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Stefano Olla

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# MICROSCOPIC DERIVATION OF AN ISOTHERMAL THERMODYNAMIC TRANSFORMATION

STEFANO OLLA

ABSTRACT. We obtain macroscopic isothermal thermodynamic transformations by space-time scalings of a microscopic Hamiltonian dynamics in contact with a heat bath. The microscopic dynamics is given by a chain of anharmonic oscillators subject to a varying tension (external force) and the contact with the heat bath is modeled by independent Langevin dynamics acting on each particle. After a diffusive space-time scaling and cross-graining, the profile of volume converges to the solution of a deterministic diffusive equation with boundary conditions given by the applied tension. This defines an irreversible thermodynamic transformation from an initial equilibrium to a new equilibrium given by the final tension applied. Quasistatic reversible isothermal transformations are then obtained by a further time scaling. Heat is defined as the total flux of energy exchanged between the system and the heat bath. Then we prove that the relation between the limit heat, work, free energy and thermodynamic entropy agree with the first and second principle of thermodynamics.

## 1. INTRODUCTION

Isothermal transformations are fundamental in thermodynamics, in particular they are one of the components of the Carnot cycle. As often in thermodynamics, they represent *idealized* transformations where the system is maintained at a constant temperature by being in constant contact with a *large* heat reservoir (*heat bath*). An isothermal thermodynamic transformations connects two equilibrium states  $A_0$  and  $A_1$  at the same temperature  $T$ , by changing the exterior forces applied. According to the first law of thermodynamics, the change in the internal energy is given by  $U_1 - U_0 = W + Q$ , where  $W$  is the work made by the exterior forces and  $Q$  is the heat (energy) exchanged with the thermal reservoir. The second law prescribes that the change of the free energy  $F = U - TS$  (where  $S$  is the thermodynamic entropy), satisfy the Clausius inequality  $F_1 - F_0 \leq W$ , with equality satisfied for *reversible quasistatic* transformations. In the quasistatic transformation we can then identify  $Q = T(S_1 - S_0)$ .

The purpose of this article is to prove mathematically that the thermodynamic behavior of isothermal transformations, as described above, can be obtained by proper space and time scaling of a microscopic dynamics. We consider a one dimensional system, where the equilibrium thermodynamic intensive parameters

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are given by the temperature  $T = \beta^{-1}$  and the tension (or pressure)  $\tau$ , or by the extensive observables: length (volume)  $\mathcal{L}$  and energy  $U$ . This simplifies the problem as only two parameters are needed to specify the equilibrium thermodynamic state and no phase transitions will appear.

The microscopic model is given by a chain of  $N$  anharmonic oscillators, where the first particle is attached to a fix point and on the last particle acts a force (tension)  $\tilde{\tau}$ , eventually changing in time. The action of the thermal bath is modeled by independent Langevin processes at temperature  $T$ , acting on each particle. A mathematically equivalent model for the heat bath is given by random collisions with the environment: at exponentially distributed independent random times, each particle has a new velocity distributed by a centered gaussian with variance  $T$ .

As a consequence of the action of the thermal bath, the time evolution of the microscopic configuration of the positions and velocities of the particles is stochastic. The distance between the first and the last particle defines the microscopic length of the system, while the energy is given by the sum of the kinetic energies of each particle and the potential energy of each spring.

For each value of the applied tension  $\tau$ , the system has an equilibrium probability distribution explicitly given by a Gibbs measure, a product measure in this case. The temperature parameter is fixed by the heat bath. Starting the system with an equilibrium given by tension  $\tau_0$ , and changing the applied tension to  $\tau_1$ , the system will go out of equilibrium before reaching the new equilibrium state. During this transformation a certain amount of energy is exchanged with the thermostats and mechanical work is done by the force applied. We prove that, under a proper macroscopic rescaling of space and time, all these (random) quantities, converge to *deterministic* values predicted by thermodynamics.

