

## Relation between Canonical and microcanonical A

We now investigate the effect that the energy fluctuations have on the canonical Helmholtz free energy  $A$ , as compared to the microcanonical Helmholtz free energy

microcanonical A:

- ① compute  $S(E) = k_B \ln \Omega(E)$  from the microcanonical partition function  $\Omega(E)$
- ② take Legendre transform of  $S$  with respect to  $E$  to get  $-\frac{A}{T} = S - \frac{E}{T}$  this gives the microcanonical A

We will write the Legendre transform as follows:

$$-\frac{A(T)}{T} = \max_E \left[ S(E) - \frac{E}{T} \right]$$

$$\text{or } A(T) = \min_E \left[ E - TS(E) \right]$$

let  $\bar{E}$  be this minimizing value of  $E$

$$A_{\text{micro}} = \bar{E} - TS(\bar{E})$$

## Canonical A

- ① compute  $A(T) = -k_B T \ln Q_N(T)$

Consider now the computation of  $Q_N = e^{-A/k_B T}$

$$Q_N = e^{-A/k_B T} = \int \frac{dE}{\Delta} \Omega(E) e^{-E/k_B T} \quad \text{use } S = k_B \ln \Omega$$

$$= \int \frac{dE}{\Delta} e^{S(E)/k_B} e^{-E/k_B T}$$

$$= \int \frac{dE}{\Delta} e^{-(E - TS(E))/k_B T}$$

Consider the exponent  $E - TS(E)$  and expand to 2nd order about its minimum at  $\bar{E}$ .  $E = \bar{E} + \delta E$

$$E - TS(E) = \underbrace{\bar{E} - TS(\bar{E})}_{\text{0th order}} + \underbrace{\delta E - T \left( \frac{\partial S}{\partial E} \right)_{V,N} \delta E}_{\text{1st order}} - \underbrace{\frac{1}{2} T \left( \frac{\partial^2 S}{\partial E^2} \right)_{V,N} \delta E^2}_{\text{2nd order}}$$

$$= A_{\text{micro}} + \underbrace{\delta E - T \left( \frac{1}{T} \right) \delta E}_{\text{cancel}} - \frac{1}{2} T \left( \frac{\partial(1/T)}{\partial E} \right)_{V,N} \delta E^2$$

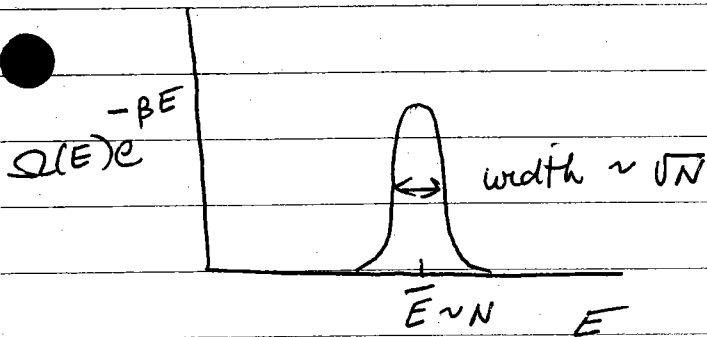
$$= A_{\text{micro}} + \frac{1}{2} \frac{1}{T} \left( \frac{\partial T}{\partial E} \right)_{V,N} \delta E^2$$

$$= A_{\text{micro}} + \frac{\delta E^2}{2 T C_V} \quad \text{where used } \left( \frac{\partial T}{\partial E} \right)_{V,N} = \frac{1}{\left( \frac{\partial E}{\partial T} \right)_{V,N}} = \frac{1}{C_V}$$

$$Q_N = e^{-A/k_B T} = \int \frac{d\delta E}{\Delta} e^{-A_{\text{micro}}/k_B T} e^{-\delta E^2 / 2 k_B T^2 C_V}$$

we have a Gaussian integral - integrand is sharply peaked at  $\delta E = 0$  with width  $\sqrt{\langle \delta E^2 \rangle} = \sqrt{k_B T^2 C_V} \sim \sqrt{N}$

$$\text{so } \frac{\sqrt{\langle \delta E^2 \rangle}}{\bar{E}} \sim \frac{\sqrt{N}}{N} = \frac{1}{\sqrt{N}} \quad \text{small fluctuations}$$



