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Article

Clausius Relation for Active Particles: What Can We Learn from Fluctuations

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Received: 12 June 2017; Accepted: 12 July 2017; Published: 13 July 2017

Abstract: Many kinds of active particles, such as bacteria or active colloids, move in a thermostatted fluid by means of self-propulsion. Energy injected by such a non-equilibrium force is eventually dissipated as heat in the thermostat. Since thermal fluctuations are much faster and weaker than self-propulsion forces, they are often neglected, blurring the identification of dissipated heat in theoretical models. For the same reason, some freedom—or arbitrariness—appears when defining entropy production. Recently three different recipes to define heat and entropy production have been proposed for the same model where the role of self-propulsion is played by a Gaussian coloured noise. Here we compare and discuss the relation between such proposals and their physical meaning. One of these proposals takes into account the heat exchanged with a non-equilibrium active bath: such an "active heat" satisfies the original Clausius relation and can be experimentally verified.

Keywords: active particles; entropy production; Clausius relation

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1. Introduction

Active particle systems have recently attracted the increasing interest of scientists of different disciplines since they sit at the intersection of biology, chemistry and physics [1,2]. A central feature of these materials is that its elementary constituents convert energy from the environment via metabolic or chemical reactions into direct motion but also dissipate energy producing heat by friction in order to move inside a surrounding solvent [3]. Therefore, the complex behavior of active particles can only be described by the tools of non equilibrium statistical physics, such as kinetic theory, statistical mechanics of non-equilibrium processes and stochastic thermodynamics [4]. A fascinating question, which naturally comes to our mind, is how thermodynamics shapes biological functions in living organisms [5] such as motility and self-propulsion and in particular which is the entropy production associated with their non equilibrium steady states [6]. This question requires a notion of heat generated by self-propulsion and dissipated in the thermostatted solvent.

Within careful calorimetric experiments, one is able to measure the heat dissipated into the solvent by a microbial colony [7]. Such total heat depends upon many biological functions which are not included in active models, but one could devise smart experiments (e.g., by varying motility without changing other functions) in order to assess the fraction of heat strictly generated by self-propulsion. Observing the associated fluctuations is perhaps a much harder task, if not impossible. However, before encountering experimental limitations, one finds limits in the theory.

At our mesoscopic level, the definition of heat has to be framed within stochastic thermodynamics [8–11]. A problem, however, arises when thermal fluctuations are discarded: such an approximation is adopted in many models of active particles, since temperature is negligible with respect to the energy associated with both self-propulsion and external forces. In active models, some noise is retained to describe the non-deterministic nature of the self-propulsion force, but it usually acts on time-scales and energy scales much larger than molecular agitation of the solvent. This "athermal" nature of active particle models is similar to that in granular models [12] or in models of macroscopic friction [13]. While it is very useful—sometimes even inevitable—for the purpose of analytic calculations or numerical simulations, it leads to a mismatch between entropy production and heat [14]. Basically, the relation between total entropy production and dissipated heat loses its similitude with the original Clausius form and involves additional terms. For this reason, it does not provide a clear constraint on heat divided by temperature, as it occurs for the Clausius relation in macroscopic thermodynamics. Such a problem has already been noticed in some models of active particles [15], and in systems with feedback [16–18].

Recently it has been shown that the above fallacy is bypassed in a model of active particles where Gaussian colored noise plays the role of self-propulsion [19–21]. Even if thermal fluctuations are neglected, a notion of "coarse-grained heat" can be introduced, together with a spatial-dependent effective temperature, such that the original Clausius relation is fully recovered. The crucial point here is that both such a "coarse-grained heat" and the effective temperature can be measured in experiments and therefore a test of this active Clausius relation can be attempted. In the last year other two proposals have appeared in the literature [22,23], devoted to define entropy production and heat in the same identical model. The purpose of the present paper is to discuss the connection between those different Clausius relations. Apart from this comparison, two novelties are present here with respect to [21]: (1) a single trajectory level of description is adopted, while in [21] an ensemble average had been considered; (2) a generalization of [21] to more than one dimension and interacting particles is presented. In order to simplify the discussion, the main discussion is focused on the 1d case with a time-independent potential, which is sufficient to show the main difference between the definitions of heat and entropy production in the three works considered [21–23]. The generalisation of the proposal in [21] to multi-dimensional cases with a time-dependent potential is also discussed at the end.

In Section 2, we review the basic facts of Clausius relation in macroscopic thermodynamics and in stochastic (or mesoscopic) thermodynamics. In Section 3, we introduce the active model with Gaussian colored noise with thermal fluctuations, where a "microscopic Clausius relation" is trivially satisfied, and then show what happens at the coarse-grained level, when inertia and thermal fluctuations are neglected. The three recipes appeared in [21–23] to connect entropy production, dissipated heat and temperature are reviewed and compared.

