A Thermalization-Fluctuation Relation near Equilibrium

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We mathematize the physical intuition that a macroscopic system near equilibrium that does not thermalize as easily will show greater fluctuations in an experiment.

I. INTRODUCTION

Let us be given a macroscopic system and we would like to measure in the laboratory the fluctuations of the system. E.g. let us have a colloidal suspension, and we measure the fluctuations in a constituent particle's position $x(t)$ by tracking the trajectory of a sample constituent particle and then computing $\overline{\Delta x^2} = \int_0^{T_{\rm ex}} (x(t) - \overline{x}^2)$. $\overline{O}$ indicates time-average over the course of the experiment. Let us assume that the duration of the experiment $T_{\rm ex}$ is much much greater than all the microscopic time-scales. If the system is at equilibrium throughout the duration of the experiment, then we apply the Ergodic hypothesis to assert that $\overline{O} = \langle O \rangle \equiv \int_\Omega O e^{-H} / \int_\Omega e^{-H}$. Ω denotes the phase space, and the observable O and the Hamiltonian H are functions of the phase space variables $\{x_i, p_i\}$. i is an index for the constituent particles. It is understood that $\{x_i, p_i\}$ is a place-holder for all the degrees of freedom of all the constituent particles. Generically in equilibrium, we expect that the equilibrium "thermal" fluctuations in position $\overline{\Delta x}$ to be greater if temperature is raised in the experiment.

We can easily imagine situations where the above equilibrium picture does not fully apply. A big arena is biology where many processes are not at equilibrium. Nonliving examples may be experiments away from equilibrium in say classical or quantum fluids, or cold atomic gases. We aim to show in this article that for such non-equilibrium situations, if a macroscopic system is inefficient at thermalization – approaching thermal equilibrium when away from equilibrium through its internal dynamics –, then it will exhibit greater fluctuations in general. This is intuitive : imagine an extreme example where there is a "non-equilibrium kick" during an experiment, in an already equilibrated system and some observable O moves very far away from its equilibrium average $\langle O \rangle$. Very far way is quantified by how far away is O from $\langle O \rangle$ in units of equilibrium fluctuations, $(O - \langle O \rangle)/\sqrt{\langle \Delta O^2 \rangle}$. After the "non-equilibrium kick event", O again moves in time towards its equilibrium in some manner during (re-)thermalization. Now it is obvious that if this movement towards equilibrium is slow, then the time average of that observable $\overline{O}$ over $T_{\rm ex}$ will be greater than if this movement is fast. We will mathematize this picture and the notion of the "non-equilibrium kick event" will be used in an integral way in order to do this.

We first show in Sec. II, the relation between fluctuations and thermalization in the somewhat fictitious quench-type scenario when only one non-equilibrium kick event occurs during the whole duration of the experiment. This will allow us to associate a time-scale with thermalization dynamics. Then in Sec. III we generalize to the more realistic scenario with many kick events occurring during the experiment. We will still simplify for tractability that the many kick events happen in a Poissonian fashion, which is not fully realistic.

II. ONE KICK EVENT

At equilibrium, the probability density of a macroscopic system in the vicinity of a phase space point $\{x_i, p_i\}$ is given by the Boltzmann distribution $P_{\rm eq}(\{x_i, p_i\}) = e^{-H(\{x_i,p_i\})/kT}/Z$ with the partition sum $Z = \int_\Omega d\{x_i, p_i\}\ e^{-H(\{x_i,p_i\})/kT}$. Therefore $\int_\Omega d\{x_i, p_i\}\ P_{\rm eq}(\{x_i, p_i\}) = 1$. The equilibrium value of some observable O is $\langle O \rangle_{\rm eq} = \int_\Omega d\{x_i, p_i\}\ P_{\rm eq}(\{x_i, p_i\})\ O(\{x_i, p_i\})$ and its equilibrium thermal fluctuations is $\langle \Delta O^2 \rangle_{\rm eq} = \int_\Omega d\{x_i, p_i\}\ P_{\rm eq}(\{x_i, p_i\})\ (O(\{x_i, p_i\}) - \langle O \rangle_{\rm eq})^2$. If the system remains at equilibrium throughout the experiment, then we would measure for that observable O its average and fluctuations to be $\overline{O} = \langle O \rangle_{\rm eq}$ and $\overline{\Delta O^2} = \langle \Delta O^2 \rangle_{\rm eq}$.

