Disruption of equilibrium due to lack of change

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A sudden change in the macroscopic parameters of a system will cause it to depart from equilibrium. In this paper we study how a lack of a sudden change can also disrupt equilibrium. Non-events can provide information pertaining the microstates of the system, essentially playing the role of a passive Maxwell demon and allowing Bayesian updates to the equilibrium distribution. We argue that this effect is present and consequential in almost every physical system, but is ignored in the standard formulation of equilibrium statistical mechanics. As a case study, we investigate the local and global thermodynamic properties of an ideal gas placed in a fragile container that does not burst. This non-event disrupts equilibrium and allows work extraction from the system. It also leads to corrections to the heat capacity of the gas.

Intuition suggests that if the macroscopic parameters of a non-equilibrium system is kept constant, the system will monotonically approach thermodynamic equilibrium [1]. This need not be the case. Here we study the thermodynamic properties of a simple system in which the absence of macroscopic changes constitute a continuous stream of information, which allows one to update the equilibrium description of the system to a non-equilibrium one.

Consider for example, a gas sampled from a thermal bath, in equilibrium, with temperature $T$ and placed in an isolated container such that neither the gas nor the container undergoes an observable macroscopic change during $\tau$. At this stage, the fact that the container has not burst or deformed or leaked so far, informs us that no molecule above a critical energy has yet hit the walls of the container. Since the original Boltzmann distribution actually included such high energies, the statistical description of the gas better be updated near the walls (but not in the bulk). In this example, a non-event informs us of a position and time dependent energy distribution. The lack of an equilibrium-disrupting event is leading to a departure from equilibrium.

In this paper we investigate how the thermodynamic properties of an ideal gas must be dynamically updated in light of the observation that its container remains unchanged. Of course, similar arguments can be made more generally for other macroscopic non-events: Lack of chemical and nuclear reactions, evaporation and condensation, adsorption and desorption, dissolution and precipitation all occur when system constituents are within a specific energy window, and typically with higher likelihood near certain locations. Any system that has a potential to undergo such processes will start revealing its microstates every moment this potential is not realized. The longer nothing happens, the further away the system departs from its original state of equilibrium.

This odd conclusion does not stem from the semantics of thermodynamic equilibrium [2, 3]. It has concrete physical consequences. Local information can often be used to extract work [4–9], and in our particular case too, the temperature variations as inferred by the non-event, as well as the evolving difference in global temperatures between the container and the original bath, can be used to generate work, $W(\tau)$. Interestingly, based off of the duration of the non-event, we can also make retrodictions and predictions (similar to [10, 11]) about the past and the future of the temperature distribution in the fragile container. Furthermore, the heat capacity $C_\nu(T) = dE/dT$ of the gas must be modified in light of the non-event as a function of time.

Of course, none of this violates any fundamental laws of physics. A system can be driven out of equilibrium by performing measurements whose outcome restricts the space of microstates available to the system [6, 7, 12–15], thereby turning the equilibrium state into a fluctuation state [16, 19]. Such deviations from equilibrium are quantified by fluctuation theorems [20, 29], and have interesting consequences such as second law violation. The study of the fluctuations of a system and the information contained in them forms the subject of stochastic thermodynamics [40, 50]. In our case study, the non-event is providing us with a continuous stream of information, essentially playing the role of a passive Maxwell’s demon.
Model. Suppose that $N$ ideal-gas particles are sampled from a heat bath of temperature $T$ and placed in an isolated cubical container of size $L$. Suppose further that the container walls undergo a macroscopically visible change when hit by a particle whose normal velocity component is greater than a critical velocity, $v_c$. We refer to this event as a detection.

Let $\tau$ be a time period of no detection and $E(\vec{r}, t)$ be the energy in an infinitesimal volume around $\vec{r}$ at time $t$. We use the Bayes’ theorem to infer the probability that the system exhibits an energy distribution $E(\vec{r}, t)$,

$$P(E(\vec{r}, t) | \tau) = \frac{P(\tau | E(\vec{r}, t)) P_a(E(\vec{r}))}{P(\tau)} \quad (1)$$

Here, $P(\tau) = \int P(\tau | E(\vec{r}, t)) P_a(E(\vec{r})) D\{E(\vec{r}, t)\}$ is a functional integral over all possible $E(\vec{r}, t)$, and the a-priori probability distribution $P_a(E)$ is the many-particle Maxwell-Boltzmann distribution. The a-priori probability that a single particle in 1D has energy $E$ and is at a point $x$ is

$$P_a(E(x)) dE dx = \exp(-E/kT)(dx/L) dE/(kT \sqrt{E})$$

whereas for $N$ particles,

$$P_a(E(x)) = \int \prod_{i=1}^{N} dE_i P_a(E_i, x) \delta(E - \sum_{i=1}^{N} E_i). \quad (2)$$