We can do the Gaussian integration to explicitly evaluate  $Q_N$

$$\text{use } \int dx e^{-x^2/2\sigma^2} = \sqrt{2\pi\sigma^2}$$

$$Q_N = e^{-A/k_B T} = e^{-A_{\text{micro}}/k_B T} \frac{\sqrt{2\pi k_B T^2 C_V}}{\Delta}$$

take logs

$$A = A_{\text{micro}} - k_B T \ln \left( \frac{\sqrt{2\pi k_B T^2 C_V}}{\Delta} \right)$$

$$A = A_{\text{micro}} - \frac{1}{2} k_B T \ln \left( \frac{2\pi k_B T^2 C_V}{\Delta^2} \right)$$

↑  
canonical  
Helmholtz  
free energy

↑  
microcanonical  
Helmholtz  
free energy

↑  
correction due to  
fluctuations in energy

$$\text{Note: } A \sim A_{\text{micro}} \sim N, \quad C_V \sim N$$

so the correction term between  $A$  and  $A_{\text{micro}}$  has relative size

$$\frac{A - A_{\text{micro}}}{A} \sim \frac{\ln N}{N} \rightarrow 0 \text{ as } N \rightarrow \infty$$

⇒ The canonical ensemble gives the same results as the microcanonical ensemble, provided one takes the thermodynamic limit  $N \rightarrow \infty$ .

This is because as  $N \rightarrow \infty$ , the most probable energy  $\bar{E}$  is the same as the average energy  $\langle E \rangle$ , and all other energies have negligible probability to occur.

Average energy  $\langle E \rangle$  vs. the most probable energy  $\bar{E}$  in the canonical ensemble.

In our earlier discussion of fluctuations in the canonical ensemble we expanded

$$E - TS(E) \cong A_{\text{micro}}(T) + \frac{\delta E^2}{2TC_V}$$

now we continue the expansion to  $O(\delta E^3)$

$$E - TS(E) \cong A_{\text{micro}}(T) + \frac{\delta E^2}{2TC_V} - \frac{1}{3!} T \frac{\partial^3 S}{\partial E^3} \Big|_{E=\bar{E}} \delta E^3$$

Note  $\frac{\partial^3 S}{\partial E^3} \sim \frac{1}{N^2}$  since  $S \sim N$  and  $E \sim N$  are both extensive

so we can write

$$E - TS(E) \cong A_{\text{micro}}(T) + \frac{\delta E^2}{2TC_V} - \frac{\gamma}{N^2} \delta E^3$$

where  $\gamma$  is some constant that does not increase with  $N$  (it can depend on  $T$ )

$$\text{Now compute } \langle \delta E \rangle = \langle E \rangle - \bar{E}$$

$$\langle SE \rangle = \frac{\int \frac{dSE}{\Delta} e^{-(E - TS(E))/k_B T} SE}{\int \frac{dSE}{\Delta} e^{-(E - TS(E))/k_B T}}$$

$$\approx \frac{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V} + \frac{\gamma SE^3}{N^2 k_B T}} SE}{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V} + \frac{\gamma SE^3}{N^2 k_B T}}}$$

$$\approx \frac{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V}} \left(1 + \frac{\gamma SE^3}{N^2 k_B T}\right) SE}{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V}} \left(1 + \frac{\gamma SE^3}{N^2 k_B T}\right)}$$

where we expanded  $e^{\frac{\gamma SE^3}{N^2 k_B T}} \approx 1 + \frac{\gamma SE^3}{N^2 k_B T}$   
for  $N \rightarrow \infty$

For a Gaussian distribution, only the even moments are non-vanishing

$$\langle SE \rangle \approx \frac{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V}} \left(\frac{\gamma}{N^2 k_B T}\right) SE^4}{\int dSE e^{-\frac{SE^2}{2k_B T^2 C_V}}}$$

$$= \left(\frac{\gamma}{N^2 k_B T}\right) \cdot (k_B T^2 C_V)^2 \cdot 3$$

where we used 
$$\frac{\int_{-\infty}^{\infty} dx e^{-\frac{1}{2} \frac{x^2}{\sigma^2}} x^4}{\int_{-\infty}^{\infty} dx e^{-\frac{1}{2} \frac{x^2}{\sigma^2}}} = 3\sigma^4$$