Let there be a non-equilibrium kick event at the start of the experiment $t = 0$ such that the non-equilibrium distribution of the phase space variables is deviated away from equilibrium distribution $P_{\rm eq}(\{x_i, p_i\})$ to $P_{\rm neq}(\{x_i, p_i\}; t = 0)$. $P_{\rm neq}$ evolves with time t as the system approaches equilibrium during thermalization. Now we make an *assumption* regarding the internal dynamics that leads to thermalization. We make this assumption to give a (mathematical) idealization to thermalization. The approach to equilibrium is assumed to be of the following form

$$\frac{dP_{\rm neq}(\{x_i, p_i\}; t)}{dt} = -\frac{P_{\rm neq}(\{x_i, p_i\}; t) - P_{\rm eq}(\{x_i, p_i\})}{T_{\rm th}} \tag{1}$$

$T_{\rm th}$ is a time-scale that captures the scale of the assumed thermalization dynamics. This dynamics can be called "linear response" since the system responds to the non-equilibrium kick in a fashion that is linear in deviation from equilibrium. It is straightforward to write down the closed-form solution of Eq. 1 as

$$P_{\rm neq}(t) = P_{\rm eq} + (P_{\rm neq}(0) - P_{\rm eq})\, e^{-t/T_{\rm th}} \tag{2}$$

In the above equation and in the following, we suppress the phase-space argument $\{x_i, p_i\}$ for brevity when there is no confusion.

Given this dynamics, we may write the following non-equilibrium average $\langle O\rangle_{\rm neq}(t) = \int_\Omega P_{\rm neq}(t)\, O$ and non-equilibrium fluctuations $\langle \Delta O^2\rangle_{\rm neq}(t) = \int_\Omega P_{\rm neq}(t)\, (O - \langle O\rangle_{\rm neq}(t))^2$. In writing this, we have made the *critical assumption* of "quasi-ergodicity" where the macroscopic system is visiting the phase space in a quasi-ergodic way so that *some* ensemble distribution $P_{\rm neq}$ can be applied to describe the non-equilibrium situation for some time window, and thus calculate non-equilibrium average and fluctuations. We posit that this assumption might be safely applied when the thermalization time-scale $T_{\rm th}$ is much bigger than the microscopic time-scales of the system. Thus we have

$$\langle O\rangle_{\rm neq}(t) = \langle O\rangle_{\rm eq} + (\langle O\rangle_{\rm neq}(0) - \langle O\rangle_{\rm eq}) e^{-t/T_{\rm th}} \tag{3a}$$

$$\begin{aligned}\langle \Delta O^2\rangle_{\rm neq}(t) &= \langle \Delta O^2\rangle_{\rm eq}(1 - e^{-t/T_{\rm th}}) \\ &+ \langle \Delta O^2\rangle_{\rm neq}(0)\, e^{-t/T_{\rm th}} \\ &+ (\langle O\rangle_{\rm neq}(0) - \langle O\rangle_{\rm eq})^2 e^{-t/T_{\rm th}}(1 - e^{-t/T_{\rm th}})\end{aligned} \tag{3b}$$

As $t \to \infty$, $\langle O\rangle_{\rm neq}(t) \to \langle O\rangle_{\rm eq}$ and $\langle \Delta O^2\rangle_{\rm neq}(t) \to \langle \Delta O^2\rangle_{\rm eq}$ signaling the (exponential) completion of thermalization.

