33**, 1275 (1910).

[2] The letter $W$ stood for phase volume in Boltzmann relation while it denotes probability in (1). I am grateful to Jiri Vala who showed me that Einstein [1], maybe for somehow related reasons, committed (eventually innocent) sign errors repeatedly confusing $e^W$ and $e^{-W}$.

[3] L.D. Landau and E.M. Lifshitz, *Statistical Physics* (Clarendon, Oxford, 1982).

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[5] L.Diósi, Katalin Kulacsy, B.Lukács and A.Rácz, J.Chem.Phys. **105**, 11220 (1996).

[6] Einstein's ansatz fails obviously beyond the Gaussian approximation. Our present proposal is first of all limited to small velocities $\dot{\bar{x}}$. In fact, the fluctuations of the thermodynamic parameters are governed by the phenomenological Langevin equation (see, e.g., in [3]):

$$\dot{x}_t = -\lambda(x_t - \bar{x}) + \sqrt{2\gamma}\ w_t$$

which can be generalized for time-dependent $\bar{x}_t$. To lowest order in $\dot{\bar{x}}$ the result (17) comes out. In higher orders the Langevin equation gives different results from the present proposal. The standard distribution functional is the Onsager-Machlup functional [7].

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