2. Heat and Entropy Production: From Macroscopic to Stochastic Thermodynamics

Here we revise a few elementary facts of thermodynamics, at the macroscopic level and at the mesoscopic one. The macroscopic level is the one presented in thermodynamic textbooks, where there are no fluctuations: we denote quantities at this level with capital letters. The mesoscopic level is the topic of an intense research exploded roughly in the last two decades, and is dominated by fluctuations: we denote quantities at this level with small letters. Averaging out the fluctuations of the mesoscopic level (an operation which—in general—is automatically obtained in the limit of a very large number of constituents) brings back the results of the macroscopic one. Through the whole paper, we set the Boltzmann constant $k_B = 1$.

2.1. Macroscopic Level

For a large system one may measure heat, for instance with a calorimeter, and call it δQ: we consider it positive when going from the bath to the system. The second principle of thermodynamics guarantees that in a transformation where entropy S changes by a quantity dS there is a non-negative entropy production

$$\delta\Sigma = dS - \frac{\delta Q}{T} \geq 0\,, \tag{1}$$

where we used a shorthand notation where—for instance $\delta\Sigma$ and δQ are non-exact differentials, while dS is an exact differential. In a "quasi-static" transformation the equal sign holds, i.e., $\delta\Sigma = 0$.

In the absence of a direct way of measuring the entropy of a system (e.g., if quasi-static transformations are not available), other relations derived from Equation (1) and involving measurable observables are useful. For instance from Equation (1) it follows

$$dS \geq \frac{\delta Q}{T} \tag{2}$$

and therefore the existence of a "minimum work" that can be extracted, also called difference of free energy dF:

$$TdS \geq dE - \delta W \rightarrow \delta W \geq dE - TdS = dF. \tag{3}$$

Another consequence that is derived way from Equation (1) is to consider a cyclical transformation ($dS = 0$), where it implies

$$\oint \frac{\delta Q(t)}{T(t)} \leq 0, \tag{4}$$

which is the celebrated Clausius relation. This can be tested in experiments and is the founding principle of the theory of heat engines, efficiency, etc.

It is important to underline that if—hypothetically—the total entropy production was something different from $dS - \delta Q/T$, i.e., if

$$\delta\Sigma = dS - \frac{\delta Q}{T} + \Sigma_{an} \geq 0, \tag{5}$$

then all the above relations, including the Clausius relation, would not hold anymore due to the presence of an "anomalous" entropy production term, Σ_{an}. However it is quite difficult to imagine Equation (5) in macroscopic thermodynamics, since the very definition of macroscopic entropy production is the difference between dS and $\delta Q/T$ [6]. On the contrary, equations similar to (5) have appeared in the literature in a stochastic thermodynamic treatment of systems with feedback and model of self-propelled particles [15–18,23].

2.2. Mesoscopic Level

When a small system is considered, a stochastic description is necessary in order to incorporate fluctuations. At thermodynamic equilibrium the stochastic evolution must be consistent with micro-reversibility. More precisely, the couple "system plus thermostat" describes all degrees of freedom of the world and therefore it has to satisfy an exact symmetry under time-reversal: when the heat bath is replaced by an effective stochastic bath force, time-reversal is mapped into the equivalence of probabilities of a trajectory and its time-reversal, which coincides with detailed balance if the process is Markovian.

When an external, non-conservative, force is applied to the system, one may expect that the stochastic bath force is not changed (for instance if the bath is very large and is weakly affected by the external force). This amounts to say that the non-equilibrium model contains the sum of two forces which both concur to change the energy of the system: the external force does work, the bath force brings heat [11]. A notion of entropy production rate σ of a trajectory $\omega(t)$, for Markovian stochastic systems, has been introduced in [8] and revisited in [9]. It can be summarized as

$$\int_0^t \delta\sigma(t') = \ln \frac{\text{prob}[\{\omega(t')\}_0^t]}{\text{prob}[\{\overline{\omega}(t-t')\}_0^t]} = \ln \frac{p[\omega(0)]}{p[\overline{\omega(t)}]} + \ln \frac{\text{prob}[\{\omega(t')\}_0^t|\omega(0)]}{\text{prob}[\{\overline{\omega}(t-t')\}_0^t|\overline{\omega}(t)]} \tag{6}$$

$$= \int_0^t ds + \int_0^t \delta s_m, \tag{7}$$

where $\overline{\omega}$ is the time-reversal of the phase-space variables (typically positions are unchanged and velocities are reflected), $s(t) = -\ln p[\omega(t)]$ is the microscopic Gibbs entropy in the point $\omega(t)$ in phase space and δs_m is the so-called entropy production of the surrounding medium [9]. In the rest of the paper we consider, for simplicity, the infinitesimal version of Equation (6), i.e., $\delta\sigma = ds + \delta s_m$. An average over noise realizations and initial conditions is expected to give back the macroscopic quantities, i.e., $\delta\Sigma = \langle \delta\sigma \rangle$ and $dS = \langle ds \rangle$, such that Equation (1) implies $\langle \delta s_m \rangle = -\delta Q/T$. Indeed in many models at constant temperature, one has $\delta s_m = -\delta q/T$ with δq the heat injected by the bath force, which satisfies $\langle \delta q \rangle = \delta Q$. The total entropy production $\int_0^t \delta\sigma(t')$ satisfies the Fluctuation-Relation at any time $t > 0$ and this guarantees that $\delta\Sigma = \langle \delta\sigma \rangle$ is non-negative [8]. In a stationary state $\langle \delta s_m \rangle \geq 0$ then follows.