When the system is out of equilibrium, either for a change in the tension applied, or by initial conditions, there is an evolution of the local length (or stretch) on a diffusive macroscopic space-time scale. This is governed by a diffusion equation that describe the inhomogeneity of the system during the isothermal transformation. After an infinite time (in this scale) it reach the new equilibrium state given by a constant value of the local lenght, corresponding to the value of the tension  $\tau_1$ . We have obtained, in this diffusive time scale, an *irreversible* thermodynamic transformation, that satisfies a strict Clausius inequality between work and change of the free energy. Under a further rescaling of time, that correspond in a slower change of the applied tension, we obtain a *reversible quasi-static* transformation that satisfies Clausius inequality. In fact, for the irreversible transformation we obtain the following relation between heat and changes of thermodynamic entropy  $S$

$$Q = T\Delta S - \mathcal{D}$$

where  $\mathcal{D}$  is a strictly positive dissipation term that has an explicit expression in terms of the solution of the diffusive equation that govern macroscopically the transformation (cf. (4.13)). In the quasi-static limit we prove that  $\mathcal{D} \rightarrow 0$ . A

similar interpretation of quasi-static transformations, for thermodynamic systems with one parameter (density), has been proposed in recent works by Bertini et al. [1, 2].

In the case of the harmonic chain, the thermodynamic entropy is a function of the temperature, so it remains constant in isothermal transformation. Then heat is equal to the dissipation term  $\mathcal{D}$ . It means that in the quasistatic limit for the harmonic chain, there is no heat produced, internal energy is changed by work in a perfectly efficient way.

Thermodynamics does not specify the time scale for the transformations, this may depend on the nature of the transformation (isothermal, adiabatic, ...) and the details of the microscopic system and of the exterior agent (heat bath etc.). In this system of oscillators, in adiabatic setting, with also momentum conservation, the relevant space-time scale is hyperbolic (cf. [4]).

The proof of the hydrodynamic limit follows the lines of [5, 7], using the relative entropy method (cf. [8, 3]). The method has to be properly adapted to deal with the boundary conditions.

## 2. ISOTHERMAL MICROSCOPIC DYNAMICS

We consider a chain of  $N$  coupled oscillators in one dimension. Each particle has the same mass that we set equal to 1. The position of atom  $i$  is denoted by  $q_i \in \mathbb{R}$ , while its momentum is denoted by  $p_i \in \mathbb{R}$ . Thus the configuration space is  $(\mathbb{R} \times \mathbb{R})^N$ . We assume that an extra particle 0 to be attached to a fixed point and does not move, i.e.  $(q_0, p_0) \equiv (0, 0)$ , while on particle  $N$  we apply a force  $\tilde{\tau}(t)$  depending on time. Observe that only the particle 0 is constrained to not move, and that  $q_i$  can assume also negative values.

Denote by  $\mathbf{q} := (q_1, \dots, q_N)$  and  $\mathbf{p} := (p_1, \dots, p_N)$ . The interaction between two particles  $i$  and  $i - 1$  will be described by the potential energy  $V(q_i - q_{i-1})$  of an anharmonic spring relying the particles. We assume  $V$  to be a positive smooth function which for large  $r$  grows faster than linear but at most quadratic, that means that there exists a constant  $C > 0$  such that

$$\lim_{|r| \rightarrow \infty} \frac{V(r)}{|r|} = \infty. \quad (2.1)$$

$$\limsup_{|r| \rightarrow \infty} V''(r) \leq C < \infty. \quad (2.2)$$

Energy is defined by the following Hamiltonian:

$$\mathcal{H}_N(\mathbf{q}, \mathbf{p}) : = \sum_{i=1}^N \left( \frac{p_i^2}{2} + V(q_i - q_{i-1}) \right).$$

Since we focus on a nearest neighbor interaction, we may define the distance between particles by

$$r_i = q_i - q_{i-1}, \quad i = 1, \dots, N.$$

The chain is immersed in a thermal bath at temperature  $\beta^{-1}$  that we model by the action of  $N$  independent Langevin processes. The dynamics is defined by the solution of the system of stochastic differential equations

$$\begin{aligned} dr_i &= N^2(p_i - p_{i-1}) dt \\ dp_i &= N^2(V'(r_{i+1}) - V'(r_i)) dt - N^2\gamma p_i dt - N\sqrt{2\gamma\beta^{-1}}dw_i, \quad i = 1, \dots, N-1, \\ dp_N &= N^2(\tilde{\tau}(t) - V'(r_N)) dt - N^2\gamma p_N dt - N\sqrt{2\gamma\beta^{-1}}dw_N \end{aligned} \quad (2.3)$$

Here  $\{w_i(t)\}_i$  are  $N$ -independent standard Wiener processes,  $\gamma > 0$  is a parameter of intensity of the interaction with the heat bath,  $p_0$  is set identically to 0. We have also already rescaled time according to the diffusive space-time scaling. Notice that  $\tilde{\tau}(t)$  changes at this macroscopic time scale.

