* **Administration:**

1.) Exam 1 will be Monday Oct. 18
(be there by 10:10 sharp.)

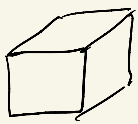
* Will cover material from the units on
  ① Classical TD
  ② Stat Mech Fundamentals
  } HW's 1-4

* We only have ~ 70 minutes, so it will be more like a "long quiz"

2) HW 4 will be posted in the next couple days with a due date of Thurs. Oct 14 to make allowances for the QM exam on Oct 13.

Recap from L11

* Ideal gas



$V = L^3$

$$Z_N = \sum_\alpha e^{-\beta E_\alpha} = \sum_{\vec{n}_1 \vec{n}_2 \cdots \vec{n}_N} e^{-\beta(\varepsilon_{\vec{n}_1} + \varepsilon_{\vec{n}_2} + \cdots + \varepsilon_{\vec{n}_N})}$$

where $\varepsilon_{\vec{n}} = \frac{\hbar^2}{2m}\frac{\pi^2}{L^2}(n_x^2 + n_y^2 + n_z^2)$ (Solving $-\frac{\hbar^2}{2m}\nabla^2\psi = \varepsilon_{\vec{n}}\psi$ w/ hard wall BC's)

$$Z_N = (Z_1)^N = (Z_{1,x})^{3N}$$

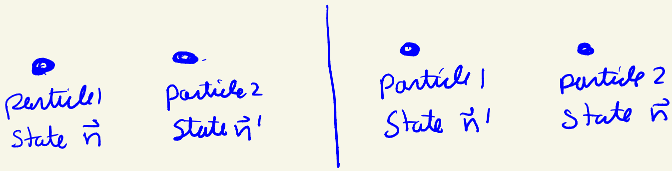
$$Z_{1,x} = \sum_{n_x} e^{-\beta \frac{\hbar^2\pi^2}{2mL^2} n_x^2} \longrightarrow \frac{L}{2\pi\hbar}\int_{-\infty}^{\infty} dp_x \, e^{-\beta \frac{p_x^2}{2m}}$$

$$\boxed{Z_N \equiv \left(\frac{L}{\ell_Q}\right)^{3N} = \left(\frac{V}{\ell_Q^3}\right)^N \qquad \ell_Q \equiv \sqrt{\frac{2\pi\hbar^2}{k_B T m}}}$$

"Thermal de-Broglie Wavelength"

expect QM effects to dominate when particle spacing $\lesssim \ell_Q$

* So far, we've not worried about the identity of the N particles (i.e., we know from QM if they are identical, then they are indistinguishable, so that



are not distinct states

* Therefore, we expect for identical particles our Z_N above runs afoul of this.

Ad-Hoc Correction (valid for dilute + high T where $\langle n_{\vec{k}} \rangle \ll 1$)

$$\boxed{Z_N^{\text{corrected}} = \frac{1}{N!}\left(\frac{V}{\ell_Q^3}\right)^N}$$

cf. our discussion of Gibbs paradox + entropy of mixing

Ensembles in classical Phase Space

* all we've done so far has kind of assumed discrete QM microstates.

* But SM was developed well before QM came into being.

* How can we develop SM working entirely in classical phase space?

* Microstate $(q_1 \ldots q_{3N}, p_1 \ldots p_{3N})$ at some time t evolves via

$$\left.\begin{aligned} \dot{q}_i &= \frac{\partial \mathcal{H}}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial \mathcal{H}}{\partial q_i} \end{aligned}\right\}$$

* Too hard to solve $\sim 10^{23}$ ODE's
* impossible to specify 10^{23} initial conditions

* as before, we expect an enormous # of microstates (points in 6N-dim phase space) to be consistent w/a given macrostate.