As a useful example, let us consider the evolution of a colloidal particle of mass m, position and velocity $x(t), u(t)$ in one dimension, under the action of an external potential $\phi(x)$ and of a non-conservative external force $f_{nc}(t)$.

$$dx(t) = u(t)dt \tag{8a}$$

$$mdu(t) = -\gamma u(t)dt + \sqrt{2\gamma T}dW(t) - \phi'[x(t)]dt + f_{nc}(t)dt, \tag{8b}$$

with $dW(t)$ the Wiener infinitesimal increment (with variance dt). Defining energy as $e = mu^2/2 + \phi(x)$, it is easy to see that heat (going from the bath into the system) reads

$$\delta q = de - \delta w = u \circ [-\gamma u dt + \sqrt{2\gamma T}dW(t)] \tag{9}$$

where we have defined the work $\delta w = u f_{nc} dt$, and $\circ$ denotes products which must be integrated according to the Stratonovich rule.

For this model, it is possible to compute the conditional probability appearing in (6) and therefore compute δs_m. The result depends upon the parity of f_{nc} under time-reversal [24]. In simple cases, for instance when magnetic fields are not involved [25], such a force is assigned even parity under time-reversal. In this case, one gets (see Appendix A)

$$\delta\sigma = ds - \frac{u \circ [-\gamma u dt + \sqrt{2\gamma T}dW]}{T} = ds - \frac{\delta q}{T}, \tag{10}$$

which is ≥ 0 on average, leading to the usual Clausius relation.

On the contrary if f_{nc} is odd, for instance if the coarse-graining has delivered a force which is proportional to odd powers of the velocity of external bodies [14,26], or if magnetic fields are involved [25], the relation (10) does not hold anymore. In such cases, things seem to improve when the so-called *conjugated* dynamics is considered, by changing the sign of odd external non-conservative forces when computing the probability of inverse paths appearing in the denominator of Equation (6) [18,24,26–29]: basically this amounts to change the parity of the force and get back the result in Equation (10). The problem of such an artificial prescription, however, is that the conjugated dynamics cannot be realized in experiments and therefore an empirical evaluation (i.e., without a detailed knowledge of the equation of motions) of the conjugated probability is not available, neither it is possible to experimentally observe the associated fluctuation relation.

3. Active Particles: The Coarse-Grained Heat and Clausius Relation

The analogy between stochastic and macroscopic thermodynamics, Equation (10), rests upon two main ingredients: (1) the heat bath must be modeled as a stochastic force which—if non-conservative forces are removed—satisfies detailed balance with respect to the equilibrium probability distribution ($\delta\sigma \equiv 0$) and (2) the non-conservative forces are even under time-reversal, a fact which is expected to be realized when the microscopic forces are not velocity-dependent (e.g., there are no Lorentz forces) and the coarse-graining does not change or mix their parity. Many models of active particles abandon such basic facts (in particular detailed balance [4]), with the aim of describing the relevant variables (such as positions or orientations of the micro-swimmers) which evolve on scales much slower than those affected by thermal agitation. An interesting example of model of active swimmers where this procedure can be analyzed is one where self-propulsion takes the form of an Ornstein-Uhlenbeck process: its non-zero correlation time represents the persistence of motion due to activity. Active particles of biophysical interest, for instance bacteria or sperms, display such a finite time decay of autocorrelation, but of course can exhibit more complicate form of the decay, i.e., not necessarily an exponential. Several authors have discussed the fair comparison, at some level (for instance comparing the spatial correlations in the presence of external potentials or the phase separation effects induced by activity), between other models or real experiments and the Ornstein-Uhlenbeck model considered here, see for instance [30–32].

Here we introduce the model at a space-time scale fine enough to describe the real velocity u of the particle and thermal fluctuations:

$$dx(t) = u(t)dt \tag{11a}$$

$$mdu(t) = -\gamma u(t)dt + \sqrt{2\gamma T_b}dW(t) + f_a(t)dt - \phi'[x(t)]dt, \tag{11b}$$

where T_b is the environmental (solvent) temperature and the active force satisfies

$$df_a(t) = -\frac{f_a(t)}{\tau}dt + \frac{\gamma\sqrt{2D_a}}{\tau}dW_2(t), \tag{12}$$

with dW_2 another (independent) Wiener increment with variance dt. Here we consider for simplicity the 1-particle case in one dimension, with a potential $\phi(x)$ which does not depend upon time. Later we generalize some of the results to many interacting particles and with a time-dependent potential.

