

Nonequilibrium Thermodynamics and Nose–Hoover Dynamics

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ABSTRACT: We show that systems driven by an external force and described by Nose–Hoover dynamics allow for a consistent nonequilibrium thermodynamics description when the thermostatted variable is initially assumed in a state of canonical equilibrium. By treating the “real” variables as the system and the thermostatted variable as the reservoir, we establish the first and second law of thermodynamics. As for Hamiltonian systems, the entropy production can be expressed as a relative entropy measuring the system–reservoir correlations established during the dynamics.

I. INTRODUCTION

The thermodynamic description of a system out of equilibrium is based on the first and second law. The first law states that, since energy is conserved, the change in the system energy (ΔH_s) is the sum of the energy added doing work on the system (W) and the energy flowing into the system from the environment under the form of heat (Q). The second law states that the change in system entropy (ΔS) is the sum of the entropy flow, a reversible term given by heat divided by temperature ($\Delta_e S = Q/T$), and the entropy production, an always positive or zero irreversible term ($\Delta_i S \geq 0$).^{1–3} During the last few years, significant progress has been achieved in establishing the relation between the nonequilibrium thermodynamics description of a system and its underlying dynamics. The discovery of fluctuation theorems, first for thermostatted deterministic dynamics^{4–9} and then for stochastic^{10–15} and Hamiltonian dynamics,^{16–23} played an important role in this regard. For stochastic dynamics, this connection is nowadays well-established and has given rise to the field of stochastic thermo dynamics.^{24–30} More recently, exact relations for the entropy production have also been obtained for Hamiltonian dynamics when considering specific class of initial conditions.^{31–34} Some work in this direction has been done for thermostatted deterministic dynamics.^{35–37}

In this paper, we explicitly construct the thermodynamics description of a driven system with an underlying Nose–Hoover thermostatted deterministic dynamics.^{9,38,39} Our result can be viewed as the analogue for Nose–Hoover dynamics of the recent result obtained in ref 34 for open systems described by Hamiltonian dynamics. A key point to establish this connection is to treat the thermostatted variable as the reservoir. Our sole assumption is that the initial probability distribution of the thermostatted variable be a canonical equilibrium one.

In Section II we briefly remind the key properties of Nose–Hoover dynamics. In Section III we operate the system–reservoir identification, and in Section IV we identify heat and work to establish the first law of thermodynamics. In Section V we identify entropy and entropy production to establish the

second law of thermodynamics. In Section VI we discuss the connection between irreversible work and entropy production, and in Section VII we discuss the interpretation of entropy production in terms of system–reservoir correlations. Conclusions are drawn in Section VIII.

II. NOSE–HOOVER DYNAMICS

We consider a N -particle system confined in a D dimensional time-dependent potential $V(\lambda(t), \{q_i(t)\})$ in contact with a Nose–Hoover thermostat at temperature T .^{9,38,39} The coordinates and conjugate momenta of the particles are denoted by q_i and p_i ($1 \leq i \leq DN$), and the time dependence of the potential occurs through the driving parameter λ . The equations of motion read:

$$\begin{aligned}\dot{q}_i(t) &= \frac{p_i(t)}{m_i} \\ \dot{p}_i(t) &= -\frac{\partial V(\lambda(t), \{q_i(t)\})}{\partial q_i(t)} - \zeta(t)p_i(t) \\ \dot{\zeta}(t) &= \frac{1}{\alpha} \left(\sum_{i=1}^{DN} \frac{p_i^2}{m_i} - DNk_b T \right)\end{aligned}\quad (1)$$

The dynamical variable ζ mimics a friction coefficient, and α is a measure of the relaxation rate. Hereafter, we abbreviate the set of variables $\{q_i, p_i, \zeta\}$ and $\{q_i, p_i\}$ by Γ and Γ_s , respectively.

