4.5: Temperature as a Control Variable for Energy (Canonical Ensemble)

Note distinction!

$\mathcal{P}(\mathbf{x})$ is the probability of falling in a particular microstate x. This happens to be a function only of the energy of the microstate, whence this function is often called $\mathcal{P}(H(\mathrm{x}))$. (For a continuous system, $\mathcal{P}(\mathbf{x})$ corresponds to $p(\Gamma)d\Gamma$. . . the probability of the system falling in some phase space point within the volume $d\Gamma$ about point Γ.)

P(H) is the probability of having a particular energy. It is equal to $\mathcal{P}(H(\Gamma))\Omega(H)$. ($\Omega(H)$: the number of microstates with energy H.)

Temperature as persuasion.

Temperature as an energy control parameter.

Analogy: "The Jim Smith effect." A man asks a statistician "What is the probability that a man named Milton Abramowitz will win the lottery?" The questioner, whose name is Milton Abramowitz, is disappointed when the statistician's answer is so tiny. So he tries again: "What is the probability that a man named Jim Smith will win the lottery?" The statistician replies with a number that is still small, but not quite so small as the first reply. In response, the man changes his name to Jim Smith.[1]

Because $P(H(\Gamma))$ decreases rapidly with H, and $\Omega(H)$ increases rapidly with H, we expect $P(H)$ to be pretty sharply peaked near some $\langle H\rangle$ (recall the arguments of section 2.7.3). We also expect this peak to become sharper and sharper as the system becomes larger and larger (approaching "the thermodynamic limit").

Even at high temperature, the most probable microstate is the ground state. However the most probable energy increases with temperature.

In the canonical ensemble (where all microstates are "accessible") the microstate most likely to be occupied is the ground state, and this is true at any positive temperature, no matter how high. The ground state energy is not the most probable energy, nor is the ground state typical, yet the ground state is the most probable microstate. In specific, even at a temperature of 1 000 000 K, a sample of helium is more likely to be in a particular crystalline microstate than in any particular plasma microstate. However, there are so many more plasma than crystalline microstates that (in the thermodynamic limit) the sample occupies a plasma macrostate with probability 1.

Economic analogy for temperature as an energy control parameter: strict regulation versus incentives. "Market-based approaches work more efficiently than clumsy command-and-control techniques"—Alan S. Blinder, "Needed: Planet Insurance", New York Times, 22 October 1997, page A23.

4.1 Probability of microstate vs. probability of energy

> $\mathcal{P}(H)$ is the probability of being in a particular microstate with energy H, whereas $\mathcal{P}(H)dH$ is the probability of being in any microstate whose energy falls within the range H to $H + dH$. The number of microstates with energy from H to $H + dH$ is $\Omega(H)dH$. Following the arguments of section 2.7.1 ("Rapidly increasing character of the $\Omega(H)$ function"), assume that $\Omega(H) = cH^\nu$. (For a classical monatomic ideal gas of N atoms, $\nu = (3/2)N$.) Show that
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> $$Z(T,V,N)=c(k_BT)^{\nu+1}\Gamma(\nu+1). \tag{4.5.1}$$
>
> Does Z have the correct dimensions? Show that
>
> $$\mathcal{P}(H)=\frac{e^{-H/k_BT}}{c(k_BT)^{\nu+1}\Gamma(\nu+1)} \quad \text{while} \quad P(H)=\frac{H^\nu e^{-H/k_BT}}{(k_BT)^{\nu+1}\Gamma(\nu+1)}. \tag{4.5.2}$$
>
> Sketch $\Omega(H)$, $\mathcal{P}(H)$, and $P(H)$.

[1]Only the most ardent students of American history know that Jim Smith signed the Declaration of Independence.