But the main point is  $C_V \sim N$

so 
$$\langle \delta E \rangle \sim \frac{1}{N^2} \cdot N^2 \sim O(1)$$

The relative difference between average and most probable energy therefore scales as

$$\frac{\langle E \rangle - \bar{E}}{\langle E \rangle} = \frac{\langle \delta E \rangle}{\langle E \rangle} \sim \frac{1}{N} \rightarrow 0 \text{ as } N \rightarrow \infty$$

# Stirling's Formula

In lecture we used the saddle point approx to discuss the relation between the Helmholtz free energy in the canonical vs. the micro canonical ensemble. The saddle pt approx is also how one derives Stirling's approx for  $n!$

Consider the integral

$$I = \int_0^{\infty} dx x^n e^{-x}$$

integrate by parts

$$I = \left[ -x^n e^{-x} \right]_0^{\infty} + \int_0^{\infty} nx^{n-1} e^{-x} dx$$

boundary term vanishes at its limits so

$$I = \int_0^{\infty} dx nx^{n-1} e^{-x}$$

integrate by parts again

$$I = \int_0^{\infty} dx n(n-1)x^{n-2} e^{-x}$$

and so on to get

$$I = \int_0^{\infty} dx n(n-1)(n-2)\dots(1)e^{-x} = n!$$



Now evaluate  $I$  in saddle pt approx.

Define  $U(x) = -x + n \ln x$

$$I = \int_0^{\infty} dx e^{U(x)}$$

expand  $U(x)$  about its maximum

$$\begin{aligned} U(\bar{x}) &= -n + n \ln n \\ U'(x) &= -1 + \frac{n}{x} \Rightarrow \bar{x} = n \text{ is the maximum} \\ U''(x) &= -\frac{n}{x^2} \Rightarrow U''(\bar{x}) = -\frac{1}{n} \\ U'''(x) &= \frac{2n}{x^3} \Rightarrow U'''(\bar{x}) = \frac{2}{n^2} \\ U^{(4)}(x) &= -\frac{6n}{x^4} \Rightarrow U^{(4)}(\bar{x}) = -\frac{6}{n^3} \end{aligned}$$

For  $\delta x = x - \bar{x}$ ,

$$U(x) \approx -n + n \ln n - \frac{\delta x^2}{2n} + \frac{1}{6} \frac{2}{n^2} \delta x^3 - \frac{1}{24} \frac{6}{n^3} \delta x^4 + \dots$$

$$= -n + n \ln n - \frac{\delta x^2}{2n} + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + \dots$$

$$I = \int_0^{\infty} dx e^{-n + n \ln n} e^{-\delta x^2/2n} e^{\frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3}} \quad \text{expand for small } \delta x$$

$$\approx \int_{-\infty}^{\infty} d\delta x e^{-n + n \ln n} e^{-\delta x^2/2n} \left[ 1 + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + o(\delta x^6) \right]$$

$$= e^{-n + n \ln n} \int_{-\infty}^{\infty} d\delta x e^{-\delta x^2/2n} \left[ 1 + \frac{\delta x^3}{3n^2} - \frac{\delta x^4}{4n^3} + \dots \right]$$

$$= e^{-n + n \ln n} \sqrt{2\pi n} \left[ 1 + \frac{\langle \delta x^3 \rangle}{3n^2} - \frac{\langle \delta x^4 \rangle}{4n^3} + \dots \right]$$

Now  $\langle \delta x^3 \rangle = 0$ ,  $\langle \delta x^4 \rangle \sim n^2$ , so

$$I = n! = e^{-n+n \ln n} \sqrt{2\pi n} \left[ 1 + o\left(\frac{1}{n}\right) \right]$$

$$\begin{aligned} \ln n! &= n \ln n - n + \frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi + \ln\left(1 + o\left(\frac{1}{n}\right)\right) \\ &= n \ln n - n + \frac{1}{2} \ln n + \frac{1}{2} \ln 2\pi + o\left(\frac{1}{n}\right) \end{aligned}$$

these are the leading terms

these are next order corrections

## Factorization of canonical partition function - the ideal gas

Consider a system of  $N$  noninteracting particles

$$\rightarrow \mathcal{H}[\vec{q}_i, \vec{p}_i] = \sum_{i=1}^N H^{(i)}(\vec{q}_i, \vec{p}_i)$$

where  $H^{(i)}$  is the single particle Hamiltonian that depends only on the three coordinates  $\vec{q}_i$  and three momenta  $\vec{p}_i$  of particle  $i$ .