Note that, when $\phi = 0$, $\langle x^2 \rangle \sim 2(D_a + T_b/\gamma)t$ for large times. Based upon such a bare diffusivity, the "active bath temperature" $T_a = \gamma D_a$ is usually defined. In [21] a "mass-less" active temperature $T_\tau = D_a/\tau$ was defined. In this paper we show that it is not necessary, if an "effective mass" $\mu = \gamma\tau$ is used, as in [23]. Of course there is no thermostat at temperature T_a, such a temperature is only useful to define a relevant energy scale.

Since active micro-swimmers are usually dispersed in viscous liquids, it is much more common to find the overdamped version of the model [19], which describes the position of the particle on a time-scale slower than the relaxation time due to inertia:

$$dx(t) = \frac{\sqrt{2\gamma T_b}dW(t) + f_a(t)dt - \phi'[x(t)]dt}{\gamma}. \tag{13}$$

3.1. Heat Dissipation into the Solvent

Interpreting f_a as an external force derived—through the coarse-graining of the full microscopic dynamics—from forces which do not depend upon velocities, it is reasonable to consider it even. According to the recipe of stochastic thermodynamics discussed above, Equation (6) applied to Equation (11) or Equation (13), see Appendix A, one gets Equation (10), with

$$\delta q_b = u \circ [-\gamma u dt + \sqrt{2\gamma T_b}dW(t)], \tag{14}$$

which is the heat absorbed from the reservoir, satisfying in the steady state the Clausius relation at constant temperature, i.e.,

$$\delta Q_b = \langle \delta q_b \rangle \leq 0. \tag{15}$$

The interpretation is obvious, the active force $f_a(t)$ acts as an external non-conservative force and transfers energy in the system which is dissipated into the bath. This can be measured by ordinary calorimetry in the solvent [33]. As discussed above, such a measurement is in principle very difficult in experiments with living micro-swimmers, since released heat is affected by many other non-equilibrium biological functions. A promising direction could be the use of artificial active particles [3].

3.2. Removing the Solvent from the Description

Since T_b is orders of magnitude smaller than active temperatures, it is very useful—also for computational purposes—to remove it from Equation (13), keeping only

$$\dot{x} = \frac{f_a(t) - \phi'(x)}{\gamma}. \tag{16}$$

At this point, an important ingredient of the bath force (its noise) has disappeared and the basic recipe of stochastic thermodynamics cannot be applied straightforwardly. Still, it is useful to find a measure of "distance from equilibrium" and relate it to parameters and observable quantities. Considering that f_a is random, one is tempted to consider $-\gamma\dot{x} + f_a(t)$ as an effective bath and define a heat as $\dot{x} \circ [-\gamma\dot{x} + f_a(t)]$. However, the random force $f_a(t)$ is non-Markovian and therefore the standard recipe of stochastic thermodynamics brings in complications [34–36].

The simplest way to get rid of the non-Markovian character of the noise is to time-derive Equation (16), obtaining

$$\begin{aligned} dx(t) &= u(t)dt && \text{(17a)} \\ \mu du(t) &= -\gamma u(t)dt + \sqrt{2\gamma T_a}dW(t) - \phi'[x(t)]dt - \tau\phi''[x(t)]u(t)dt && \text{(17b)} \\ &= -\gamma\Gamma(x)u(t)dt + \gamma\sqrt{2D_a}dW(t) - \phi'[x(t)]dt && \text{(17c)} \end{aligned}$$

where we have introduced the effective mass $\mu = \gamma\tau$ and the space-dependent viscosity correction $\Gamma(x) = 1 + \frac{\tau}{\gamma}\phi''(x)$.

As highlighted by the two versions in Equations (17b)–(17c), the evolution of the effective velocity u is affected by the conservative force $-\phi'(x)$ and by an additional force that can be interpreted in two different ways: (1) an equilibrium bath at temperature T_a plus a non conservative force $f_{nc} = -\tau\phi''(x)u$ which is *odd* under time-reversal; or (2) a non-equilibrium bath with space-dependent viscosity modulated according to the function $\Gamma(x)$. In the next two subsections, we see the consequences of such different interpretations, which change both the definition of entropy production as well as of heat.