The generator of this diffusion is given by

$$\mathcal{L}_N^{\tilde{\tau}(t)} := N^2 A_N^{\tau(t)} + N^2 \gamma S_N. \quad (2.4)$$

Here the Liouville operator  $A_N^\tau$  is given by

$$\begin{aligned} A_N^\tau &= \sum_{i=1}^N (p_i - p_{i-1}) \frac{\partial}{\partial r_i} + \sum_{i=1}^{N-1} (V'(r_{i+1}) - V'(r_i)) \frac{\partial}{\partial p_i} \\ &\quad + (\tau - V'(r_N)) \frac{\partial}{\partial p_N}, \end{aligned} \quad (2.5)$$

while

$$S = \sum_{i=1}^N (\beta^{-1} \partial_{p_i}^2 - p_i \partial_{p_i}) \quad (2.6)$$

For  $\tilde{\tau}(t) = \tau$  constant, the system has a unique stationary measure given by the product

$$d\mu_{\tau,\beta}^N = \prod_{i=1}^N e^{-\beta(\mathcal{E}_i - \tau r_i) - \mathcal{G}_{\tau,\beta}} dr_i dp_i = g_\tau^N d\mu_{0,\beta}^N \quad (2.7)$$

where we denoted  $\mathcal{E}_i = p_i^2/2 + V(r_i)$ , the energy we attribute to the particle  $i$ , and

$$\mathcal{G}_{\tau,\beta} = \log \left[ \sqrt{2\pi\beta^{-1}} \int e^{-\beta(V(r) - \tau r)} dr \right]. \quad (2.8)$$

Observe that the function  $\mathfrak{r}(\tau) = \beta^{-1} \partial_\tau \mathcal{G}_{\tau,\beta}$  gives the average equilibrium length in function of the tension  $\tau$ , and we denote the inverse by  $\boldsymbol{\tau}(\mathfrak{r})$ .

We will need also to consider local Gibbs measure (inhomogeneous product), corresponding to profiles of tension  $\{\tau(x), x \in [0, 1]\}$ :

$$d\mu_{\tau,\beta}^N = \prod_{i=1}^N e^{-\beta(\mathcal{E}_i - \tau(i/N)r_i) - \mathcal{G}_{\tau(i/N),\beta}} dr_i dp_i = g_{\tau(\cdot)}^N d\mu_{0,\beta}^N \quad (2.9)$$

Given an initial profile of tension  $\tau(0, x)$ , we assume that initial probability state is given by an absolutely continuous measure (with respect to the Lebesgue measure), whose density with respect to  $d\mu_{0,\beta}^N$  is given by  $f_0^N$ , such that the relative entropy with respect to  $\mu_{\tau(0,x),\beta}^N$

$$H_N(0) = \int f_0^N \log \left( \frac{f_0^N}{g_{\tau(0,\cdot)}^N} \right) d\mu_{0,\beta}^N \quad (2.10)$$

satisfies

$$\lim_{N \rightarrow \infty} \frac{H_N(0)}{N} = 0 \quad (2.11)$$

This implies the following convergence in probability with respect to  $f_0^N$ :

$$\frac{1}{N} \sum_{i=1}^N G(i/N) r_i(0) \longrightarrow \int_0^1 G(x) \mathfrak{r}(\tau(0, x)) dx \quad (2.12)$$

The macroscopic evolution for the stress will be given by

$$\begin{aligned} \partial_t r(t, x) &= \gamma^{-1} \partial_x^2 \boldsymbol{\tau}(r(t, x)), \quad x \in [0, 1] \\ \partial_x r(t, 0) &= 0, \quad \boldsymbol{\tau}(r(t, 1)) = \tilde{\tau}(t), \quad t > 0 \\ \boldsymbol{\tau}(r(0, x)) &= \tau(0, x), \quad x \in [0, 1] \end{aligned} \quad (2.13)$$

Observe that we do not require that  $\tau(r(0, 1)) = \tilde{\tau}(0)$ , so we can consider initial profiles of equilibrium with tension different than the applied  $\tilde{\tau}$ .

The main result is the following

**Theorem 2.1.**

$$\lim_{N \rightarrow \infty} \frac{H_N(t)}{N} = 0 \quad (2.14)$$

where

$$H_N(t) = \int f_t^N \log \left( \frac{f_t^N}{g_{\tau(t,\cdot)}^N} \right) d\mu_{0,\beta}^N \quad (2.15)$$

with  $\tau(t, x) = \boldsymbol{\tau}(r(t, x))$ , and  $f_t^N$  the density of the configuration of the system at time  $t$ .