Any probability distribution $f(t, \Gamma(t))$ on the phase space Γ , due to conservation, satisfies

$$\frac{\partial f}{\partial t} = -\frac{\partial}{\partial \Gamma}(\dot{\Gamma}f) = -\left(\frac{\partial \dot{\Gamma}}{\partial \Gamma}\right)f - \frac{\partial f}{\partial \Gamma}\dot{\Gamma}\quad (2)$$

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As a result, from

$$\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial \Gamma} \dot{\Gamma} \quad (3)$$

we get that

$$\frac{df}{dt} = -\left(\frac{\partial \Gamma}{\partial \Gamma}\right) f = \frac{d \ln f}{dt} f = -\Lambda f \quad (4)$$

where Λ is the phase space compression factor. For Hamiltonian dynamics, the Liouville theorem implies $\Lambda = 0$, but for the Nose–Hoover dynamics (eq 1), the phase space compression factor is given by $\Lambda = -DN\dot{\zeta}(t)$. This means that any probability distribution evolves in time according to

$$f(t, \Gamma(t)) = \exp[DN \int_0^t d\tau \zeta(\tau)] f(0, \Gamma(0)) \quad (5)$$

which also implies

$$d\Gamma(t) = d\Gamma(0) \exp[-DN \int_0^t d\tau \zeta(\tau)] \quad (6)$$

These two relations will often be used in the following sections.

III. SYSTEM BATH SEPARATION

We are now going to consider that the Γ_s variables constitute the system, while ζ constitutes the reservoir. This is reasonable since Γ_s are the true physical variables, while ζ is only an artificial variable introduced to mimic the effect of a reservoir on the system dynamics. As a result, we define the (reduced) system and reservoir probability distributions as

$$f_s(t, \Gamma_s(t)) = \int d\zeta(t) f(t, \Gamma(t)) \quad (7)$$

$$f_r(t, \zeta(t)) = \int d\Gamma_s(t) f(t, \Gamma(t))$$

and the system and reservoir Hamiltonian as

$$H_s(\lambda, \Gamma_s) = \sum_{i=1}^{DN} \frac{p_i^2}{2m_i} + V(\lambda, \{q_i\}) \quad (8)$$

$$H_r(\zeta) = \frac{\alpha \zeta^2}{2}$$

It should be stressed that these are not real Hamiltonians since the Nose–Hoover dynamics (eq 1) is not Hamiltonian. They are used to define the system and reservoir canonical distributions

$$f_s^{\text{eq}}(\lambda, \Gamma_s) = \frac{\exp[-\beta H_s(\lambda, \Gamma_s)]}{Z_s(\lambda)}$$

$$f_r^{\text{eq}}(\zeta) = \frac{\exp[-\beta H_r(\zeta)]}{Z_r} \quad (9)$$

Note that $\beta = (k_b T)^{-1}$ and that Z_r and $Z_s(\lambda)$ are the system and reservoir partition functions

$$Z_s(\lambda) = \int d\Gamma_s \exp[-\beta H_s(\lambda, \Gamma_s)] \quad Z_r = \int d\zeta \exp[-\beta H_r] \quad (10)$$

We finally introduce the canonical distribution of the total system

$$f^{\text{eq}}(\lambda, \Gamma) = \frac{\exp[-\beta H_0(\lambda, \Gamma)]}{Z_r Z_s(\lambda)} = f_s^{\text{eq}}(\lambda, \Gamma_s) f_r^{\text{eq}}(\zeta) \quad (11)$$

associated to the system–reservoir Hamiltonian

$$H_0(\lambda, \Gamma) = H_s(\lambda, \Gamma_s) + H_r(\zeta) \quad (12)$$

These definitions are a posteriori justified by the important property that the canonical distribution (eq 11) is invariant under the Nose–Hoover dynamics for a constant value of the driving parameter λ . Indeed, using eq 1, we verify that $\Gamma(\partial f^{\text{eq}}/\partial \Gamma) = -\Lambda f^{\text{eq}}$, and that, using eqs 3 and 4, $(\partial f^{\text{eq}}/\partial t) = 0$.