$$Q_N = \frac{1}{N! h^{3N}} \left( \prod_{i=1}^N \int d\vec{q}_i d\vec{p}_i \right) e^{-\beta \mathcal{H}}$$

$$= \frac{1}{N!} \left( \prod_{i=1}^N \int \frac{d\vec{q}_i d\vec{p}_i}{h^3} \right) e^{-\beta \sum_j H^{(j)}(\vec{q}_j, \vec{p}_j)}$$

factor the exponential

$$= \frac{1}{N!} \prod_{i=1}^N \left( \int \frac{d\vec{q}_i d\vec{p}_i}{h^3} e^{-\beta H^{(i)}(\vec{q}_i, \vec{p}_i)} \right)$$

↑  
factor for particle  $i$  is  
identical to factor for particle  $j$

$$\rightarrow \boxed{Q_N = \frac{1}{N!} (Q_1)^N} \text{ for noninteracting particles}$$

where  $Q_1$  is the one particle partition function

$$Q_1 = \int \frac{d\vec{q} d\vec{p}}{h^3} e^{-\beta H^{(1)}(\vec{q}, \vec{p})}$$

Apply to the ideal gas.

$$H^{(1)}(\vec{q}, \vec{p}) = \frac{p^2}{2m}$$

$$Q_1 = \int \frac{d\vec{q}}{h^3} \int d\vec{p} e^{-\beta \frac{p^2}{2m}}$$

$$\int d\vec{q} = V \quad \text{volume of system}$$

$$\int d\vec{p} e^{-\beta \frac{p^2}{2m}} = \left( \frac{2\pi m}{\beta} \right)^{3/2} \quad \text{3D Gaussian integral}$$

$$Q_1 = \frac{V}{h^3} (2\pi m k_B T)^{3/2}$$

$$\Rightarrow Q_N = \frac{1}{N!} \left( \frac{V}{h^3} \right)^N (2\pi m k_B T)^{3N/2}$$

$$A(T, V, N) = -k_B T \ln Q_N$$

$$\ln N! = N \ln N - N$$

using Stirling's formula

$$= -k_B T \left\{ N \ln \left[ \frac{V}{h^3} (2\pi m k_B T)^{3/2} \right] - N \ln N + N \right\}$$

$$A(T, V, N) = -k_B T N - k_B T N \ln \left[ \frac{V}{h^{3N}} (2\pi m k_B T)^{3/2} \right]$$

### Compute average energy

$$\langle E \rangle = -\frac{\partial}{\partial \beta} (\ln \Omega_N) = -\frac{\partial}{\partial \beta} (-\beta A)$$

$$= -\frac{\partial}{\partial \beta} \left( N + N \ln \left[ \frac{V}{h^{3N}} \left( \frac{2\pi m}{\beta} \right)^{3/2} \right] \right)$$

$$= -N \frac{\partial}{\partial \beta} (\ln \beta^{-3/2}) = \frac{3}{2} N \frac{\partial}{\partial \beta} \ln \beta = \frac{3}{2} N \frac{1}{\beta}$$

$$\langle E \rangle = \frac{3}{2} N k_B T \quad \text{as expected}$$

### entropy

$$S = -\left( \frac{\partial A}{\partial T} \right)_{V,N} = k_B N + k_B N \ln \left[ \frac{V}{h^{3N}} (2\pi m k_B T)^{3/2} \right]$$

$$+ k_B T N \frac{3}{2} \left( \frac{1}{T} \right)$$

↪ from derivative of log

$$S = \frac{5}{2} N k_B + N k_B \ln \left[ \frac{V}{h^{3N}} (2\pi m k_B T)^{3/2} \right]$$

substitute in  $k_B T = \frac{2}{3} \frac{E}{N}$  to get

$$\Rightarrow S(E, V, N) = \frac{5}{2} N k_B + N k_B \ln \left[ \frac{V}{h^{3N}} \left( \frac{4\pi m E}{3N} \right)^{3/2} \right]$$

we have recovered the Sackur-Tetrode equation which we earlier derived from the microcanonical ensemble! Canonical and microcanonical approaches are equivalent.

Because in computing  $\Omega_N$  we sum over all states with any energy, as compared to computing  $\Omega$  where we restrict the sum to states in a particular energy shell  $E$ , it is usually easier to compute  $\Omega_N$ , rather than  $\Omega$ .

We introduced the canonical distribution as a means of describing a physical system in contact with a heat bath.