* Imagine $\mathcal{N} \to \infty$ mental copies of these microstates distributed as a swarm of points in phase space.

let $\boxed{\rho(q,p;t)\, d^3q_1 \ldots d^3q_N\, d^3p_1 \ldots d^3p_N = \text{\# of points in volume about } (p,q)}$

$\Rightarrow \rho(p,q;t)\, d\Gamma = \dfrac{d\mathcal{N}(p,q;t)}{\mathcal{N}}$ $\quad (d\Gamma \equiv d^{3N}p\, d^{3N}q)$

# of points in $d\Gamma$ about $\{p_i, q_i\}$

total # of points (# ensemble members)

Then the ensemble avg. of some qty. $f(q,p)$

$$\boxed{\langle f(t) \rangle = \frac{\int d^{3N}p\, d^{3N}q\; f(q,p)\, \rho(q,p;t)}{\int d^{3N}p\, d^{3N}q\; \rho(q,p;t)}}$$

* any function of (q,p) evolves via

$$\frac{d}{dt} f(q,p) = \frac{\partial f}{\partial t} + \sum_i \frac{\partial f}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial f}{\partial p_i}\frac{dp_i}{dt}$$

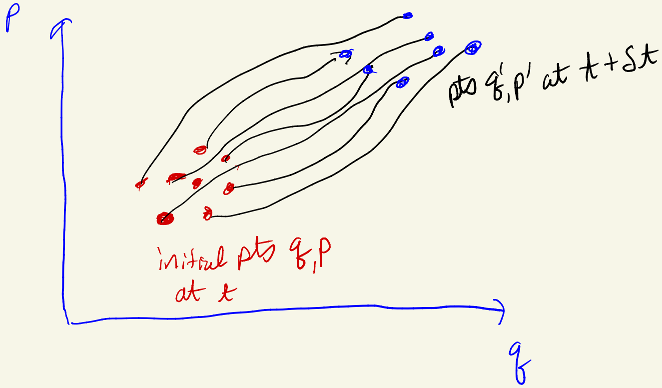
$$= \frac{\partial f}{\partial t} + \underbrace{\sum_i \frac{\partial f}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial f}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i}}$$

$$= \frac{\partial f}{\partial t} + \{f, \mathcal{H}\}_{PB}$$

poisson bracket

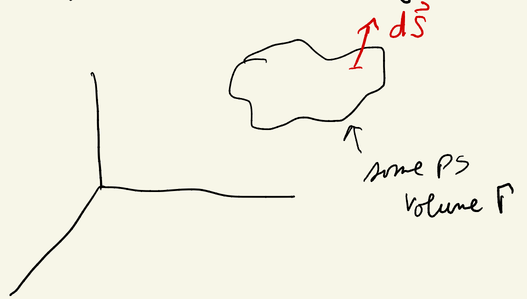
∴ We can ask how our swarm of ensemble members moves about in 6N-dim PS.

By computing $\frac{d}{dt}\rho(p,q)$



* Consider the evolution of ensemble points as a "flow of particles" in 6N-dim phase space with "velocity" vector

$$\vec{v}_{q,p} \equiv \begin{pmatrix} \dot{q}_1 \\ \vdots \\ \dot{q}_{3N} \\ \dot{p}_1 \\ \vdots \\ \dot{p}_{3N} \end{pmatrix}$$



$$\int_\Gamma \rho(q,p;t)\, d\Gamma = \text{\# of pts in } \Gamma \text{ at } t$$

$$\therefore \frac{\partial}{\partial t} \int_\Gamma \rho(q,p;t)\, d\Gamma = \underbrace{-\oint_{\partial\Gamma} (\rho \vec{v}_{q,p}) \cdot d\vec{S}}_{\text{flow out thru the surface of } \Gamma}$$

$$= -\int_\Gamma \vec{\nabla} \cdot (\rho \vec{v}_{q,p})\, d\Gamma$$

$$\Rightarrow \frac{\partial}{\partial t}\int_\Gamma \rho \, d\Gamma = -\int_\Gamma \vec{\nabla}\cdot(\rho \vec{v}_{q,p})\, d\Gamma$$

* Taking Γ arbitrary + infinitesimal

$$\Rightarrow \boxed{\frac{\partial}{\partial t}\rho(p,q;t) + \vec{\nabla}\cdot\left(\rho(p,q;t)\,\vec{v}_{q,p}\right) = 0}$$

Continuity equation just like in hydrodynamics (fluid flow) or electrodynamics (charge + current density)