In a 1D container, a detection can occur at either at 0 or $L$. For this to happen before some time $\tau$, there must be a particle with a velocity greater than $v_c$ and that particle should reach one of the walls before time $\tau$. Therefore, the conditional probability of no detection before $\tau$ given the energies and positions of the $N$ particles is,

$$P(\tau \{ E_i, x_i \}, t) = \prod_{i=1}^{N} \theta(E_i - E_c) \eta(E_i, x_i) \quad (3)$$

$$\eta(E_i, x_i) = \frac{1}{2} \left[ \theta(t - \tau - x_i \sqrt{\frac{2mE_i}{kT}}) + \theta(t - \tau - (L - x_i) \sqrt{\frac{2mE_i}{kT}}) \right]$$

where $\theta$ is the unit step function, and $E_c = mv_c^2/2$. The two step functions in time are for two possible velocities, $\pm v_c$ that would lead to detection at $x = L$ and $x = 0$. $E(x, t)$ can easily be obtained from particle energies and positions by binning. We can then marginalize this by taking a functional integral over all $E(x, t)$,

$$P(\tau) = \int D\{E(x, t)\} \int dx P(\tau | E(x, t)) P_a(E(x)) \quad (4)$$

2D and 3D analogs of the above equations can be obtained by the same procedure.

Variations in local mean energy. The probability distributions given by eqns 2,3 and 4 are then plugged into eqn 1 to yield an energy distribution $P(E(\vec{r}, t) | \tau)$ at every location $\vec{r}$. In Fig.1 and Fig.2 we use this distribution to plot the local mean energy $\langle E(\vec{r}) \rangle$ for various values of $\tau$. We can interpret this as the temperature variations within the container, as local mean energy is a convenient proxy for local temperature [3][5].

We evaluate the integrals in eqns 2,3 and their respective 2D analogs by Monte-Carlo integration. To do so, we first generate $10^6$ sets of initial positions and velocities with the a priori distributions for $N$ particles. We then select the configurations that lead to detection times greater than $\tau$ and calculate the local mean energy of those configurations.

In the one dimensional system, we observe a higher energy density near the detecting end-points for small $\tau$, indicating that high energy particles are close to the end-points and moving towards them. As $\tau$ increases, the high energy particles must be closer to the center, hence a single peak appears near center. For $\tau > (L/2v_c)$ (where $L/2v_c = 0.25$ in Fig.1), the time it takes for a critical velocity particle to go from the center to any one end, we see that two high energy peaks appear. This is because these values of $\tau$ can only arise when all the high velocity particles are close to one of end-points and are moving in a direction opposite to the closest end-point.

In 2D, we only observe events where $\tau$ is much smaller than $(L/2v_c)$ since they are already very rare (see Fig.3 for the distribution of detection times). In this regime...
we infer a local mean energy distribution consisting of a combination of the high and low energy peaks similar to the \( \tau = 0.1 \) curve in Fig.4. Videos of the time dependent energy distribution in 1D and 2D are included as supplementary material.

Fig.3 shows how non-detection events get rarer as \( \tau \) increases. We see that non-detection at greater \( \tau \) is less likely if the initial temperature of the particles is higher, as we would intuitively expect.

Since we are considering non-interacting particles, we can exactly determine the past and future trajectories of all particles given their present state. This allows us to evaluate the probability distribution of the local mean energy at all times from the distribution at any one point of time. This means that we can infer the initial state of a system in which we know that no detection occurred, and predict its future. Fig.2 also shows the retrodicted and predicted local mean energy. We see that even if the container walls were to lose their potential to respond to high energy particles at some time, the local temperature variations would persist afterwards. This is important in the context of work extraction, which we will study in more detail in the next section.

**Updating the heat capacity.** As the particles bounce off the container walls, their direction of motion changes, but their speed remains constant. This means that a high velocity particle, if any, must already be present in the initial state of the system. This puts an upper limit on \( \tau \). The maximum time required for the first detection, if any, is \( \tau_{\text{max}} = L/v_c \), which occurs when the high velocity particle starts at one edge of the box and is detected at the opposite edge. If no particles are detected before \( \tau_{\text{max}} \), one can infer that there exist no particles with velocity greater than \( v_c \) anywhere in the box. This simple inference will have significant thermodynamic outcomes.