IV. WORK AND HEAT

We start by noting that, under the Nose–Hoover dynamics (eq 1), the Hamiltonian (eq 12) evolves according to

$$\frac{dH_0(\lambda(t), \Gamma(t))}{dt} = \frac{\partial H_s(\lambda(t), \Gamma_s(t))}{\partial \lambda(t)} \dot{\lambda}(t) - DN k_b T \zeta(t) \quad (13)$$

This shows that, even in absence of external driving, that is, for a fixed value of λ , the Hamiltonian (eq 12) is not conserved. Since the work performed on the system by the external driving from 0 to t is naturally defined as^{16,17,31}

$$W[t, \Gamma_s] = \int_0^t d\tau \frac{\partial H_s(\lambda(\tau), \Gamma_s(\tau))}{\partial \lambda(\tau)} \dot{\lambda}(\tau) \quad (14)$$

using eq 13, we can express this work as

$$W[t, \Gamma_s] = \Delta H_s[t, \Gamma_s] + \Delta H_r[t, \zeta] + DN k_b T \int_0^t d\tau \zeta(\tau) \quad (15)$$

where the energy change in the system and reservoir along the trajectory Γ reads

$$\Delta H_s[t, \Gamma_s] = H_s(\lambda(t), \Gamma_s(t)) - H_s(\lambda(0), \Gamma_s(0))$$

$$\Delta H_r[t, \zeta] = H_r(\zeta(t)) - H_r(\zeta(0)) \quad (16)$$

We use square brackets to denote a quantity that depends on an entire trajectory and not just on a specific point in the phase space. We note however that the energy changes $\Delta H_s[t, \Gamma_s]$ and $\Delta H_r[t, \zeta]$ only depend on the initial and final states. Since the first law of thermodynamics should apply for the system energy

$$\Delta H_s[t, \Gamma_s] = W[t, \Gamma_s] + Q[t, \zeta] \quad (17)$$

it becomes natural to define heat as

$$Q[t, \zeta] = -\Delta H_r[t, \zeta] - DN k_b T \int_0^t d\tau \zeta(\tau) \quad (18)$$

In the following sections, the statistical average of a trajectory dependent quantity $X[t, \Gamma(t)]$ will be denoted by

$$X(t) = \langle X[t, \Gamma(t)] \rangle_t = \int d\Gamma(t) f(t, \Gamma(t)) X[t, \Gamma(t)] \quad (19)$$

V. ENTROPY AND ENTROPY PRODUCTION

Our key assumption is that we are going to consider initial conditions of the form

$$f(0, \Gamma(0)) = f_s(0, \Gamma_s(0)) f_r^{\text{eq}}(\zeta(0)) \quad (20)$$

where $f_s(0, \Gamma_s(0))$ is an arbitrary system distribution and $f_r^{\text{eq}}(\zeta(0))$ is the canonical equilibrium distribution of the reservoir.

The second law of thermodynamics reads^{1–3}

$$\Delta S(t) = \Delta_e S(t) + \Delta_i S(t) \quad (21)$$

The left-hand side $\Delta S(t) = S(t) - S(0)$ is the change in the system entropy and will be expressed as the change in Shannon entropy associated with the reduced probability distribution of the system

$$S(t) = -k_b \int d\Gamma_s(t) f_s(t, \Gamma_s(t)) \ln f_s(t, \Gamma_s(t)) \quad (22)$$

The first term on the right-hand side is the entropy flow expressed as the heat (eq 18) divided by temperature

$$\Delta_e S(t) = \frac{Q(t)}{T} \quad (23)$$

while the second term $\Delta_i S(t)$ defines the entropy production. The central result of this paper is that, using eqs 5, 6, 18, and 20, the entropy production can be expressed as

$$\Delta_i S(t) = k_b \left\langle \ln \frac{f(t, \Gamma(t))}{f_s(t, \Gamma_s(t)) f_r^{\text{eq}}(\zeta(t))} \right\rangle_t \quad (24)$$