3.2.1. Equilibrium Bath with a Non-Conservative Force: Conjugated Entropy Production

This interpretation is considered in [23]. The authors propose to define heat as the energy injected by the force $-\gamma u dt + \gamma\sqrt{2D_a}dW$, as if it were an equilibrium bath

$$\delta q_1 = u \circ (-\gamma u dt + \gamma\sqrt{2\gamma T_a}dW). \tag{18}$$

To derive the entropy production, the authors consider the formula (6) with the probability of the time-reversed path (which appears in the denominator) computed according to a dynamics where the force $f_{nc}(t)$ is replaced by $-f_{nc}(t)$, as discussed at the end of Section 2.2. This idea is justified by the authors by showing that such a change of sign is necessary in order to make invariant under time-reversal the dynamics without the bath. However such an argument is not really compelling. The terms $-\gamma u dt + \gamma\sqrt{2\gamma T_a}dW$ do not correspond to any well-defined part of the physical system which could be identified as an equilibrium bath: the first term is the viscous damping due to the solvent, the second term is the fluctuating part of the derivative of the self-propulsion. It is a mathematical coincidence that together they form a Ornstein-Uhlenbeck process of the same form of equilibrium bath forces. In our opinion, it is quite arbitrary detaching them from Equation (17) and there is no reason why the rest of the equation (once those terms are removed) should satisfy the invariance under time-reversal.

According to the "conjugated" prescription, one gets for the case of a single particle considered here (see Appendix A)

$$\delta\Sigma = ds - \frac{\delta q_1}{T_a} + \frac{\tau^2}{2T_a}(du)^2\phi'', \tag{19}$$

where $(du)^2 \approx 2T_a dt/(\gamma\tau^2)$. The average can be written as

$$\delta\Sigma = dS - \frac{\delta Q_1}{T_a} + \frac{dt}{\gamma}\langle\phi''\rangle \geq 0, \tag{20}$$

with $\delta Q_1 = \langle\delta q_1\rangle$.

A peculiarity of this recipe is that it gives a non-zero average entropy production also for the harmonic case $\phi(x) \sim x^2$. Since in the harmonic case Equation (17) satisfies detailed balance, it is unclear if such a peculiarity is an advantage or not. Moreover, as already discussed, entropy production computed with the conjugated reversed dynamics is not accessible in experiments. Most importantly, in our opinion Equation (20) hardly deserves the name "Clausius relation", as it does not give the same important information about the sign of the average heat.

3.2.2. Equilibrium Bath with a Non-Conservative Force: Standard Entropy Production

In [22] the authors consider Formula (6) (without conjugation for the reversed dynamics) applied to the dynamics in Equation (17c). However all terms giving exact deterministic differentials are thrown away, leading to an approximate formula (see Appendix A)

$$\delta\Sigma \approx \frac{\tau^2 u\phi'' \circ du}{T_a}. \tag{21}$$

In the steady state the neglected terms have zero average, and indeed only the average formula is reported in [22]. Fluctuations and large deviations functions, however, may keep the memory of those terms [37–39].

Another difficulty of formula (21) is its connection with heat. In the end of their paper, the authors manage to show that Equation (16) can be mapped exactly into a generalized Langevin equation with memory. This equation can be broken into a viscoelastic bath at equilibrium at temperature T plus a non-conservative force. Within such a description, the average of the entropy production rate in Equation (21) can be written as $\mathcal{J}/T$, where $\mathcal{J}$ is the heat flux dissipated into the bath. A simple formula for such a "viscoelastic" heat or its—local or global—average is not given in [22]. Most importantly, some terms of fluctuations of entropy production are neglected which could be relevant for large deviation functions and the validity of the Fluctuation Relation [37–39].

3.2.3. Non-Equilibrium Bath

If the standard recipe of stochastic thermodynamics, Equation (6), is used without neglecting any term, one gets (see Appendix A)

$$\delta\sigma = ds - \frac{\delta q_2}{\theta(x)}, \tag{22}$$

with the "active bath heat" defined as

$$\delta q_2 = u \circ df_{ab}, \tag{23}$$

the "active bath force" as

$$\begin{aligned} df_{ab}(t) &= -\gamma\Gamma[x(t)]u(t)dt + \gamma\sqrt{2D_a}dW(t) & (24)\\ &= -\gamma\Gamma[x(t)]u(t)dt + \sqrt{2\gamma\Gamma[x(t)]\theta(x)dW(t)} & (25) \end{aligned}$$

and the "local active temperature" $\theta(x) = T_a/\Gamma(x)$. It is clear that—as in the general formulation, Equation (9)—δq_2 corresponds to the variation of the total energy $e = \frac{\mu u^2}{2} + \phi(x)$ due to the bath force. The interpretation of $\theta(x)$ as a local active temperature is supported by the observation that a local Maxwellian with temperature $\theta(x)$ is an approximate solution for the local velocity distribution, with "small" violations of detailed balance, see [21] for details. We underline that $\theta(x)$ is immediately accessible in experiments: indeed the external potential $\phi(x)$ is directly controlled by the experimentalist (for instance by means of optical fields). The parameters γ, τ and D_a can be measured by independent measurements with single particles in the fluid without potential.