* Now, $\vec{\nabla}\cdot(\rho \vec{v}_{qp}) = \vec{\nabla}\rho\cdot\vec{v}_{qp} + \rho\,\vec{\nabla}\cdot\vec{v}_{qp}$

+ recall $\vec{\nabla} = \left(\frac{\partial}{\partial q_1} \cdots \frac{\partial}{\partial q_{3N}}\ \frac{\partial}{\partial p_1} \cdots \frac{\partial}{\partial p_{3N}}\right)$

$$\therefore \rho\,\vec{\nabla}\cdot\vec{v}_{qp} = \rho \sum_{i=1}^{3N}\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right)$$

$$= \rho \sum_{i=1}^{3N} \cancel{\frac{\partial^2 \mathcal{H}}{\partial q_i \partial p_i}} - \cancel{\frac{\partial^2 \mathcal{H}}{\partial p_i \partial q_i}}$$ (by Hamiltons eqns.)

$$\rho\,\vec{\nabla}\cdot\vec{v}_{qp} = 0$$

and $\vec{\nabla}\rho\cdot\vec{v}_{qp} = \sum_{i=1}^{3N} \frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i$

$$= \sum_{i=1}^{3N} \frac{\partial \rho}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i}$$ (by Hamilton's eqns.)

$$\therefore \quad \vec{\nabla}\cdot(\rho\vec{v}_{qp}) = \sum_i \left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right) = \sum_i \left(\frac{\partial \rho}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial \rho}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i}\right)$$

$$\Rightarrow \boxed{\vec{\nabla}\cdot(\rho\vec{v}_{qp}) = \{\rho, \mathcal{H}\}_{PB}}$$

$*$ Now, $\displaystyle \frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{i=1}^{3N} \dot{q}_i \frac{\partial}{\partial q_i} + \dot{p}_i \frac{\partial}{\partial p_i} = \{\ ,\mathcal{H}\}_{PB}$

total derivative

(aka "convective derivative")

$$\Rightarrow \boxed{\frac{d}{dt}\rho(p,q;t) = 0 = \frac{\partial \rho}{\partial t} + \{\rho, \mathcal{H}\}_{PB}} \quad (**)$$

"Liouville's Theorem": ρ is constant along the phase space trajectories

(i.e., imagine you start in some neighborhood $d\Gamma$ about some point in PS and flow along with the "fluid" trajectories. at all subsequent times the density of points will remain constant)

[[i.e., ρ evolves like an incompressible fluid flow.]]

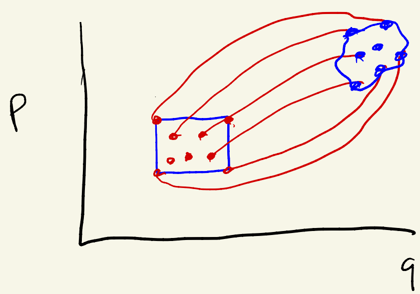
Since $\rho(p,q;t)\,d\Gamma = \dfrac{d\mathcal{N}(p,q;t)}{\mathcal{N}}$

$$\Rightarrow \boxed{\rho(p,q;t) = \frac{1}{\mathcal{N}} \cdot \frac{d\mathcal{N}(p,q;t)}{d\Gamma}}$$

And:

$$\rho(p',q';t+\delta t) = \rho(p,q;t)$$ (where $q' = q + \dot{q}\,\delta t$, $p' = p + \dot{p}\,\delta t$ and we used $\frac{d}{dt}\rho = 0$)

$$\Rightarrow d\Gamma = d\Gamma'$$



i.e., all initial points in $d\Gamma$ get mapped to a new volume $d\Gamma'$ that might be distorted in shape, but it has the same size as $d\Gamma$

* This is what it means to say if you "ride along" with one of the phase points the density of points doesn't change.

