

3.20

virial:  $\langle \sum_i \vec{q}_i \cdot \dot{\vec{p}}_i \rangle = - \langle \sum_i \vec{q}_i \cdot \frac{\partial H}{\partial \vec{q}_i} \rangle = 3NkT$

for ~~range~~ homogeneous function of degree  $n$  (potential)

$$q_i \cdot \frac{\partial H}{\partial q_i} = q_i \cdot \frac{\partial \tilde{V}}{\partial q_i} = n \tilde{V}$$

virial consists of two terms:

- 1.) surface of container (pressure)
- 2.) contribution from forces between atoms

$$\begin{aligned} \langle \sum_i \vec{q}_i \cdot \dot{\vec{p}}_i \rangle &= - \langle \sum_i \vec{q}_i \cdot \frac{\partial H}{\partial \vec{q}_i} \rangle = \langle \sum_i \vec{q}_i \cdot \vec{F}_i \rangle \\ &= \langle \vec{q}_i \cdot \vec{F}_i \rangle_{\text{surface}} + \underbrace{\langle \sum_{i,j} \vec{r}_{ij} \cdot \vec{F}_{ij} \rangle}_{\text{force}} \end{aligned}$$

$$\begin{aligned} - \sum_i \left\langle \vec{q}_i \cdot \frac{\partial H}{\partial \vec{q}_i} \right\rangle &= - \left\langle \sum_i \vec{q}_i \cdot \frac{\partial V(\vec{q}_1, \dots, \vec{q}_N)}{\partial \vec{q}_i} \right\rangle \\ &= - \left\langle \sum_i \vec{q}_i \cdot \sum_{j \neq i} \frac{\partial V(|\vec{q}_i - \vec{q}_j|)}{\partial \vec{q}_i} \right\rangle \\ &= - \left\langle \sum_i \vec{q}_i \cdot \sum_{j \neq i} \frac{\partial V(|\vec{q}_i - \vec{q}_j|)}{\partial \vec{q}_i} \right\rangle \end{aligned}$$

for each  $\vec{q}_i \frac{\partial V}{\partial \vec{q}_{ij}}$  we also have  $\vec{q}_j \frac{\partial V}{\partial \vec{q}_{ji}} = - \vec{q}_j \frac{\partial V}{\partial \vec{q}_{ij}}$

$$= - \left\langle \sum_{i,j} \vec{q}_{ij} \frac{\partial V}{\partial \vec{q}_{ij}} \right\rangle$$

if  $V$  homogeneous function of degree  $n$

$$= - \left\langle \sum_{i,j} \vec{q}_{ij} \frac{\partial V}{\partial \vec{q}_{ij}} \right\rangle = -n \langle V \rangle = -nU$$

surface term:  $- \langle \sum_i \vec{q}_i \cdot \vec{F}_i \rangle_{\text{surface}} = -P \oint \vec{r} \cdot d\vec{S} = -3PV$

$\Rightarrow$   $V_{\text{virial}} = -3PV - nU$

mean kinetic energy:

$$K = -\frac{1}{2} \text{Virial} = \frac{1}{2} (3PV + nU)$$

$$E = -\frac{1}{2} \text{Virial} + U$$

$$\text{Virial} = -3PV - nU$$

$$\frac{n \text{Virial}}{2} = \frac{1}{2} (U - E) n$$

$\Rightarrow$

$$(1 - \frac{n}{2}) \text{Virial} = -3PV + nE$$

$$\frac{1}{2} [3PV + n(E + \frac{1}{2} \text{Virial})] = -\frac{1}{2} \text{Virial}$$

$$3PV + nE = -\text{Virial} - \frac{n}{2} \text{Virial}$$

$$= -(1 + \frac{n}{2}) \text{Virial}$$

$$= -\frac{(2+n)}{2} \text{Virial}$$

$$K = \frac{1}{n+2} (3PV + nE)$$

3.28

4.)

$$g(E) = \frac{(R+N-1)!}{R!(N-1)!} \rightarrow \text{total number of microstates}$$