A schetch of the proof is postponed to section 5.

**Remark 2.2.** *The proof and the result are identical (up to some constant) if we use a different modelling of the heat bath, where the particles undergo independent*

random collisions such that after the collision they get a new value distributed by a gaussian distribution with variance  $\beta^{-1}$ , i.e.

$$Sf(\mathbf{r}, \mathbf{p}) = \sum_{i=1}^N \int (f(\mathbf{r}, p_1, \dots, p'_i, \dots) - f(\mathbf{r}, \mathbf{p})) \frac{e^{-\beta(p'_i)^2/2}}{\sqrt{2\pi\beta^{-1}}} dp'_i \quad (2.16)$$

### 3. THERMODYNAMIC CONSEQUENCES

Consider the case where we start our system with a constant tension  $\tau(0, x) = \tau_0$  and we apply a tension  $\tilde{\tau}(t)$  going smoothly from  $\tilde{\tau}(0) = \tau_0$  to  $\tilde{\tau}(t) = \tau_1$  for  $t \geq t_1$ . It follows from standard arguments that

$$\lim_{t \rightarrow \infty} \boldsymbol{\tau}(r(t, x)) = \tau_1, \quad \forall x \in [0, 1] \quad (3.1)$$

so on an opportune time scale, this evolution represents an isothermal thermodynamic transformation from the equilibrium state  $(\tau_0, \beta^{-1})$  to  $(\tau_1, \beta^{-1})$ . Clearly this is an irreversible transformation and will satisfy a strict Clausius inequality.

The length of the system at time  $t$  is given by

$$L(t) = \int_0^1 r(t, x) dx \quad (3.2)$$

and the work done by the force  $\tilde{\tau}$ :

$$\begin{aligned} W(t) &= \int_0^t \tilde{\tau}(s) dL(s) = \gamma^{-1} \int_0^t ds \tilde{\tau}(s) \int_0^1 dx \partial_x^2 \boldsymbol{\tau}(r(s, x)) \\ &= \gamma^{-1} \int_0^t \tilde{\tau}(s) \partial_x \boldsymbol{\tau}(r(s, 1)) ds \end{aligned} \quad (3.3)$$

The free energy of the equilibrium state  $(r, \beta)$  is given by the Legendre transform of  $\beta^{-1} \mathcal{G}_{\tau, \beta}$ :

$$F(r, \beta) = \inf_{\tau} \{ \tau r - \beta^{-1} \mathcal{G}_{\tau, \beta} \} \quad (3.4)$$

Since  $\beta$  is constant, we will drop the dependences on it in the following. It follows that  $\boldsymbol{\tau}(r) = \partial_r \mathcal{F}$ . Thanks to the local equilibrium, we can define the free energy at time  $t$  as

$$\mathcal{F}(t) = \int_0^1 F(r(t, x), \beta) dx. \quad (3.5)$$

Its time derivative is (after integration by parts):

$$\frac{d}{dt} \mathcal{F}(t) = -\gamma^{-1} \int_0^1 (\partial_x \boldsymbol{\tau}(r(t, x)))^2 dx + \gamma^{-1} \tilde{\tau}(t) \partial_x \boldsymbol{\tau}(r(t, x)) \Big|_{x=1}$$

i.e.

$$\mathcal{F}(t) - \mathcal{F}(0) = W(t) - \gamma^{-1} \int_0^t ds \int_0^1 (\partial_x \boldsymbol{\tau}(r(s, x)))^2 dx$$

Because of initial condition,  $\mathcal{F}(0) = F(\tau_0)$ , and because (3.1) we have  $\mathcal{F}(t) \rightarrow F(\tau_1)$ , and we conclude that

$$F(\tau_1) - F(\tau_0) = W - \gamma^{-1} \int_0^{+\infty} ds \int_0^1 (\partial_x \boldsymbol{\tau}(r(s, x)))^2 dx \quad (3.6)$$

where  $W$  is the total work done by the force  $\tilde{\tau}$  in the transformation up to reaching the new equilibrium and is expressed by taking the limit in (3.3) for  $t \rightarrow \infty$ :

$$W = \int_0^\infty \tilde{\tau}(s) dL(s) = \gamma^{-1} \int_0^\infty \tilde{\tau}(s) \partial_x \boldsymbol{\tau}(r(s, 1)) ds \quad (3.7)$$

By the same argument we will use in the proof of Proposition 3.1 we have that the second term of the righthand side of (3.6) is finite, that implies the existence of  $W$ .