Stationary (equilibrium) PS densities

* Since SM deals w/ equilibrium properties, let's consider properties of a stationary ensemble $\partial_t \rho = 0$

$$\therefore \cancel{\partial_t \rho}^{\,0} + \{\mathcal{H}, \rho\}_{PB} = 0$$

$$\Rightarrow \boxed{\rho_{\text{stationary}} = \rho(\mathcal{H})}$$

Microcanonical Ensemble

* Every member has fixed $E \rightarrow \boxed{\rho \propto \delta(\mathcal{H} - E)}$

* $\Omega(E) \propto$ Surface area of $(6N-1)$ dimensional manifold corresponding to $\mathcal{H}(p,q) = E$.

* In practice, it's easier to calculate volumes in Γ-space, also, it's usually impractical to "know"/control E with infinite precision.

* What is often done is to say every ensemble member has $E - \frac{\Delta E}{2} \leq \mathcal{H}(p,q) \leq E + \frac{\Delta E}{2}$

where $\Delta E \ll E$

$$\Rightarrow \Omega(E) = \int \frac{d\Gamma}{\Gamma_0} \left[\Theta\left(\mathcal{H} - \left(E + \frac{\Delta E}{2}\right)\right) - \Theta\left(\mathcal{H} - \left(E - \frac{\Delta E}{2}\right)\right)\right]$$

* here Γ_0 = factor of dimensions $(qp)^{3N}$ to keep $\Omega(E)$ dimensionless

* For $\Delta E \ll E$, we can Taylor expand

$$\Theta\left(\mathcal{H}-\left(E+\frac{\Delta E}{2}\right)\right)-\Theta\left(\mathcal{H}-\left(E-\frac{\Delta E}{2}\right)\right)$$

$$\simeq \cancel{\Theta(\mathcal{H}-E)}+\frac{\Delta E}{2}\Theta'(\mathcal{H}-E)+\mathcal{O}(\Delta E^2)$$

$$-\cancel{\Theta(\mathcal{H}-E)}+\frac{\Delta E}{2}\Theta'(\mathcal{H}-E)+\mathcal{O}(\Delta E^2)$$

$$=\Delta E\,\Theta'(\mathcal{H}-E)+\mathcal{O}(\Delta E^2)$$

* but $\Theta'(\mathcal{H}-E)=\delta(\mathcal{H}-E)$

$$\therefore \boxed{\Omega(E)=\Delta E\int\frac{d\Gamma}{\Gamma_0}\,\delta(\mathcal{H}-E)}$$

Comments

1. As you might expect, the precise value ΔE doesn't matter for computed TD quantities as we take $N \gg 1$.

2. Γ_0 has dimensions of h^{3N}. Comparing to our ideal gas calc. last lecture, we strongly suspect $\Gamma_0=(2\pi\hbar)^{3N}=h^{3N}$.

*One simple way to understand Γ_0 is that it is the PS volume of <u>one</u> microstate

i.e., $\Omega(E) = $ # of microstates for $E < \mathcal{H} < E + \Delta E$

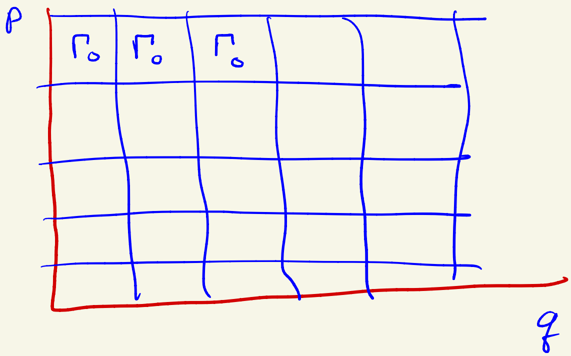
$$= \frac{1}{\Gamma_0} \int d\Gamma \underbrace{\left[\Theta(\mathcal{H} - (E+\Delta E)) - \Theta(\mathcal{H} - E)\right]}_{\substack{\text{Volume of PS in the} \\ \text{hypershell between the} \\ \text{radii } \mathcal{H} = E+\Delta E \text{ \& } \mathcal{H} = E}}$$

$$= \frac{\Gamma}{\Gamma_0} = \# \text{ microstates.}$$

*Pre-QM, people didn't know what Γ_0 was, so they didn't have a value for Γ_0

(<u>Actually</u>, they didn't even bother with inserting Γ_0. So $\Omega(E)$ was dimensionful, and correspondingly $S = k_B \log \Omega(E)$ had the strange feature that a change of units for p & q would lead to a unit-dependent shift in S! But this was back when only ΔS mattered (pre 3rd-Law), so it doesn't matter.)