$\rightarrow$  total number of arrangements

probability that  $n$  are in a particular state

$n$  in state  $i$

$R-n$  will be in  $N-1$  states

number of possible arrangements

$R-n$  quanta into  $N-1$  states

$$P_n = \frac{\frac{(R-n+N-2)!}{(R-n)!(N-2)!} R! (N-1)!}{(R-n)!(N-2)! (R+N-1)!} \rightarrow$$

$$= \frac{(R-n+1) \times (N-1)}{(R+N-1) \dots (R-n+N-1)} \rightarrow \frac{R^n N}{(N+R)^{n+1}} = \frac{\bar{n}^n}{(1+\bar{n})^{n+1}} N$$

for  $N \gg 1$   $R \gg n$

6.)  $g(E) = \frac{1}{N!} \left(\frac{V}{n^3}\right)^N \frac{(2\pi m)^{3N/2}}{[(3N/2)-1]!} E^{(3N/2)-1}$

$E$  - total energy  
 $\epsilon$  - energy of subsystem

$$g(E_r, E_r') = \frac{1}{N!} \left(\frac{V}{n^3}\right)^N \frac{(2\pi m)^{3N/2}}{[(3N/2)-1]!} (E_r + E_r')^{(3N/2)-1}$$

$$\ln P(E_r) = \ln \Omega'(E_r') = \ln \Omega'(E_r'') = \frac{\partial \ln \Omega'}{\partial E'} \bigg|_{E'=E} E_r$$

$$\frac{\partial \ln g}{\partial E} = \left(\frac{3N}{2} - 1\right) \frac{1}{E} \rightarrow \frac{3N}{2E}$$

$N \rightarrow \infty$

$$\Rightarrow P(E_r) = e^{-\frac{3N}{2E} E_r}$$

3.36

$$V = -\frac{\mu\mu'}{R^5} [3\cos\theta\cos\theta' - \hat{r} \cdot \hat{r}'] = -\frac{1}{R^5} [3\mu_z\mu_z' - \hat{r} \cdot \hat{r}']$$

mean force = gradient of mean potential  $U$

$$U = \frac{\int d\Omega d\Omega' e^{-\beta V(\Omega, \Omega')} V(\Omega, \Omega')}{\int d\Omega d\Omega' e^{-\beta V(\Omega, \Omega')}} \\ = \frac{\int d\Omega d\Omega' [1 - \beta V(\Omega, \Omega')] V(\Omega, \Omega')}{\int d\Omega d\Omega' 1}$$

$\Rightarrow$  the first term will not contribute to force

$$\Rightarrow U' = -\beta \frac{\int d\Omega d\Omega' V(\Omega, \Omega') V(\Omega, \Omega')}{(4\pi)^2}$$

$$= -\frac{\beta}{R^6} \int d\Omega d\Omega' [\hat{r} \cdot \hat{r}']^2$$

$$= -\frac{\beta(\mu\mu')^2}{R^6} \frac{\int d\Omega d\Omega' [2\cos\theta\cos\theta' - \sin\theta\sin\theta'\cos(\theta-\theta')]^2}{(4\pi)^2}$$

$$= -\frac{\beta(\mu\mu')^2}{R^6} \frac{\int d\Omega d\Omega' [4\cos^2\theta\cos^2\theta' - 4\cos\theta\cos\theta'\sin\theta\sin\theta'\cos(\theta-\theta') + \sin^2\theta\sin^2\theta'\cos^2(\theta-\theta')]}{(4\pi)^2}$$

$$\int_0^{2\pi} d\phi \int_0^{2\pi} d\phi' \cos(\theta-\theta') = 2\pi \int_0^{2\pi} d\phi \cos\phi = 0$$

$$2\pi \int_0^{2\pi} d\phi \cos^2(\phi) = 2\pi^2$$

$$= -\frac{\beta(\mu\mu')^2}{R^6} \frac{\int \sin\theta d\theta \int \sin\theta' d\theta' [4\cos^2\theta\cos^2\theta' (2\pi)^2 + \sin^2\theta\sin^2\theta' 2\pi^2]}{16\pi^2}$$

$$= -\frac{\beta(\mu\mu')^2}{R^6} \frac{\int \sin\theta d\theta \int \sin\theta' d\theta' [16\cos^2\theta\cos^2\theta' + 2\sin^2\theta\sin^2\theta']}{16}$$

$$= -\frac{\beta}{16R^6} \left[ 16 \left[ \int_0^\pi \sin \theta \cos^2 \theta d\theta \right]^2 + 2 \left[ \int_0^\pi \sin^3 \theta d\theta \right]^2 \right] (\mu \mu')^2$$

$$\int_0^\pi \cos^2 \theta \sin \theta d\theta = \int_{-1}^1 x^2 dx = \frac{2}{3}$$

$$\int_0^\pi \sin^3 \theta d\theta = \int_{-1}^1 (1-x^2) dx = \frac{4}{3}$$

$$= -\frac{\beta}{16R^6} \left[ 16 \times \left( \frac{2}{3} \right)^2 + 2 \left( \frac{4}{3} \right)^2 \right] = -\frac{\beta}{R^6} \frac{2}{3}$$

$$\text{force} = -\frac{\partial U}{\partial r} = \frac{\beta}{R^7} = \frac{4\beta}{R^7} (\mu \mu')^2$$