The quasi-ergodicity assumption will now allow us to replace the instantaneous values of an observable $O(t)$ by its (non-equilibrium) ensemble averages appropriate to the right time window *while doing the experimental time average*. If we label the quasi-ergodic time window in which *some* ensemble distribution can be applied to calculate averages as $T_{\rm qe}$ and the (biggest) microscopic time-scale as $T_{\rm mic}$, then the arguments below apply when $T_{\rm mic} \ll T_{\rm qe} \ll T_{\rm th}$ and $T_{\rm mic} \ll T_{\rm qe} \ll T_{\rm ex}$.

The average that gets measured in the experiment would be

$$\begin{aligned}\overline{O} &= \frac{1}{T_{\rm ex}}\int_0^{T_{\rm ex}} dt\, O(t) \\ &\to \text{under quasi-ergodicity} \\ &\cong \frac{1}{T_{\rm ex}}\int_0^{T_{\rm ex}} dt\, \langle O\rangle_{\rm neq}(t) \\ &= \langle O\rangle_{\rm eq} + (\langle O\rangle_{\rm neq}(0) - \langle O\rangle_{\rm eq})\frac{T_{\rm th}}{T_{\rm ex}}(1 - e^{-T_{\rm ex}/T_{\rm th}}) \\ &\to T_{\rm ex} \gg T_{\rm th} \\ &\approx \langle O\rangle_{\rm eq} + \frac{T_{\rm th}}{T_{\rm ex}}\langle O\rangle_{\rm neq}(0)\end{aligned} \tag{4}$$

The fluctuations that get measured in the experiment would be

$$\begin{aligned}\overline{\Delta O^2} &= \frac{1}{T_{\rm ex}}\int_0^{T_{\rm ex}} dt\, (O(t) - \overline{O})^2 \\ &\to \text{under quasi-ergodicity} \\ &\cong \frac{1}{T_{\rm ex}}\int_0^{T_{\rm ex}} dt\, \langle \Delta O^2\rangle_{\rm neq}(t) \\ &= \langle \Delta O^2\rangle_{\rm eq}\left(1 - \frac{T_{\rm th}}{T_{\rm ex}}(1 - e^{-T_{\rm ex}/T_{\rm th}})\right) \\ &\quad + \langle \Delta O^2\rangle_{\rm neq}(0)\frac{T_{\rm th}}{T_{\rm ex}}(1 - e^{-T_{\rm ex}/T_{\rm th}}) \\ &\quad + (\langle O\rangle_{\rm neq}(0) - \langle O\rangle_{\rm eq})^2\frac{T_{\rm th}}{T_{\rm ex}}\times \\ &\quad \left((1 - e^{-T_{\rm ex}/T_{\rm th}}) - \frac{1}{2}(1 - e^{-2T_{\rm ex}/T_{\rm th}})\right) \\ &\to T_{\rm ex} \gg T_{\rm th} \\ &= \langle \Delta O^2\rangle_{\rm eq} + \frac{T_{\rm th}}{T_{\rm ex}}\left(\langle \Delta O^2\rangle_{\rm neq}(0) + \frac{1}{2}(\langle O\rangle_{\rm neq}(0) - \langle O\rangle_{\rm eq})^2\right)\end{aligned} \tag{5}$$

The above equation already contains our basic intuition, i.e. if $T_{\rm th}$ is comparable to $T_{\rm ex}$ then the measured fluctuations $\overline{\Delta O^2}$ will be greater than equilibrium fluctuations $\langle \Delta O^2\rangle_{\rm eq}$ and will be bigger in magnitude for larger $\frac{T_{\rm th}}{T_{\rm ex}}$. In the following section, we will generalize to a more realistic scenario with many kick events.

III. MANY KICK EVENTS

IV. REMARKS

- Discuss non-equilibrium kick events in physical terms.
- Treat the kick events as a Poissonian process for mathematical tractability.
- Treatment of kick events as a Poissonian process will introduce a new time scale associated with the average rate of these kicks (which is physically well-motivated as well).