Nonequilibrium thermodynamics and Nose-Hoover dynamics

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(Dated: May 26, 2010)

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 is the sum of the energy added doing work on the system and the energy flowing into the system from the environment under the form of heat. The second law states that the change in system entropy is the sum of the entropy flow, a reversible term given by heat divided by temperature, and the entropy production, an always positive or zero irreversible term [1–3]. During the last 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 thermodynamics [24–28]. More recently, exact relations for the entropy production have also been obtained for Hamiltonian dynamics when considering specific class of initial conditions [29–32]. Some work in this direction has been done for thermostatted deterministic dynamics [33–35].

In this paper, we explicitly construct the thermodynamics description of a driven system with an underlying Nose-Hoover thermostatted dynamics [3, 36, 37]. Our result can be viewed as the analogue for Nose-Hoover dynamics of the recent result obtained in [32] for open systems described by Hamiltonian dynamics. A key point in 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 term 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 $T \neq 0$. 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 $\lambda$. The equations of motion read:

$$\dot{q}_i(t) = \frac{p_i(t)}{m_i}$$

$$\dot{p}_i(t) = -\frac{\partial V(\lambda(t), \{q_i(t)\})}{\partial q_i(t)} - \zeta(t)p_i(t)$$

$$\dot{\zeta}(t) = \frac{1}{\alpha} \left( \sum_{i=1}^{DN} \frac{p_i^2}{m_i} - DNk_bT \right).$$

(1)

The dynamical variable $\zeta$ mimics a friction coefficient and $\alpha$ 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 $\Gamma$ and $\Gamma_s$, respectively.

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

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

(2)
As a result, from
\[
\frac{df}{dt} = \frac{\partial f}{\partial t} + \frac{\partial f}{\partial \Gamma} \Gamma,
\]
we get that
\[
\frac{df}{dt} = -\left(\frac{\partial \Gamma}{\partial t}\right)f = \frac{d\ln f}{dt} = -\Lambda f
\]
where \(\Lambda\) is the phase space compression factor. For Hamiltonian dynamics, Liouville theorem implies \(\Lambda = 0\), but for the Nose-Hoover dynamics [1], the phase space compression factor is given by \(\Lambda = -DN\partial t\zeta(t)\). This means that any probability distribution evolves in time according to
\[
f(t, \Gamma(t)) = e^{\int_0^t ds\zeta(s)} f(0, \Gamma(0))
\]
which also implies
\[
d\Gamma(t) = d\Gamma(0) e^{-\int_0^t ds\zeta(s)}.
\]
These two relations will often be used in what follows.

### III. SYSTEM BATH SEPARATION

We are now going to consider that the \(\Gamma_s\) variables constitute the system, while \(\zeta\) constitutes the reservoir. This is reasonable since \(\Gamma_s\) are the true physical variables while \(\zeta\) 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
\[
f_s(t, \Gamma_s(t)) = \int d\zeta(t) f(t, \Gamma(t))
\]
\[
f_r(t, \zeta(t)) = \int d\Gamma_s(t) f(t, \Gamma(t))
\]
and the system and reservoir Hamiltonian as
\[
H_s(\lambda, \Gamma_s) = \sum_{i=1}^{DN} \frac{p_i^2}{2m_i} + V(\lambda, \{q_i\})
\]
\[
H_r(\zeta) = \frac{\alpha\zeta^2}{2}.
\]

The system and reservoir canonical distributions are therefore defined as
\[
f^eq_s(\lambda, \Gamma_s) = \frac{e^{-\beta H_s(\lambda, \Gamma_s)}}{Z_s(\lambda)}, \quad f^eq_r(\zeta) = \frac{e^{-\beta H_r(\zeta)}}{Z_r}.
\]

Note that \(\beta = (k_b T)^{-1}\) and that \(Z_r\) and \(Z_s(\lambda)\) are the system and reservoir partition functions
\[
Z_s(\lambda) = \int d\Gamma_s e^{-\beta H_s(\lambda, \Gamma_s)}, \quad Z_r = \int d\zeta e^{-\beta H_r(\zeta)}.
\]

We finally introduce the canonical distribution of the total system
\[
f^eq(\lambda, \Gamma) = \frac{e^{-\beta H(\lambda, \Gamma)}}{Z_r Z_s(\lambda)} = f^eq_s(\lambda, \Gamma_s) f^eq_r(\zeta),
\]
associated to the system-reservoir Hamiltonian
\[
H_0(\lambda, \Gamma) = H_s(\lambda, \Gamma_s) + H_r(\zeta).
\]

An important property of the canonical distribution \(\{\zeta\}\) is that it is invariant under the Nose-Hoover dynamics for constant value of the driving parameter \(\lambda\). Indeed, using [11], we verify that \(\frac{\partial f^eq}{\partial \tau} = -\Lambda f^eq\) and that, using [3] and [11], \(\frac{d\Gamma}{d\tau} = 0\).