Averaging Equation (22), one gets

$$\delta\Sigma = dS - \left\langle \frac{\delta q_2(x)}{\theta(x)} \right\rangle \geq 0, \tag{26}$$

which in the steady state ($dS = 0$) is identical to the Clausius relation [21]. Interestingly, the local average $\dot{\bar{q}}(x)$ of the dissipated heat flux reads

$$\dot{\bar{q}}(x) = \gamma\Gamma(x)\left[\frac{\theta(x)}{\mu}n(x) - \int dvu^2 p(x,u)\right], \tag{27}$$

where $n(x) = \int dvp(x,u)$. This is an additional argument in favour of the simplicity and consistency of the picture discussed in the present section: the "active heat" is exactly proportional to the difference between the local active temperature $\theta(x)$ and the empirical temperature $\langle u^2\rangle_x$. The empirical temperature is "attracted" by the local active temperature but the non-uniformity of such a temperature prevents full relaxation: the mismatch is a source of flowing heat. Equation (27) shows a straightforward way to measure such "active heat". Indeed such a measurement only amounts to measure $n(x)$ and $\langle u^2\rangle_x$ (for instance by means of a fast camera attached to a microscope), while all other variables are parameters of the experimental setup, controlled by the experimentalist. Once one has measured the local heat $\dot{\bar{q}}(x)$ an experimental verification of the Clausius relation, Equation (26), is immediately accessible, since

$$\left\langle \frac{\delta q_2(x)}{\theta(x)} \right\rangle = \int dx \frac{\dot{\bar{q}}(x)}{\theta(x)} \tag{28}$$

We note that when the potential does not depend upon time, as in all our equations up to this point, the active heat δq_2 has zero average. Nevertheless, the average entropy production $\delta\Sigma$ has non-zero average, apart from the harmonic case $\phi(x) \sim x^2$ which is a special case where $\theta(x)$ is uniform [21].

When more particles are involved, a (local and time-dependent) diagonalisation procedure can always set back the problem in the case of a single particle. The multi-particles and multi-dimensional version of Equation (17) reads

$$\mu du_i = -\gamma\Gamma_{ij}(\mathbf{r})u_j dt - \partial_i\phi(\mathbf{r})dt + \gamma\sqrt{2D_a}dW_i, \tag{29}$$

with $\Gamma_{ij} = \delta_{ij} + \frac{\tau}{\gamma}\partial_j\partial_i\phi$ and indexes running over all particles and all Cartesian components and the Einstein summation convention is assumed. The potential ϕ includes both external and internal forces. Since the matrix $\Gamma_{ij}(\mathbf{r})$ is symmetric, an orthogonal matrix $P_{ij}(\mathbf{r})$ always exists such that $P\Gamma P^T = D$ with $D_{ij}(\mathbf{r}) = \lambda_i(\mathbf{r})\delta_{ij}$. By defining the rotated coordinates $\mathbf{R} = P\mathbf{r}$ and velocities $\mathbf{U} = P\mathbf{u}$, and recalling that the gradient rotates as a vector and the rotation of the vector of independent white noises gives again a vector of independent white noises, it is straightforward to get the formula:

$$\mu dU_i = -\gamma\lambda_i(\mathbf{R})U_i dt - \partial_{R_i}\phi + \gamma\sqrt{2D_a}dW_i. \tag{30}$$

Computation of the entropy production leads, therefore, to

$$\delta\sigma(t) = ds(t) - \sum_i \frac{\delta q_{2,i}(t)}{\theta_i[\mathbf{R}(t)]}, \tag{31}$$

with $\theta_i(\mathbf{R}) = T_a/\lambda_i(\mathbf{R})$ the i-th component of the local active temperature and

$$\delta q_{2,i} = U_i \circ [-\gamma\lambda_i(\mathbf{R})U_i dt + \gamma\sqrt{2D_a}dW]. \tag{32}$$

Notice that Equation (31) generalizes the Clausius relation to a system with different temperatures θ_i.

As an example, in the case of an active particle moving in a plane a subject to a central potential $\phi(r) = \phi(\mathbf{r})$, we have the following Cartesian representation of the matrix $D_{ij}(r) = D_r(r)\hat{r}_i\hat{r}_j + D_t(r)(\delta_{1j} - \hat{r}_i\hat{r}_j)$ with $D_r(r) = 1 + \frac{\tau}{\gamma}\phi''(r)$ and $D_t(r) = 1 + \frac{\tau}{\gamma}\phi'(r)/r$. The two temperatures are $\theta_r(r) = 1/D_r(r)$ and $\theta_t(r) = 1/D_t(r)$.

3.3. Time-Dependent Potential

When an external transformation is considered, i.e., a time-dependent potential $\phi(x,t)$ is taken into account, Equation (17c) is replaced with

$$\mu du(t) = -\gamma\Gamma(x)u(t)dt + \gamma\sqrt{2D_a}dW(t) - \partial_x\phi[x(t),t]dt - \tau\partial_t\partial_x\phi[x(t),t]dt \tag{33}$$

Also, in this case, we get (see Appendix A) the validity of the mesoscopic Clausius relation Equation (22) with the active heat Equation (23). Time-dependent potentials are at the basis, for instance of realizations of heat engines [40].