Details of the derivation are given in the appendix. As expected from thermodynamics, the entropy production is always positive or zero since it can be rewritten as a relative entropy

$$\Delta_i S(t) = k_b D[f(t, \Gamma(t)) | f_s(t, \Gamma_s(t)) f_r^{\text{eq}}(\zeta(t))] \geq 0 \quad (25)$$

Properties of relative entropies are discussed in detail in ref 40. The entropy production will be zero only when $f(t, \Gamma(t)) = f_s(t, \Gamma_s(t)) f_r^{\text{eq}}(\zeta(t))$. It thus becomes clear that eq 21 constitutes the second law of thermodynamics stating that the change in the system entropy $\Delta S(t)$ is the sum of two contributions, the irreversible entropy production $\Delta_i S(t) \geq 0$ and the reversible entropy flow due to heat exchanges $\Delta_e S(t)$.^{1–3} Because a relative entropy is a measure of how different two distributions are from each other, we get a appealing physical interpretation of entropy production as a measure of how different the actual distribution $f(t, \Gamma(t))$ is from the product of the actual reduced probability distribution of the system and the equilibrium distribution of the reservoir. The same result was found for Hamiltonian dynamics in ref 34. By introducing the nonequilibrium free energy

$$F(t) = H_s(t) - TS(t) \quad (26)$$

and using eqs 21 and 23 and the average of eq 17, we can also express entropy production as

$$T\Delta_i S(t) = W(t) - \Delta F(t) \geq 0 \quad (27)$$

VI. IRREVERSIBLE WORK

We now consider the special case where the initial probability distribution of the system (eq 20) is the canonical equilibrium distribution (eq 9), that is, $f_s(0, \Gamma_s(0)) = f_s^{\text{eq}}(\lambda(0), \Gamma_s(0))$. In this case it is interesting to compare the entropy production (eq 27) with the irreversible work defined by^{31–33}

$$W_{\text{diss}}(t) = W(t) - \Delta F^{\text{eq}}(t) \quad (28)$$

where $\Delta F^{\text{eq}}(t) = F^{\text{eq}}(t) - F^{\text{eq}}(0)$ is the change in the equilibrium free energy $F^{\text{eq}}(t) = -\beta^{-1} \ln Z_s(\lambda(t))$. Indeed, by proceeding similarly as for the proof of eq 24 in the appendix, but using eq 15 instead of 18, we verify that the irreversible work can be expressed as

$$W_{\text{diss}}(t) = k_b TD[f(t, \Gamma(t)) | f_s^{\text{eq}}(\lambda(t), \Gamma_s(t))] \geq 0 \quad (29)$$

At time zero $W_{\text{diss}}(0) = 0$, but as the dynamics takes place, the actual probability distribution in the join system–reservoir space starts to

differ from the canonical probability distribution and the irreversible work is a direct measure of that difference. The same result was obtained in eq 10 of ref 33 for an externally driven Hamiltonian dynamics and can be seen as a special case of results obtained in refs 31 and 32.

We can now express the difference between the irreversible work and the entropy production as a relative entropy between the actual and the equilibrium system distribution

$$W_{\text{diss}}(t) - T\Delta_i S(t) = k_b TD[f_s(t, \Gamma_s(t)) | f_s^{\text{eq}}(\lambda(t), \Gamma_s(t))] \geq 0 \quad (30)$$

This relation implies two important inequalities. First, due to the positivity of relative entropies, we get that

$$W_{\text{diss}}(t) \geq T\Delta_i S(t) \quad (31)$$

This inequality only becomes an equality if the final state reached by the system at time t is the canonical equilibrium distribution. A direct consequence of eq 31 obtained using eq 27 with 29 is that the equilibrium free energy is the minimum of the nonequilibrium free energy

$$F(t) \geq F^{\text{eq}}(t) \quad (32)$$

The second inequality following from eq 30 is due to the positivity of the entropy production and reads

$$W_{\text{diss}}(t) \geq k_b TD[f_s(t, \Gamma_s(t)) | f_s^{\text{eq}}(\lambda(t), \Gamma_s(t))] \quad (33)$$