### IV. WORK AND HEAT

We start by noting that under the Nose-Hoover dynamics [1], the Hamiltonian [13] evolves according to
\[
\frac{dH_0(\lambda(t), \Gamma(t))}{dt} = \frac{\partial H_s(\lambda(t), \Gamma_s(t))}{\partial \lambda(t)} \dot{\lambda}(t) - D N k_b T \dot{\zeta}(t).
\]

This shows that even in absence of external driving, i.e. for a fixed value of \(\lambda\), the Hamiltonian [11] is not conserved. Since the work performed on the system by the external driving from 0 to \(t\) is naturally defined as
\[
W[t, \Gamma_s] = \int_0^t d\tau \frac{\partial H_s(\lambda(\tau), \Gamma_s(\tau))}{\partial \lambda(\tau)} \dot{\lambda}(\tau),
\]
using [14], we can express this work as
\[
W[t, \Gamma_s] = \Delta H_s[t, \Gamma_s] + \Delta H_r[t, \zeta]
\]
\[
+ D N k_b T \int_0^t d\zeta(s),
\]
where the energy change in the system and reservoir along the trajectory \(\Gamma\) reads
\[
\Delta H_s[t, \Gamma_s] = H_s(\lambda(t), \Gamma_s(t)) - H_s(\lambda(0), \Gamma_s(0))
\]
\[
\Delta H_r[t, \zeta] = H_r(\zeta(t)) - H_r(\zeta(0)).
\]

Since the first law of thermodynamics should apply for the system energy
\[
\Delta H_s[t, \Gamma_s] = W[t, \Gamma_s] + Q[t, \zeta],
\]
it becomes natural to define heat as
\[
Q[t, \zeta] = -\Delta H_r[t, \zeta] - D N k_b T \int_0^t d\tau \dot{\zeta}(\tau).
\]

In the following, the statistical average of a trajectory dependent quantity \(X[t, \Gamma(t)]\) will be denoted by
\[
X(t) = \langle X[t, \Gamma(t)] \rangle_t = \int d\Gamma(t) f(t, \Gamma(t)) X[t, \Gamma(t)].
\]
V. ENTROPY AND ENTROPY PRODUCTION

Our key assumption is that we are going to consider initial conditions of the form
\[ f(0, \Gamma(0)) = f_s(0, \Gamma_s(0)) f^{eq}_s(\zeta(0)), \]
where \( f_s(0, \Gamma_s(0)) \) is an arbitrary system distribution and \( f^{eq}_s(\zeta(0)) \) is the canonical equilibrium distribution of the reservoir.

The central result of this paper is that the entropy production is given by
\[ \Delta_i S(t) = k_b \left< \ln \frac{f(t, \Gamma(t))}{f_s(t, \Gamma_s(t)) f^{eq}_s(\zeta(t))} \right>_t. \]
Indeed, using (5) and (19), we can express (22) as
\[ \Delta_i S(t) = \Delta S(t) - \Delta_c S(t), \]
where the first term \( \Delta S(t) = S(t) - S(0) \) is the change in the entropy associated with the reduced system probability distribution
\[ S(t) = -k_b \int d\Gamma_s(t) f_s(t, \Gamma_s(t)) \ln f_s(t, \Gamma_s(t)), \]
and the second term is the entropy flow expressed as the heat divided by temperature
\[ \Delta_c S(t) = \frac{Q(t)}{T}. \]

VI. IRREVERSIBLE WORK

We now consider the special case where the initial distribution of the system (21) is the canonical equilibrium distribution (10). In this case it is interesting to compare the entropy production (23) with the irreversible work defined as
\[ W_{diss}(t) = \frac{W(t) - \Delta F^{eq}(t)}{k_b T}, \]
where \( \Delta F^{eq}(t) = F^{eq}(t) - F^{eq}(0) \) is the change in the equilibrium free energy \( F^{eq}(t) = -\beta^{-1} \ln Z_s(\lambda(t)) \). Indeed, using (5) and (19), we find that the irreversible work can be expressed as
\[ W_{diss}(t) = k_b D \left[ f_s(t, \Gamma_s(t)) \middle\| f^{eq}_s(\lambda(t), \Gamma_s(t)) \right]. \]

Due to the positivity of relative entropies we get the inequality
\[ W_{diss}(t) \geq \Delta_i S(t) \geq 0, \]
which only becomes an equality when the final state of the system (at time \( t \)) is the canonical equilibrium distribution. Using (28) with (30), we also find that the equilibrium free energy is the minimum of the nonequilibrium free energy
\[ F(t) \geq F^{eq}(t). \]

VII. CORRELATION ENTROPY

Using (5), we start by noting that the change in the total Shannon entropy
\[ S_{tot}(t) = -k_b \int d\Gamma(t) f(t, \Gamma(t)) \ln f(t, \Gamma(t)) \]
is given by (32, 39)
\[ \Delta S_{tot}(t) = -k_b DN \int_0^t ds \langle \zeta(s) \rangle_s. \]
We define the correlation entropy as minus the mutual system-reservoir information, i.e. the difference between the Shannon entropy of the total system \( S_{tot}(t) \) and the
For the initial conditions that we consider, $S_c(0) = 0$ and the correlation entropy at time $t$ can be expressed as the relative entropy

$$S_c(t) = S_{tot}(t) - S(t) - S_r(t).$$

(36)

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

$$S_c(t) + \Delta_iS(t) = k_BT\left[f_r(t, \zeta(t))|f_r^{eq}(t, \zeta(t))\right] \geq 0.$$  

(37)

which implies the inequality

$$\Delta_iS(t) \geq -S_c(t) \geq 0.$$  

(38)

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, i.e. 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 class of initial conditions of the kind. We identified the microscopic expressions for heat, work, system entropy and entropy production and where able to establish the first and second law of thermodynamics starting from the underlying dynamics. This work can be viewed as the analog for thermostatted deterministic dynamics of the recent results obtained for Hamiltonian dynamics in [32]. Our microscopic expression for entropy production in term of a relative entropy is reminiscent of results such as [18, 19, 22, 29, 40].

ACKNOWLEDGMENTS

M. E. is supported by the Belgian Federal Government (IAP project “NOSY”). T. M. owes much to the financial support from JSPS research fellowship for young scientists.

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