Since the second term on right hand side is always strictly positive, we have obtained a strict Clausius inequality. This is not surprising since we are operating an irreversible transformation.

If we want to obtain a *reversible quasistatic isothermal transformation*, we have introduce another larger time scale, i.e. introduce a small parameter  $\varepsilon > 0$  and apply a tension slowly varying in time  $\tilde{\tau}(\varepsilon t)$ . The diffusive equation becomes

$$\partial_t r_\varepsilon(t, x) = \gamma^{-1} \partial_x^2 \boldsymbol{\tau}(r_\varepsilon(t, x)) \quad (3.8)$$

with boundary conditions

$$\begin{aligned} \partial_x r_\varepsilon(t, 0) &= 0 \\ \boldsymbol{\tau}(r_\varepsilon(t, 1)) &= \tilde{\tau}(\varepsilon t) \end{aligned} \quad (3.9)$$

Then (3.6) became

$$F(r_1) - F(r_0) = W_\varepsilon - \gamma^{-1} \int_0^\infty ds \int_0^1 (\partial_x \boldsymbol{\tau}(r_\varepsilon(s, x)))^2 dx \quad (3.10)$$

**Proposition 3.1.**

$$\lim_{\varepsilon \rightarrow 0} \int_0^\infty ds \int_0^1 (\partial_x \boldsymbol{\tau}(r_\varepsilon(s, x)))^2 dx = 0 \quad (3.11)$$

*Proof.* To simplify notations, let set here  $\gamma = 1$ . We look at the time scale  $\mathbf{t} = \varepsilon^{-1}t$ , then  $\tilde{r}_\varepsilon(\mathbf{t}, x) = r_\varepsilon(\varepsilon^{-1}t, x)$  satisfy the equation

$$\partial_{\mathbf{t}} \tilde{r}_\varepsilon(\mathbf{t}, x) = \varepsilon^{-1} \partial_x^2 \boldsymbol{\tau}(\tilde{r}_\varepsilon(\mathbf{t}, x)) \quad (3.12)$$

with boundary conditions

$$\begin{aligned} \partial_x \tilde{r}_\varepsilon(\mathbf{t}, 0) &= 0 \\ \boldsymbol{\tau}(\tilde{r}_\varepsilon(\mathbf{t}, 1)) &= \tilde{\tau}(\mathbf{t}) \end{aligned} \quad (3.13)$$

$$\begin{aligned} & \frac{1}{2} \int_0^1 (\tilde{r}_\varepsilon(\mathbf{t}, x) - \mathbf{r}[\tilde{\tau}(\mathbf{t})])^2 d\mathbf{t} \\ &= \int_0^{\mathbf{t}} ds \int_0^1 dx (\tilde{r}_\varepsilon(s, x) - \mathbf{r}(\tilde{\tau}(s))) \left( \varepsilon^{-1} \partial_x^2 \boldsymbol{\tau}[\tilde{r}_\varepsilon(s, x)] - \frac{d}{ds} \mathbf{r}[\tilde{\tau}(s)] \right) \\ &= -\varepsilon^{-1} \int_0^{\mathbf{t}} ds \int_0^1 dx (\partial_x \tilde{r}_\varepsilon(s, x))^2 \frac{d\boldsymbol{\tau}}{dr}[\tilde{r}_\varepsilon(s, x)] \\ & \quad - \int_0^{\mathbf{t}} ds \frac{d\mathbf{r}}{d\tau}(\tilde{\tau}(s)) \tilde{\tau}'(s) \int_0^1 dx (\tilde{r}_\varepsilon(s, x) - \tilde{r}_\varepsilon(s, 1)) \end{aligned} \quad (3.14)$$



Rewriting

$$\begin{aligned} \left| \int_0^1 dx (\tilde{r}_\varepsilon(s, x) - \tilde{r}_\varepsilon(s, 1)) \right| &= \left| \int_0^1 dx \int_x^1 dy \partial_y \tilde{r}_\varepsilon(s, y) \right| \\ &= \left| \int_0^1 dy y \partial_y \tilde{r}_\varepsilon(s, y) \right| \leq \frac{\alpha}{2\varepsilon} \int_0^1 dx (\partial_x \tilde{r}_\varepsilon(s, x))^2 + \frac{\varepsilon}{4\alpha} \end{aligned}$$