The inequality becomes an equality when the system becomes isolated from the reservoir and thus follows an Hamiltonian dynamics, that is, when $\alpha \rightarrow \infty$. Equation 33 is the Nose–Hoover version of the central result of ref 33 in eq 2. By comparing 29 with 33, we recover the important result that evaluating the dissipative work using relative entropies at a coarse grained level (in eq 33 the coarse graining results from tracing out the thermostatted variable) underestimates the true dissipative work $W_{\text{diss}}(t)$.^{31,32}

VII. CORRELATION ENTROPY

Using eq 5, we start by noting that the change in the total Shannon entropy

$$S_{\text{tot}}(t) = -k_b \int d\Gamma(t) f(t, \Gamma(t)) \ln f(t, \Gamma(t)) \quad (34)$$

is given by^{37,41}

$$\Delta S_{\text{tot}}(t) = -k_b DN \int_0^t d\tau \langle \zeta(\tau) \rangle_\tau \quad (35)$$

We define the correlation entropy as minus the mutual system–reservoir information, that is, the difference between the Shannon entropy of the total system $S_{\text{tot}}(t)$ and the sum of the Shannon entropy of the system $S(t)$ and of the reservoir $S_r(t)$

$$S_c(t) = S_{\text{tot}}(t) - S(t) - S_r(t) \quad (36)$$

For the initial conditions that we consider (eq 20), $S_c(0) = 0$ and the correlation entropy at time t can be expressed as the relative entropy

$$-S_c(t) = k_b D[f(t, \Gamma(t)) | f_s(t, \Gamma_s(t)) f_r(\zeta(t))] \geq 0 \quad (37)$$

As suggested by its name, the correlation entropy measures the amount of negative entropy stored in the system–reservoir correlations by the dynamics. The correlation entropy is related

to the entropy production by

$$S_c(t) + \Delta_i S(t) = k_b D [f_r(t, \zeta(t)) | f_r^{eq}(t, \zeta(t))] \geq 0 \quad (38)$$

which implies the inequality

$$\Delta_i S(t) \geq -S_c(t) \quad (39)$$

The equality is satisfied when the reservoir can be assumed at equilibrium at time t . In such case the entropy production can be interpreted as minus the correlation entropy, that is, as the mutual system–reservoir information.

VIII. CONCLUSIONS

We have shown in this paper that Nose–Hoover dynamics can be made fully consistent with thermodynamics for a class of initial conditions (eq 20). We identified the microscopic expressions for heat, work, system entropy, and entropy production and were able to establish the first and second law of thermodynamics starting from the underlying dynamics. This work can be viewed as the analogue for thermostatted deterministic dynamics of the recent results obtained for Hamiltonian dynamics in ref 34. Our microscopic expression for entropy production in term of a relative entropy is reminiscent of results such as refs 18, 19, 22, 31, and 42.

APPENDIX

We can rewrite eq 24, by expanding the logarithm and using eqs 7 and 22, as

$$\begin{aligned} \Delta_i S(t) = & k_b \int d\Gamma(t) f(t, \Gamma(t)) \ln f(t, \Gamma(t)) + S(t) \\ & + \frac{\langle H_r(\zeta(t)) \rangle_t - F_r^{eq}}{T} \end{aligned} \quad (40)$$

where $F_r^{eq} = -\beta^{-1} \ln Z_r$. Using eqs 5 and 6, the first term on the right-hand side can be rewritten as

$$\begin{aligned} & k_b \int d\Gamma(0) f(0, \Gamma(0)) \ln f(0, \Gamma(0)) + DNk_b \int_0^t d\tau \langle \zeta(\tau) \rangle_\tau \\ & = -S(0) - \frac{\langle H_r(\zeta(0)) \rangle_0 - F_r^{eq}}{T} + DNk_b \int_0^t d\tau \langle \zeta(\tau) \rangle_\tau \end{aligned}$$

To go from the first to the second line we used eq 20. Using now the definition of heat (eq 18), we find that eq 40 can be rewritten as eq 21 with eqs 22 and 23.

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