The canonical distrib gives the same result as the microcanonical because in the  $N \rightarrow \infty$  (thermodynamic) limit, the canonical probability distribution

$$p(E) = \frac{\Omega(E) e^{-E/k_B T}}{\Delta Q_N(V, T)}$$

approaches a delta-function\* at the most probable energy = average energy, as set by the temperature  $T$ .

We could alternatively introduce the canonical ensemble just as a mathematical trick for computing  $\Omega(E)$ , removing the constraint of constant energy  $E$  by means of a Lagrange multiplier.

\* since  $E \sim N$  increases as  $N \rightarrow \infty$

and  $\langle E^2 \rangle - \langle E \rangle^2$  increases as  $\sqrt{N}$

it is not really  $p(E)$  that approaches a well defined function as  $N \rightarrow \infty$ . Rather it is the distribution

$p(e \equiv E/N)$ , the probability density to have an energy per particle  $e$ , that approaches a delta function as  $N \rightarrow \infty$

Note:

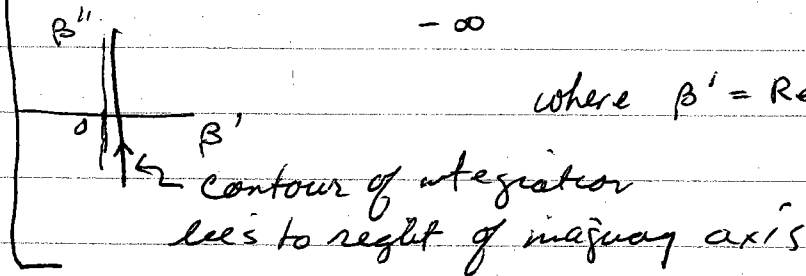
$$Q_N(\beta) = \int \frac{dE}{\Delta} \Omega(E) e^{-\beta E}$$

$Q_N(\beta)$  is Laplace transform of  $\frac{\Omega(E)}{\Delta}$

$\Rightarrow \frac{\Omega}{\Delta}$  is inverse Laplace transform of  $Q_N$

$$\frac{\Omega(E)}{\Delta} = \frac{1}{2\pi i} \int_{\beta' - i\infty}^{\beta' + i\infty} e^{\beta E} Q_N(\beta) d\beta \quad (\beta' > 0)$$

$$= \frac{1}{2\pi} \int_{-\infty}^{\infty} e^{i(\beta' + \epsilon\beta'')} Q_N(\beta' + \epsilon\beta'') d\beta''$$



entropy  $S = k_B \ln \Omega$

Helmholtz  $-\frac{A}{T} = k_B \ln Q_N$

$$-\frac{A}{T} = S - \frac{E}{T}$$

Helmholtz free energy  
is Legendre transform of  $S$  with  
respect to  $E$

Thermodynamic potentials which are Legendre transforms  
of each other, have ensemble partition functions  
that are Laplace transforms of each other.

## Virial Theorem    - Classical Systems Only

Consider  $\langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{\int dg_i dp_i x_i \frac{\partial H}{\partial x_j} e^{-\beta H}}{\int dg_i dp_i e^{-\beta H}}$

where  $x_i$  and  $x_j$  are any of the  $6N$  generalized coordinates  
 $g, p \quad i=1, \dots, 3N$ .

$$\int dg_i dp_i x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = -\frac{1}{\beta} \int dg_i dp_i x_i \frac{\partial}{\partial x_j} (e^{-\beta H})$$

integrate by parts with respect to  $x_j$

$$= -\frac{1}{\beta} \int dg_i dp_i x_i e^{-\beta H} \Big|_{x_j^{(1)}}^{x_j^{(2)}} + \frac{1}{\beta} \int dg_i dp_i \left( \frac{\partial x_i}{\partial x_j} \right) e^{-\beta H}$$

↑ integral over all coordinates except  $x_j$ 
↑  $x_j^{(1)}$  and  $x_j^{(2)}$  are the extremal values of  $x_j$

- the boundary integral vanishes because  $H$  becomes infinite at the extremal values of any coordinate
- if  $x_j$  is a momentum  $p$ , then extremal values are  $p = \pm \infty$  and  $H \propto p_{2m}^2 \rightarrow \infty$ .
  - if  $x_j$  is a spatial coord  $q$ , then extremal values are at boundary of ~~ster~~ system, where the potential energy confining the particle to the volume  $V$  becomes infinite.