Recall that the free energy  $F$  is strictly convex and that  $0 < C_- \leq \frac{dx}{d\tau} \leq C_+ < +\infty$ , and furthermore we have chosen  $\tilde{\tau}$  such that  $|\tilde{\tau}'(t)| \leq 1_{t \leq t_1}$ . Regrouping positive terms on the left hand side we obtain the bound:

$$\frac{1}{2} \int_0^1 (\tilde{r}_\varepsilon(\mathbf{t}, x) - \mathbf{r}[\tilde{\tau}(\mathbf{t})])^2 dx + \varepsilon^{-1} \left( C_- - \frac{C_+ \alpha \mathbf{t}}{2} \right) \int_0^{\mathbf{t}} ds \int_0^1 dx (\partial_x \tilde{r}_\varepsilon(s, x))^2 \leq \frac{\varepsilon C_+ \mathbf{t}}{4\alpha} \quad (3.15)$$

By choosing  $\alpha = \frac{C_-}{C_+ \mathbf{t}}$ , we obtain, for any  $\mathbf{t} > t_1$ :

$$\frac{1}{C_-} \int_0^1 (\tilde{r}_\varepsilon(\mathbf{t}, x) - \mathbf{r}[\tilde{\tau}(t_1)])^2 dx + \varepsilon^{-1} \int_0^{\mathbf{t}} ds \int_0^1 dx (\partial_x \tilde{r}_\varepsilon(s, x))^2 \leq \frac{\varepsilon}{2} \quad (3.16)$$

then we can take the limit as  $\mathbf{t} \rightarrow \infty$ , the first term on the right hand side of (3.16) will disappear, and we obtain

$$\varepsilon^{-1} \int_0^{+\infty} ds \int_0^1 dx (\partial_x \tilde{r}_\varepsilon(s, x))^2 \leq \frac{\varepsilon}{2} \quad (3.17)$$

that implies (3.11).  $\square$

Consequently we obtain the Clausius identity for the quasistatic reversible isothermal transformation.

Along the lines of the proof above it is also easy to prove that

$$\lim_{\varepsilon \rightarrow 0} \int_0^1 (r_\varepsilon(t, x) - \mathbf{r}[\tilde{\tau}(\varepsilon t)])^2 dx = 0 \quad (3.18)$$

that gives a rigorous meaning to the *quasistatic* definition.

The internal energy of the thermodynamic equilibrium state  $(r, T)$  is defined as  $U = F + TS$ , where  $S$  is the thermodynamic entropy. The first principle of thermodynamics defines the heat  $Q$  transferred as  $\Delta U = W + Q$ .

The change of internal energy in the isothermal tranformation is given by

$$\Delta U = \Delta F + T\Delta S = W - \gamma^{-1} \int_0^{+\infty} ds \int_0^1 dx (\partial_x \boldsymbol{\tau}(r(s, x)))^2 + T\Delta S \quad (3.19)$$

Then for the irreversible transformation we have  $Q \leq T\Delta S$ , while equality holds in the quasistatic limit.

The linear case is special, it corresponds to the microscopic harmonic interaction. In this case  $S$  is just a function of the temperature ( $S \sim \log T$ ), so  $\Delta S = 0$  for any isothermal transformation. Correspondingly the heat exchanged with the thermostat is always negative and given by  $Q = -\gamma^{-1} \int_0^{+\infty} ds \int_0^1 dx (\partial_x r(s, x))^2$ , and null in the quasistatic limit.

#### 4. WORK AND MICROSCOPIC HEAT

The microscopic total length is defined by  $q_N = \sum_i r_i$ , the position of the last particle. To connect it to the macroscopic space scale we have to divide it by  $N$ , so we define

$$\mathcal{L}_N(t) = \frac{q_N(t)}{N} = \frac{1}{N} \sum_{i=1}^N r_i(t). \quad (4.1)$$

The time evolution in the scale considered is given by

$$\mathcal{L}_N(t) - \mathcal{L}_N(0) = \int_0^t N p_N(s) ds. \quad (4.2)$$

If we start with the equilibrium distribution with length  $r_0$ , the law of large numbers guarantees that

$$\mathcal{L}_N(0) \xrightarrow{N \rightarrow \infty} r_0, \quad (4.3)$$

in probability.

