# Lanford on StatMech, Jan 22 2010

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10:10 AM

Canonical Ensemble: $N$ particles in a box $\Lambda$, a given temperature $T$. $\left(\beta = \frac{1}{kT}\right)$

Introduce the "canonical" probability measure:

$$\mu^{(c)}_{\beta,N,\Lambda} = \rho^{(c)}_{\beta,N,\Lambda}(x)\,dx,$$

$\left( x \in (\Lambda \times \mathbb{R}^d)^N \right.$ (momenta)

i.e. $x = \vec{q}_1, \vec{p}_1 \ldots \vec{q}_N, \vec{p}_N$

$dx = \frac{1}{N!} dq_1 \wedge dp_1 \ldots$

$\left. \right)$ [The $p$ integrals are easy to do explicitly]

where $\rho = \frac{1}{Z} \exp(-\beta H(x))$

where $Z$ is chosen to make the total measure be 1.

The equilibrium value of "any" function $f$ on phase space is $\bar{f} := \langle f \rangle_{\beta,N,\Lambda} = \int f(x)\rho(x)\,dx$

E.g., $E = \bar{H} = \dfrac{\int H(x) e^{-\beta H}\,dx}{\int e^{-\beta H}\,dx}$

(should be a function only of $\beta$ & $\frac{V(\Lambda)}{N}$, at least at the high-$N$ limit)

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The entropy: $S = k \int \rho(x)(-\log \rho(x))\,dx$ (Boltzman-Gibbs)

$$= k\langle -\log \rho \rangle \underset{\substack{\uparrow \\ \text{arithmetic, at } k=1}}{=} \beta E + \log Z =$$

So $\log Z = -\beta(E - TS)$

or $\frac{1}{N} \log Z = -\beta f$, where $f$ is the specific Helmholtz free energy.

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Also,

$\langle H \rangle = -\frac{d}{d\beta} \log Z = \ldots$

So $\epsilon = -\frac{d}{d\beta}(-\beta f)$, a thermodynamic identity.

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Also can derive $dE = TdS - \delta W$, where $\delta W$ is computed by averaging a pointwise mechanical quantity.

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$$\frac{d^2}{d\beta^2} \log Z \overset{\text{by computation}}{=} = \langle (H - \langle H \rangle)^2 \rangle \geq 0$$

So $\log(Z)$ is convex as a function of $\beta$, so $-\beta f$ is convex (in $\beta$) — a thermo-fact.

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Other prescriptions for deriving thermodynamics from microscopic physics:

The "grand canonical ensemble": Fix the box, have energy fluctuate with exponential decay, and same for particle number:

phase space $= \coprod_N (\Lambda \times \mathbb{R}^d)^N =: \mathcal{X}_\Lambda$, with measure proportional to

$$e^{-\beta H(x)} e^{+\beta\mu N} dx_N$$

where $\mu$ is "the chemical potential" $\frac{1}{N}(E - TS + pV)$

($dx :=$ the "a-priori measure", whose restriction to $\mathcal{X}_n$ is $dx_n$)