* Heuristically, we can imagine cutting phase space up into little cells of volume Γ_0



* but QM tells us $\Delta p \Delta x \gtrsim \hbar$, so no sense in using smaller cells

* If you want more rigor, you can always look at a QM calculation + take the classical limit. You'll always find $\Gamma_0 = h^{3N}$ (See P+B for some unnecessarily tedious examples.)

Canonical + Grand Canonical

Since $\rho_{eq} = \rho(\mathcal{H})$, other possibilities like the CE + GCE are perfectly good choices

$$\rho_{CE} \propto e^{-\beta \mathcal{H}}$$

$$\rho_{GCE} \propto e^{-\beta(\mathcal{H} - \mu N)}$$

The derivation of these is no different than what we already did - the microstates are just no longer discrete.

$$\Rightarrow Z_{CE} = \frac{1}{N!}\int \frac{d^{3N}q\, d^{3N}p}{(2\pi\hbar)^{3N}}\, e^{-\beta \mathcal{H}(p,q)}$$

if identical particles (see L1)

$$\Rightarrow Z_{GCE} = \sum_N \frac{1}{N!}\int \frac{d^{3N}q\, d^{3N}p}{(2\pi\hbar)^{3N}}\, e^{-\beta[\mathcal{H}(p,q;N)-\mu N]}$$

e.g. classical gas of N identical particles

$$Z = \frac{1}{N!}\int \frac{d^3x_1\cdots d^3x_N\, d^3p_1\cdots d^3p_N}{(2\pi\hbar)^{3N}}\, e^{-\beta\left[\sum_i \frac{p_i^2}{2m} + \frac{1}{2}\sum_{i\neq j} u(\vec{x}_i-\vec{x}_j)\right]}$$

$$= \frac{1}{N!}\underbrace{\int \frac{d^3p_1\cdots d^3p_N}{(2\pi\hbar)^{3N}}\, e^{-\beta\sum_i \frac{p_i^2}{2m}}}_{\text{easy}}\ \underbrace{\int d^3x_1\cdots d^3x_N\, e^{-\frac{\beta}{2}\sum_{i\neq j} u_{ij}}}_{\text{Hard!}}$$

ideal gas $u_{ij}=0$

$$\Rightarrow Z = \frac{1}{N!}V^N\int \frac{d^3p_1\cdots d^3p_N}{(2\pi\hbar)^{3N}}\, e^{-\beta\sum_i \frac{p_i^2}{2m}}$$

as before in L1

Equipartition Theorem (Classical $\mathcal{H}$)

Simple form: Consider the thermal average of a single cartesian component $\frac{p_x^2}{2m}$ of s.p. KE

$$\left\langle \frac{p_x^{(1)2}}{2m} \right\rangle = \frac{\cancel{\frac{1}{(2\pi\hbar)^{3N}}} \int d\vec{p}_1 \cdots d\vec{p}_N \, \frac{p_x^{(1)2}}{2m} \, e^{-\beta \sum_i \frac{p_i^2}{2m}} \cancel{\int d\vec{r}_1 \cdots d\vec{r}_N \, e^{-\beta \sum_{i \neq j} u_{ij}}}}{\cancel{\frac{1}{(2\pi\hbar)^{3N}}} \int d\vec{p}_1 \cdots d\vec{p}_N \, e^{-\beta \sum_i \frac{p_i^2}{2m}} \cancel{\int d\vec{r}_1 \cdots d\vec{r}_N \, e^{-\beta \sum_{i \neq j} u_{ij}}}}$$

$$= \frac{\int dp_x^{(1)} \, \frac{p_x^{(1)2}}{2m} \, e^{-\beta \frac{p_x^{(1)2}}{2m}}}{\int dp_x^{(1)} \, e^{-\beta \frac{p_x^{(1)2}}{2m}}}$$