For an ideal gas with total energy \( E \), the global temperature is given by

\[
T = (\partial S/\partial E)^{-1} = (k_B \partial \log(\Omega)/\partial E)^{-1}.
\]

where the initial volume of allowed microstates is

\[
\Omega(t = 0) = L^{3N} \int d^3v_1 ... d^3v_N \delta[(m/2)(v_1^2 + ... + v_N^2) - E].
\]

This integral is the surface area of a 3\( N \) dimensional sphere. For \( t > \tau_{\text{max}} \), since there can be no velocity component greater than \( v_c \), the volume of allowed microstates becomes

\[
\Omega(t) = L^{3N} \int \delta[(m/2)(v_1^2 + ... + v_N^2) - E] 
\theta(v_1 - v_c)... \theta(v_N - v_c) \, d^3v_1 ... d^3v_N.
\]

This integral is the surface area of intersection of a 3\( N \) dimensional sphere with a 3\( N \) dimensional cube. The radius of the sphere depends on the total energy and the side of the cube depends on the critical velocity. Analytical formulas for this surface area can be found in [38].

Changing the total energy \( (E) \) of the particles inside the box corresponds to changing the radius of the 3\( N \)–sphere. The volume of allowed microstates, \( \Omega(E) \), is not differentiable at points where the sphere touches various hyperplanes of intersection of the faces of the cube. This causes the temperature to be a discontinuous func-
tion of energy, as shown in Fig. 4. For example, for the special case of a single particle (where the velocity space is three dimensional), these singularities occur when the sphere touches the faces, edges and vertices of the cube (see Fig. 4(a)).

At higher dimensions (i.e., for systems with larger number of particles) there will be a larger number of such singularities, as we move up the energy scale, i.e., whenever the hypersphere crosses hyper-faces, lesser dimensional hyper-faces, faces, edges and finally the corners of the hypercube. The heat capacity $C_v$, which is the derivative of energy with respect to temperature, has singularities at these points.

When the total energy is very small, we do not see any deviation from the ideal gas law. This is because even if all the energy were due to one velocity component of a single particle, the velocity would not exceed $v_c$. When the total energy exceeds a critical value, the temperature of the system becomes negative. This indicates that the system is in a population-inverted state and confirms that it must be out of equilibrium [39][41]. This transition occurs when the high total energy along with the constraint, $v < v_c$ for every particle causes there to be more high energy particles than low energy particles. Finally, when the energy is so large that there can be no particles with $v < v_c$, the number of microstates becomes exactly zero, implying that such an event is impossible.

We evaluate the integral in Eq. (6) by Monte Carlo integration by generating $10^9$ sets of random $3N$-dimensional vectors with norm $\sqrt{2m/E}$ and finding the fraction of sets where no component of the vector exceeds $v_c$. We then multiply this by the surface area of the entire sphere to get the area of intersection.

Work extraction. We now proceed to finding the maximum possible work that can be extracted from the system using the inferences derived from the non-event. The maximum work that can be extracted from the system by coupling it to the heat bath from which the particles were sampled is equal to the free energy difference between the inferred state and the equilibrium state.

Using $\Delta F = \Delta U - T \Delta S$, and the equations for the entropy of an ideal gas in $d$-dimensions,

$$\Delta F = \int dx \left[ (U(x) - \bar{U}) - \bar{U} \log \left( \frac{U(x)}{\bar{U}} \right) \right]$$

(7)

where $\bar{U} = (d/2)Nk_BT$ and $U(x)$ is the inferred mean energy, which is plotted in Fig. 2. We have also assumed constant particle density in space.

Fig. 3 shows the variation of $\Delta F$ with bath temperature $T$ and non-detection time $\tau$. We observe that as inferred state becomes rarer, we can extract more work from it. As $\tau \to 0$ at a fixed temperature, non-detection is more common and system has not yet moved far from equilibrium. Therefore the free energy differences decrease to zero. When $\tau = 0$, we have no information about the system, hence the free energy differences are exactly zero.

Discussion. Any finite ensemble is expected to fluctuate about its equilibrium state [16][19]. Then the non-detection of macroscopic changes in the finite system informs us of the degree of the departure from equilibrium as much as the detection of such changes.

The thermodynamic effects considered in this article all occur due to the finite number of particles. As the number of particles increases, the probability of non-detection events decreases. Many other finite size effects such as second law violations also vanish in the thermodynamic limit [20][25][27][29].

As we see in Fig 2, the local energy distribution has features that depend on the shape of the container. This effect may also be extended to quantum mechanics, where confinement is already known to play a role. In particular, the effect of finite size and confinement geometry on quantum gases and their phase transitions has been studied [12][30].

Here we used the Bayes theorem to find the local mean energy of the system. Bayesian methods and the general relation between thermodynamics and information theory were developed in [17][50]. However, the use Bayesian methods to determine thermodynamic quantities can lead to conceptual problems [51].

While we only considered the local mean energy in the article, the problem of using it to define a local temperature has been a subject of considerable debate. Conventionally, local temperature is defined either through a mapping to the ensemble average of energy, or as the temperature measured by a model thermometer after coupling for a sufficiently long time. For further discussion
on this issue, see [12, 13, 37, 52, 54].

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