We use an EXTENDED ENSEMBLE. We add a new variable s $(s>0)$
a corresponding momentum p_s

Hamiltonian

$$H_{ext} = \sum_i \frac{p_i^2}{2ms^2} + U(r_1 \dots r_N) + \frac{p_s^2}{2Q} + gkT \ln s$$

NON CANONICAL KINETIC ENERGY

Q : "mass" of s (a parameter that can be tuned)

g : a second parameter that can be appropriately fixed.

AIM : Relate

- microcanonical averages with respect to H_{ext} [they can be compute using MD]
- canonical averages

We have an observable $A(\vec{p}, \vec{q})$

We want to compute $\langle A(\bar{p}, \bar{q}) \rangle_{canonical}$

$$\left\langle \frac{1}{s^\alpha} A\left(\frac{\bar{p}}{s}, \vec{q}\right) \right\rangle_{ext,\ microcanonical}$$

$$= \frac{1}{\Omega} \int d^{3N}p\, d^{3N}q\, ds\, dp_s\, \frac{1}{s^\alpha} A\left(\frac{p}{s}, \bar{q}\right) \delta\left(H_{ext} - E\right)$$

$\Omega \equiv$ normalization (same integral without A)

Let us change variables : $\bar{p}' = \frac{\bar{p}}{s}$

Define $\quad H_0 = \sum_i \frac{p'^2}{2m} + U(r_1, \dots r_N) \quad$ [std. Hamiltonian]

$$H_1 = H_0 + \frac{p_s^2}{2Q}$$

We obtain

$$\langle \quad \rangle = \frac{1}{\Omega} \int s^{3N} d^{3N}p'\, d^{3N}q\, ds\, dp_s\, \frac{A(p', q)}{s^\alpha}\, \delta(H_1 + gkT \ln s - E)$$

$$= \frac{1}{\Omega} \int d^{3N}p'\, d^{3N}q\, dp_s\, A(p', q) \int_0^\infty ds\, s^{3N-\alpha}\, \delta(H_1 + gkT \ln s - E)$$

We perform the integral over s

$$\int_0^\infty ds\, s^{3N-\alpha}\, \delta(H_1 + gkT \ln s - E)$$

Define $x = gkT \ln s$

$s = \exp\left(\frac{x}{gkT}\right)$

$$= \frac{1}{gkT} \int_{-\infty}^{+\infty} dx \exp\left((3N+1-\alpha)\frac{x}{gkT}\right) \delta(x + H_1 - E)$$

$\downarrow$ use $\delta(\text{—})$.

$$= \frac{1}{gkT} \cancel{\int dx} \exp\left[(3N+1-\alpha)\frac{E-H_1}{gkT}\right]$$

Thus

$$\langle\ \rangle = \frac{1}{\Omega}\frac{1}{gkT} \int d^{3N}p'\, d^3q\, dp_s\, A(p',q) \exp\left[(3N+1-\alpha)\frac{E-H_1}{gkT}\right]$$

$$= \frac{1}{\Omega}\frac{1}{gkT} \int d^{3N}p'\, d^3q\, A(p',q) \exp\left[-\frac{(3N+1-\alpha)}{gkT} H_0\right]$$

$$\times \underbrace{\int dp_s \exp\left[(3N+1-\alpha)\frac{E - p_s^2/2Q}{gkT}\right]}$$

This is a number that DOES NOT depend on $A(p,q)$: call it M

$$\langle\ \rangle = \frac{M}{\Omega gkT} \underbrace{\int d^{3N}p'\, d^{3N}q\, A(p',q) \exp\left[-\frac{(3N+1-\alpha)}{gkT} H_0\right]}$$

This looks like a canonical average

if $\quad \dfrac{(3N+1-\alpha)}{g} = 1$

If we fix $\boxed{g = 3N+1-\alpha}$

$$\left\langle \frac{1}{s^\alpha} A\left(\frac{\bar{p}}{s}, \bar{q}\right) \right\rangle = \frac{M}{\Omega g k T} \int d^{3N}p' \, d^{3N}q \; A(p', q) e^{-\beta H_0}$$

$$= \frac{ZM}{\Omega g k T} \langle A \rangle_{\text{canonical}}$$

[note: canonical partition function]

To eliminate the prefactor

Set $A = 1$

$$\left\langle \frac{1}{s^\alpha} \right\rangle = \frac{ZM}{\Omega g k T} \langle 1 \rangle_{\text{canonical}} = \frac{ZM}{\Omega g k T}$$

Therefore

$$\langle A \rangle_{\text{canonical}} = \frac{\left\langle \frac{1}{s^\alpha} A\left(\frac{\bar{p}}{s}, \bar{q}\right) \right\rangle_{\text{ext, microcanonical}}}{\left\langle \frac{1}{s^\alpha} \right\rangle_{\text{ext, microcanonical}}}$$

Physical meaning of s: reservoir variable

Note: $\boxed{\alpha \text{ and } g \text{ are CORRELATED}}$

TIME AVERAGES

Using the ergodic hypothesis

$$\langle A(\bar{p},\bar{q})\rangle_{can} = \frac{\frac{1}{T}\int_0^T dt\, A\left(\frac{p(t)}{s(t)}, q(t)\right)\frac{1}{s^{\alpha}(t)}}{\frac{1}{T}\int_0^T dt\, \frac{1}{s^{\alpha}(t)}} \quad \text{for } T\to\infty$$

$$\boxed{[g = 3N+1-\alpha]}$$

Now we introduce a new "time" variable

$$\tau(t) = \int_0^t dt' \frac{1}{s(t')^{\alpha}}$$

Note: $s(t) > 0$, so $\tau(t)$ is an increasing function of t' therefore there is a one-to-one correspondence between t and τ.

Define $\tau_{max} = \tau(T)$

We change variables $t \to \tau$ $\quad dt/s(t)^{\alpha} = d\tau$

$$\langle A(\bar{p},\bar{q})\rangle_{can} = \frac{\frac{1}{T}\int_0^{\tau_{max}} d\tau\, A\left(\frac{p}{s}, q\right)}{\frac{\tau_{max}}{T}} = \frac{1}{\tau_{max}}\int_0^{\tau_{max}} d\tau\, A(p', q)$$

with $p' = \frac{p}{s}$

<u>Therefore</u>: if we express the dynamics in terms of $\overset{a}{\tau}$ and $\vec{p}'(\tau)$, canonical averages are equivalent to time averages in the extended ensemble with $g = N+1-\alpha$