$$\Rightarrow \int dg_i dp_i x_i \frac{\partial H}{\partial x_j} e^{-\beta H} = \frac{1}{\beta} \int dg_i dp_i \left( \frac{\partial x_i}{\partial x_j} \right) e^{-\beta H}$$



but  $\frac{\partial x_i}{\partial x_j} = \delta_{ij}$

$$\Rightarrow \langle x_i \frac{\partial H}{\partial x_j} \rangle = \frac{1}{\beta} \delta_{ij} \frac{\int dx_i \int dp_i e^{-\beta H}}{\int dx_i \int dp_i e^{-\beta H}}$$

$$\boxed{\langle x_i \frac{\partial H}{\partial x_j} \rangle = k_B T \delta_{ij}} \quad \leftarrow \text{Virial Theorem}$$

If  $x_i = x_j = p_i$  then

$$\langle p_i \frac{\partial H}{\partial p_i} \rangle = \langle p_i \dot{q}_i \rangle = k_B T$$

If  $x_i = x_j = q_i$ , then

$$\langle q_i \frac{\partial H}{\partial q_i} \rangle = -\langle q_i \dot{p}_i \rangle = k_B T$$

where we used Hamilton's eqn's of motion

$$\partial H / \partial p_i = \dot{q}_i \quad \text{and} \quad \partial H / \partial q_i = -\dot{p}_i$$

$$\Rightarrow \left\langle \sum_{i=1}^{3N} p_i \dot{q}_i \right\rangle = 3N k_B T$$

$$- \left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = 3N k_B T \quad - \text{Virial Theorem} \\ \text{Clausius (1870)}$$

## Equipartition Theorem - Classical systems only

Suppose the Hamiltonian is quadratic in some particular degree of freedom  $x_j$  ( $x_j$  is either a coord or a momentum)

$$H[g_i, p_i] = H'[g_i, p_i] + \alpha_j x_j^2$$

↑  
depends on all degrees of freedom  
except  $x_j$

$$\text{Then } \langle H \rangle = \langle H' \rangle + \alpha_j \langle x_j^2 \rangle$$

↑  
Contribution to total average  
energy from the degree of  
freedom  $x_j$

$$\langle x_j^2 \rangle = \frac{\prod_i \int dg_i dp_i x_j^2 e^{-\beta(H' + \alpha_j x_j^2)}}{\prod_i \int dg_i dp_i e^{-\beta(H' + \alpha_j x_j^2)}}$$

$$= \frac{\left( \prod_i' \int dg_i dp_i e^{-\beta H'} \right) \int dx_j x_j^2 e^{-\beta \alpha_j x_j^2}}{\left( \prod_i' \int dg_i dp_i e^{-\beta H'} \right) \int dx_j e^{-\beta \alpha_j x_j^2}}$$

where  $\prod_i'$  is over all degrees of freedom except  $x_j$

$$\langle x_j^2 \rangle = \frac{\int dx_j x_j^2 e^{-\beta \alpha_j x_j^2}}{\int dx_j e^{-\beta \alpha_j x_j^2}} = \frac{1}{2\beta \alpha_j} = \frac{1}{2} \frac{k_B T}{\alpha_j}$$

(follows from  $\int dx e^{-x^2/2\sigma^2} = \sqrt{2\pi\sigma^2}$  and  $\frac{\int dx e^{-x^2/2\sigma^2} x^2}{\sqrt{2\pi\sigma^2}} = \sigma^2$ )

So the contribution to  $\langle H \rangle$  from the degree of freedom  $x_j$

$$\text{is } \alpha_j \langle x_j^2 \rangle = \alpha_j \frac{1}{2} \frac{k_B T}{\alpha_j} = \frac{1}{2} k_B T$$

$\Rightarrow$  each quadratic degree of freedom in the Hamiltonian contributes  $\frac{1}{2} k_B T$  to the total average energy.

Ideal gas:  $H = \sum_{i=1}^N \frac{|\vec{p}_i|^2}{2m}$

There are  $3N$  quadratic degrees of freedom:  
the three momenta  $\vec{p}_i$  components for each particle

$$\Rightarrow E = \langle H \rangle = \frac{3N}{2} k_B T$$

or average energy per particle

$$\langle \epsilon \rangle = \frac{E}{N} = \frac{3}{2} k_B T$$

as we saw earlier from the simple kinetic theory of the ideal gas