By theorem 2.1, we also have the convergence at time  $t$ :

$$\mathcal{L}_N(t) \xrightarrow{N \rightarrow \infty} L(t) \xrightarrow{t \rightarrow \infty} r_1 = \mathfrak{r}(\tau_1), \quad (4.4)$$

where  $L(t)$  is defined by (3.2). Notice that in (4.2) while  $N p_N(s)$  fluctuates wildly as  $N \rightarrow \infty$ , its time integral is perfectly convergent and in fact converges to a deterministic quantity.

The microscopic work done up to time  $t$  by the force  $\tilde{\tau}$  is given by

$$\mathcal{W}_N(t) = \int_0^t \tilde{\tau}(s) d\mathcal{L}_N(s) = \int_0^t \tilde{\tau}(s) N p_N(s) ds \quad (4.5)$$

We adopt here the convention that positive work means energy increases in the system. Notice that  $\mathcal{W}_N(t)$  defines the actual microscopic work divided by  $N$ .

It is a standard exercise to show that, since  $\tilde{\tau}(t)$  and  $L(t)$  are smooth functions of  $t$ , by (4.4) it follows that

$$\mathcal{W}_N(t) \xrightarrow{N \rightarrow \infty} W(t) = \int_0^t \tilde{\tau}(s) dL(s) \quad (4.6)$$

given by (3.3).

Microscopically the energy of the system is defined by

$$E_N = \frac{1}{N} \sum_i \mathcal{E}_i \quad (4.7)$$

Energy evolves in time as

$$E_N(t) - E_N(0) = \mathcal{W}_N(t) + \mathcal{Q}_N(t) \quad (4.8)$$

$$\mathcal{Q}_N(t) = -\gamma \int_0^t N \sum_{i=1}^N (p_i^2(s) - T) ds + \sqrt{2\gamma\beta^{-1}} \sum_{i=1}^N \int_0^t p_i(s) dw_i(s)$$

where  $\mathcal{Q}_N$  is the energy exchanged with the heat bath, what we call *heat*.

The law of large numbers for the initial distribution gives

$$E_N(0) \xrightarrow{N \rightarrow \infty} U(\beta, \tau_0)$$

in probability. By the hydrodynamic limit, we expect that

$$E_N(t) \xrightarrow{N \rightarrow \infty} \int_0^1 U(\beta, \boldsymbol{\tau}(r(t, x))) dx \xrightarrow{t \rightarrow \infty} U(\beta, \tau_1). \quad (4.9)$$

This is not a consequence of Theorem 2.1, because the relative entropy does not control the convergence of the energy. In the harmonic case it can be proven by using similar argument as in [6] (in fact in this case  $f_N(t)$  is a gaussian distribution where we have control of any moments).

Assuming (4.9), we have that  $Q_N(t)$  converges, as  $N \rightarrow \infty$ , to the deterministic

$$Q(t) = \int_0^1 [U(\beta, \boldsymbol{\tau}(r(t, x))) - U(\beta, \tau_0)] dx - W(t) \quad (4.10)$$

and as  $t \rightarrow \infty$ :

$$Q = U(\beta, \tau_1) - U(\beta, \tau_0) - W, \quad (\text{first principle}). \quad (4.11)$$

Recalling that the free energy is equal to  $F = U - \beta^{-1}S$ , then we can compute the variation of the entropy  $S$  as

$$\beta^{-1}(S_1 - S_0) = -(F_1 - F_0) + W + Q \quad (4.12)$$

or also that

$$Q = \beta^{-1}(S_1 - S_0) - \gamma^{-1} \int_0^\infty dt \int_0^1 dx (\partial_x \boldsymbol{\tau}(r(t, x)))^2 \quad (4.13)$$

In the quasi static limit, we have seen that  $F_1 - F_0 = W$ , and consequently  $\beta Q = S_1 - S_0$ , in accord to what thermodynamics prescribe for quasistatic transformations.