Very Slow Transformations

Imagine a very slow transformation from a $\phi(x,t_1)$ to a new $\phi(x,t_2)$: this means transforming the original non-equilibrium steady state ("NESS", at $t < t_1$) to a new non-equilibrium steady state (for $t \gg t_2$). As discussed above, in the initial and final NESS there is heat going steadily to the bath, even without the transformation. Therefore for very slow transformations $\Delta Q \to -\infty$ and the Clausius relation becomes useless. For this reason, Oono-Paniconi [41], then Hatano-Sasa [42], Bertini et al. [43] and Maes [44] have found expressions for the so-called "excess heat", i.e., heat which is released for the sole purpose of the transformation: this heat is obtained removing the "housekeeping heat" (necessary for the steady states) from the total ΔQ. All the mentioned proposals have been given for overdamped systems, where certain symmetries are more clear but also less general. Active particles have some kind of inertia or persistence which cannot be disregarded and therefore do not comply with such an assumption. It would be interesting to see the above simple ideas applied to the model in Equation (16) with a slow transformation of the potential.

4. Conclusions

In this paper, we have reviewed and compared three different prescriptions to extend the Clausius formula to active systems, i.e. to particles able to self-propel by means of metabolic processes or chemical reactions and to dissipate energy by a frictional mechanism. Those relations between the heat dissipation, entropy and work appear at the mesoscopic level, where fluctuations are taken into account by means of a stochastic description, but the contribution to these fluctuations coming from the molecular bath is neglected, leaving a certain freedom in defining heat and entropy production.

While all three methods are admissible and do not contradict any general principle, our point of view gives indications that only one of these prescriptions can be considered as a stochastic version of the original Clausius heat theorem, that is Equation (22) with "active heat" defined in (23).

The stochastic "active" version of Clausius formula we have derived coincides with the one recently presented by using ensemble averaged quantities [21].

We conclude offering a physical interpretation of our finding. In this model there is a level of coarse-graining which is sufficiently *isolated* from the fastest (neglected) degrees of freedom: at such a level of description the system behaves as a microscopic heat engine in contact with a continuum spectrum of temperatures, i.e., a particle which transfers heats between different positions of space in an environment where each position is thermostatted at a different temperature $\theta(x)$. Basically there are regions (where $\theta(x) > \langle u^2 \rangle_x$) where heat enters the system and other regions where heat leaves the system.

Acknowledgments: We warmly akcnowledge useful discussions and communications with Luca Cerino, Alessandro Sarracino and Frederic van Wijland.

Author Contributions: A.P. and U.M.B.M. equally contributed to the work reported.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A. Entropy Production

We consider here a generalization of the dynamics in Equation (8) with $f_{nc}(x,u,t)$ representing any kind of time-dependent term: it can be external or internal (that is function also of system's degrees of freedom), odd or even under time-reversal, and we consider both the normal or the conjugated dynamics for the probability of the time-reversed path. In particular, we assume $dx = udt$ and

$$mdu = d\alpha(x,u,t) = -\gamma u(t)dt + \sqrt{2\gamma T}dW(t) - \phi'[x(t)]dt + f_{nc}(x,u,t)dt \tag{A1}$$

$$mdu = d\alpha^*(x,u,t) = -\gamma u(t)dt + \sqrt{2\gamma T}dW(t) - \phi'[x(t)]dt + \overline{f}_{nc}(x,u,t)dt \tag{A2}$$

to generate the dynamics of the forward and reversed paths, respectively. The Wiener increments $dW(t)$ have variance dt. When the standard entropy production is computed, the dynamics is the same, i.e., $\overline{f}_{nc}(x,u,t) = f_{nc}(x,u,t)$. On the contrary for the conjugated entropy production $\overline{f}_{nc}(x,u,t) = -f_{nc}(x,u,t)$.

Following Equation (6) (factorized for the Markovian dynamics), the infinitesimal entropy discharged into the surrounding medium reads

$$\delta s_m(t) = \ln \frac{\exp\{-[mdu_t - d\alpha(x_t,u_t,t)]^2/(4\gamma Tdt)\}}{\exp\{-[mdu_t - d\alpha^*(x_{t+dt},-u_{t+dt},t+dt)]^2/(4\gamma Tdt)\}} \tag{A3}$$

$$\begin{aligned} &= -\frac{1}{4\gamma Tdt}\Big\{[mdu_t + \gamma u_t dt + \phi'(x_t)dt - f_{nc}(x_t,u_t,t)dt]^2 \\ &\quad -[mdu_t - \gamma u_{t+dt}dt + \phi'(x_{t+dt})dt - \overline{f}_{nc}(x_{t+dt},-u_{t+dt},t+dt)dt]^2\Big\} \end{aligned} \tag{A4}$$