3.43

$$Q = \int d\vec{p}^N e^{-\frac{p}{2m} \sum_{i=1}^N \vec{p}_i} \int d\vec{q}^N e^{-\beta V(\vec{q}^N)} = \left(\frac{2m\beta}{\pi}\right)^{3N/2} \int d\vec{q}^N e^{-\beta V}$$

$\Rightarrow$  magnetic field

$$Q' = \int d\vec{p}^N e^{-\frac{p}{2m} \sum_{i=1}^N (\vec{p}_i + \frac{e}{c} \vec{A}_i)^2} \int d\vec{q}^N e^{-\beta V(\vec{q}^N)}$$

$$\mu \Rightarrow \text{also equals} \Rightarrow \left[ \int d\vec{p}^N e^{-\beta V} \right] \left(\frac{2m\beta}{\pi}\right)^{3N/2}$$

magnetic susceptibility

$$\frac{\partial^2 \ln Q'}{\partial H^2} \Rightarrow \text{since } Q' = Q \text{ no change!}$$

$Q$  is independent of field

3.44

9.)  $I = - \sum_r p_r \ln p_r$  normalization:  $\sum_r p_r = 1$

~~maximize:  $\frac{\partial I}{\partial p_r} = -1 + \lambda = 0$~~

maximize  $I + \lambda \left( \sum_{r=1}^N p_r - 1 \right)$

$$\frac{\partial I}{\partial p_r} = -\ln p_r - 1 + \lambda = 0$$

$$\Rightarrow p_r = e^{\lambda-1} = \text{constant}$$

fix  $\lambda$  w

$$\sum_{r=1}^N p_r = 1 \Rightarrow$$

$$p_r = \frac{1}{N} \Rightarrow \sum_r p_r = 1$$

~~$\frac{\partial^2 I}{\partial p_r^2} = -\frac{1}{p_r^2}$~~

$$N e^{\lambda-1} = 1$$

$$e^{\lambda-1} = \frac{1}{N}$$

b.)  $G_{rr'} = 1$  case

$$I^{(1)} = - \sum_{rr'} P_r P_{r'} G_{rr'} \ln P_r P_{r'} G_{rr'}$$

$$= - \sum_{rr'} P_r P_{r'} G_{rr'} [\ln P_r + \ln P_{r'} + \ln G_{rr'}]$$

$$= - \sum_{rr'} P_r P_{r'} G_{rr'} \ln P_r - \sum_{rr'} P_r P_{r'} G_{rr'} \ln P_{r'} - \sum_{rr'} P_r P_{r'} G_{rr'} \ln G_{rr'}$$

$$= - 2 \sum_r P_r \ln P_r$$


---

$G_{rr'} \neq 1$

$$I^{(2)} = - \sum_{rr'} P_r P_{r'} G_{rr'} \ln P_r P_{r'} G_{rr'}$$

$$= - 2 \sum_r P_r \ln P_r - \sum_{rr'} P_r P_{r'} G_{rr'} \ln G_{rr'}$$

Optimize

$$\frac{\partial I^{(2)}}{\partial P_r} = - 2 (\ln P_r + 1) - 2 \sum_{r'} P_{r'} G_{rr'} \ln G_{rr'} = 0$$

$$\Rightarrow \ln P_r + 1 = - \sum_{r'} P_{r'} G_{rr'} \ln G_{rr'}$$

$$I^{(2)} = - 2 \sum_r P_r \ln P_r + \sum_r P_r (\ln P_r + 1)$$

$$= - \sum_r P_r \ln P_r + 1$$

difference between  $G_{rr'} = 1$  and  $G_{rr'} \neq 1$

$$- \sum_r P_r^* \ln P_r^* - 1$$

$$P_r^* = 1/N$$

for if the number of states  $N > 1$

$$- \sum_r P_r^* \ln P_r^* - 1 > 0 \Rightarrow \ln N - 1 > 0$$