$$= \frac{1}{\int dp_x \, e^{-\frac{\beta p_x^2}{2m}}} \times -\frac{\partial}{\partial \beta} \int dp_x \, e^{-\beta \frac{p_x^2}{2m}}$$

$$= \frac{1}{\sqrt{\frac{2m\pi}{\beta}}} \, -\frac{\partial}{\partial \beta} \sqrt{\frac{2m\pi}{\beta}}$$

$$= \frac{1}{\cancel{\sqrt{\frac{2m\pi}{\beta}}}} \cdot \frac{1}{2} \cancel{\sqrt{\frac{2m\pi}{\beta}}} \, \frac{1}{\beta}$$

$$\Rightarrow \left\langle \frac{p_x^2}{2m} \right\rangle = \frac{k_B T}{2}$$

$$\boxed{\therefore \left\langle \sum_{i=1}^{N} \frac{p_i^2}{2m} \right\rangle = \frac{3}{2} N k_B T}$$

i.e., each DOF has avg KE $= \frac{k_B T}{2}$

generalized form

* Let ξ_i + ξ_j be any 2 components of $(p_1 \dots p_{3N}, q_1 \dots q_{3N})$

$$\left\langle \xi_i \frac{\partial \mathcal{H}}{\partial \xi_j} \right\rangle = \frac{\int d\Gamma \, e^{-\beta \mathcal{H}} \xi_i \frac{\partial \mathcal{H}}{\partial \xi_j}}{\int d\Gamma \, e^{-\beta \mathcal{H}}}$$

* Focus on the numerator:

$$\int d\Gamma \, e^{-\beta \mathcal{H}} \xi_i \frac{\partial \mathcal{H}}{\partial \xi_j} = \int d\Gamma \left(-\frac{1}{\beta} \frac{\partial}{\partial \xi_j} e^{-\beta \mathcal{H}} \right) \xi_i$$

$$\overset{\text{partial}}{\underset{\text{integration}}{=}} \underbrace{\cancel{\text{Surface term}}}_{0} + \frac{1}{\beta} \int d\Gamma \, e^{-\beta \mathcal{H}} \overbrace{\cancel{\frac{\partial \xi_i}{\partial \xi_j}}}^{\delta_{ij}}$$

$$\boxed{\therefore \left\langle \xi_i \frac{\partial \mathcal{H}}{\partial \xi_j} \right\rangle = \frac{1}{\beta} \delta_{ij} \frac{\cancel{\int d\Gamma \, e^{-\beta \mathcal{H}}}}{\cancel{\int d\Gamma \, e^{-\beta \mathcal{H}}}} = k_B T \, \delta_{ij}}$$

Special case: 1) $\xi_i = \xi_j = p_i \Rightarrow \left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = \langle p_i \dot{q}_i \rangle = k_B T$

2) $\xi_i = \xi_j = q_i = \left\langle q_i \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle = -\langle q_i \dot{p}_i \rangle = k_B T$

$\Downarrow$ Summing over $i = 1 \dots 3N$

$$\left\langle \sum_i p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = \left\langle \sum_i p_i \dot{q}_i \right\rangle = 3N k_B T$$

$$\left\langle \sum_i q_i \frac{\partial \mathcal{H}}{\partial q_i} \right\rangle = \left\langle -\sum_i q_i \dot{p}_i \right\rangle = 3N k_B T$$

* Now, in problems where $\mathcal{H}$ is a quadratic form
(or can be brought to one with a canonical transformation
$q_i, p_i \rightarrow Q_i, P_i$)

$$\mathcal{H} = \sum_j A_j P_j^2 + \sum_j B_j Q_j^2 \qquad (X)$$

$$\Downarrow$$

$$\sum_j \left(P_j \frac{\partial \mathcal{H}}{\partial P_j} + Q_j \frac{\partial \mathcal{H}}{\partial Q_j} \right) = 2\mathcal{H}$$

$$\boxed{\therefore \langle \mathcal{H} \rangle = \frac{1}{2} f \, k_B T \qquad f = \text{\# of non-vanishing coefficients } A_j \,\&\, B_j \text{ in } (X)}$$