$$\begin{aligned} &= -\frac{1}{\gamma T}\Bigg[m\gamma du_t \circ u_t + \gamma u_t\phi'(x_t)dt - \gamma\frac{u_t f_{nc}(x_t,u_t,t) + u_{t+dt}\overline{f}_{nc}(x_{t+dt},-u_{t+dt},t+dt)}{2}dt \\ &\quad - mdu\frac{f_{nc}(x_t,u_t,t) - \overline{f}_{nc}(x_{t+dt},-u_{t+dt},t+dt)}{2} \\ &\quad - \frac{\phi'(x_t)f_{nc}(x_t,u_t,t) - \phi'(x_{t+dt})\overline{f}_{nc}(x_{t+dt},-u_{t+dt},t+dt)}{2}dt\Bigg]. \end{aligned} \tag{A5}$$

In the first passage we have used the fact that the time-reversal of du_t is $-u_t - (-u_{t+dt}) = du_t$. In the second passage we have neglected terms which goes to zero faster than dt and we have replaced $du_t(u_t + u_{t+dt})/2$ with $du_t \circ u_t$.

The cases considered in this paper are the following:

- The standard case in Equation (8) where $f_{nc}(t)$ is even and external (i.e., it does not depend upon x, v): $\overline{f}_{nc}(t) = f_{nc}(t)$. In this case, the last two terms in Equation (A5) become of higher order in dt and one gets:

  $$\delta s_m(t) = -\frac{1}{T} u_t \circ [m du_t + \phi'(x_t) dt - f_{nc}(t) dt] \tag{A6}$$

  which immediately gives Equation (10).
- The case considered in [23], where $f_{nc}(x, u, t) = -\tau u \phi''(x)$ and (“conjugated entropy production”) $\overline{f}_{nc}(x, u, t) = \tau u \phi''(x)$. In this case the last term becomes of higher order in dt, while the term du^2 cannot be discarded (as it contains $dW^2 \sim dt$), and therefore one gets

  $$\delta s_m(t) = -\frac{1}{T} \left\{ u_t \circ [m du_t + \phi'(x_t) dt - f_{nc}(x_t, v_t, t) dt] + \frac{\tau^2}{2} du_t^2 \phi''(x_t) \right\}, \tag{A7}$$

  (where we have used $m \equiv \mu = \gamma\tau$), that is Equation (19).
- The case considered in [21,22], where $f_{nc}(x, u, t) = -\tau u \phi''(x)$ and (according to the standard definition of stochastic entropy production) $\overline{f}_{nc}(x, u, t) = -\tau u \phi''(x)$. In this case the third term in Equation (A5) is of higher order in dt. All the other terms must be kept, giving

  $$\delta s_m(t) = -\frac{1}{T} \left(1 + \frac{\tau}{\gamma} \phi''(x_t) \right) u_t \circ [m du_t + \phi'(x_t) dt]. \tag{A8}$$

  If no terms are neglected, it gives exactly Equation (22).
- If in Equation (A8) the exact differentials ($u_t \circ du_t = du_t^2/2$, $u_t \phi'(x_t) dt = d\phi(x_t)$ and $u_t \phi'(x_t) \phi''(x_t) dt = d[\phi'(x_t)]^2/2$) are removed, then only one terms remains:

  $$\delta s_m(t) \approx -\frac{1}{T} \tau^2 \phi''(x_t) u_t \circ du_t, \tag{A9}$$

  i.e., Equation (21).
- If a time-dependent potential is considered, then a second non-conservative force appears $f_{nc,2}(x, t) = -\tau \partial_x \partial_t \phi(x, t)$. We stress that the dependence upon time of $\phi(x, t)$ is external, i.e., (keeping the standard recipe of stochastic thermodynamics) the probability of the reversed dynamics is generated by the same equation, that is no change of sign is attributed to ∂_t. Basically we have $\overline{f}_{nc,2}(x, t) = -\tau \partial_x \partial_t \phi(x, t)$. Introducing $f_{nc,2}$ in Equation (A3) leads to the appearance of two new addends in the brackets [...] of Equation (A5): one totally new term $-\tau u_t \partial^2 \phi(x_t, t) f_{nc,2}(x_t, t)$ coming from the product $f_{nc} f_{nc,2}$; one surviving term $-\gamma u_t f_{nc,2}(x_t, t)$ in the third addend. No new terms appear inside the fourth and fifth addend. In conclusion one gets

  $$\delta s_m(t) = -\frac{1}{T} \left(1 + \frac{\tau}{\gamma} \partial_x^2 \phi(x_t, t) \right) u_t \circ [m du_t + \phi'(x_t) dt - f_{nc,2}(x_t, t)], \tag{A10}$$

  which gives again Equation (22).

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