**Remark 4.1.** Assume that the distribution of  $p_i(t)$  is best approximated by

$$e^{\frac{\beta}{N\gamma} \sum_i \partial_x \tau(t, i/N) p_i} g_{\tau(t, \cdot)}^N \prod_{i=1}^N dr_i dp_i$$

properly normalized. Then the average of  $p_i$  is  $\frac{1}{N\gamma} \partial_x \tau(t, i/N)$ , and (4.8) can be rewritten as

$$\begin{aligned} N\gamma \sum_{i=1}^N \left( \left( p_i(t) - \frac{1}{N\gamma} \partial_x \tau(t, i/N) \right)^2 - \beta^{-1} \right) \\ - \frac{1}{N\gamma} \sum_{i=1}^N \partial_x \tau(t, i/N)^2 + 2 \sum_{i=1}^N \partial_x \tau(t, i/N) p_i(t) \end{aligned}$$

Taking expectation, the first term is null (as well as the martingale not written here) while the last two terms converge to  $\gamma^{-1} \int_0^1 (\partial_x \tau(t, x))^2 dx$ . This is correct only in the harmonic case, i.e. the fluctuation inside the time integral are very important in order to get the changes in entropy  $S$ .

## 5. PROOF OF THE HYDRODYNAMIC LIMIT

Define the modified local Gibbs density

$$\tilde{g}_{\tau(t,\cdot)}^N = e^{\frac{\beta}{\gamma N} \sum_i \partial_x \tau(t, i/N) p_i} g_{\tau(t,\cdot)}^N Z_{N,t}^{-1} \quad (5.1)$$

where  $Z_{N,t}$  is a normalization factor. Then define the corresponding relative entropy

$$\tilde{H}_N(t) = \int f_t^N \log \left( \frac{f_t^N}{\tilde{g}_{\tau(t,\cdot)}^N} \right) d\mu_{0,\beta}^N \quad (5.2)$$

It is easy to see that  $\lim_{N \rightarrow \infty} N^{-1} (\tilde{H}_N(t) - H_N(t)) = 0$ .

Computing the time derivative

$$\frac{d}{dt} \tilde{H}_N(t) = \int f_t^N \mathcal{L}_N^{\tilde{\tau}(t)} \log f_t^N d\mu_{0,\beta}^N - \int f_t^N (\mathcal{L}_N^{\tilde{\tau}(t)} + \partial_t) \log \tilde{g}_{\tau(t,\cdot)}^N d\mu_{0,\beta}^N \quad (5.3)$$

Using the inequality

$$f_t^N \mathcal{L}_N^{\tilde{\tau}(t)} \log f_t^N \leq \mathcal{L}_N^{\tilde{\tau}(t)} f_t^N$$

and since  $d\mu_{0,\beta}^N$  is stationary for  $\mathcal{L}_N^0$ , we have

$$\int f_t^N \mathcal{L}_N^{\tilde{\tau}(t)} \log f_t^N d\mu_{0,\beta}^N \leq N^2 \tau \int \partial_{p_N} f_t^N d\mu_{0,\beta}^N = N^2 \tau \beta \int p_N f_t^N d\mu_{0,\beta}^N$$

By explicit calculation

$$\begin{aligned} \mathcal{L}_N^{\tilde{\tau}(t)} \log \tilde{g}_{\tau(t,\cdot)}^N &= -\beta N^2 \sum_i \tau(i/N, t) (p_i - p_{i-1}) \\ &+ \beta \gamma^{-1} N \sum_i \partial_x \tau(t, i/N) (V'(r_{i+1}) - V'(r_i)) - N \beta \sum_i \partial_x \tau(t, i/N) p_i \\ &= N^2 \tau \beta p_N - \beta \gamma^{-1} \sum_i \partial_x^2 \tau(t, i/N) V'(r_i) + o(N) \end{aligned}$$

and

$$\partial_t \log \tilde{g}_{\tau(t,\cdot)}^N = -\beta \sum_i \partial_t \tau(t, i/N) (r_i - r(t, i/N)) + O(1).$$

Then we can estimate

$$\begin{aligned} \frac{d}{dt} \tilde{H}_N(t) &\leq \beta \int \sum_i [\gamma^{-1} \partial_x^2 \tau(t, i/N) V'(r_i) + \partial_t \tau(t, i/N) (r_i - r(t, i/N))] f_t^N d\mu_{0,\beta}^N \\ &\quad + o(N) \end{aligned}$$

and the rest of the proof follows by the standard arguments of the relative entropy method (cf. [4, 7, 3, 8]).

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CEREMADE, UMR CNRS 7534, UNIVERSITÉ PARIS-DAUPHINE, 75775 PARIS-CEDEX  
16, FRANCE, [OLLA@CEREMADE.DAUPHINE.FR](mailto:OLLA@CEREMADE.DAUPHINE.FR)