

Lec 22

Sat 15 ①

② Examples of ^{Thermo calculations for} classical systems of N , independent ($\equiv$ non-interacting) particles

A) Recipe

- 1) write Hamiltonian for either N ptcls or 1 ptcl. in phase space form
- 2) calculate partition FN. Q :

$$Q = Q(N, \beta, \sigma) = \frac{1}{N! h^{3N}} \int_{\Omega} e^{-\beta H(p, q)} d\underline{p} d\underline{q}$$

$\downarrow \left(\frac{1}{N! h^{3N}} \right)$
 $d\underline{p} = d^3 p_{ptcl 1} d^3 p_{ptcl 2} \dots d^3 p_{ptcl N}$
 $d\underline{q} = d^3 q_{ptcl 1} d^3 q_{ptcl 2} \dots d^3 q_{ptcl N}$

- 3) Use Bridge - relation

$$\underline{A = -kT \ln Q}$$

Lec 22

[Because of $A = -kT \ln Q$ we're spg 15 (2)
~~we're~~ ^{we're} modeling a ^{constant} system mass
 That exchanges energy w/
 it's surroundings, i.e.,
 we're using a canonical
ensemble approach.]

4) CALCULATE dA in order
 to get at formulae for
 μ , P , and S :

i) $A \equiv U - TS$

$$\begin{aligned} dA &= dU - Tds - SdT \\ &\quad \downarrow \text{1st law} \\ &= -PdV + Tds + \mu dN - Tds + SdT \\ &= -PdV + \mu dN + SdT \end{aligned}$$

ii) $\therefore$

$\mu = \frac{\partial A}{\partial N} \bigg _{T, V}$
$P = - \frac{\partial A}{\partial V} \bigg _{N, T}$
$S = - \frac{\partial A}{\partial T} \bigg _{N, V}$

5) Get U using following:

$$U = - \frac{\partial}{\partial \beta} \ln Q$$

$$= - \frac{1}{Q} \int H(p, q) e^{-\beta H} dp dq \checkmark$$

6) if needed,

$$G = \mu N = \left. \frac{\partial R}{\partial N} \right|_{V, T} N$$

4) EXAMPLE 1: N-particle Ideal Gas (CLASSICAL)

A) See text 3.6

$$B) H(p, q) = \frac{1}{2m} \sum_{i=1}^N p_i^2$$

$$(p_i^2 = p_{x_i}^2 + p_{y_i}^2 + p_{z_i}^2) \\ (i=1, \dots, N)$$

$$C) \therefore Q = \frac{1}{N! h^{3N}} \int_P e^{-\frac{\beta}{2m} \sum p_i^2} dp \int_{\mathcal{H}} dq_1^{(1)} dq_1^{(2)} dq_1^{(3)} \dots \int_{\mathcal{H}} dq_N^{(1)} dq_N^{(2)} dq_N^{(3)}$$

lec 22
509 15 (e)

$$a) \int_{\underline{p}} e^{-\frac{\beta}{2m} \sum_{i=1}^N p_i^2} d\underline{p} = \int e^{-\frac{\beta}{2m} p_1^2} d^3 p_1 \cdot \int e^{-\frac{\beta}{2m} p_2^2} d^3 p_2 \dots \int e^{-\frac{\beta}{2m} p_N^2} d^3 p_N$$

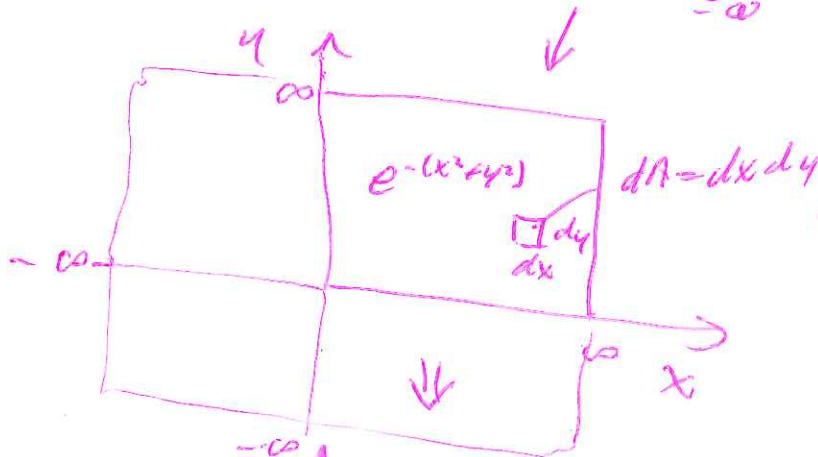
$$c2) \int_0^\infty e^{-\frac{\beta p^2}{2m}} d^3 p = \int_{-\infty}^\infty e^{-\frac{\beta p_x^2}{2m}} dp_x \int_{-\infty}^\infty e^{-\frac{\beta p_y^2}{2m}} dp_y \int_{-\infty}^\infty e^{-\frac{\beta p_z^2}{2m}} dp_z$$

ASIDE

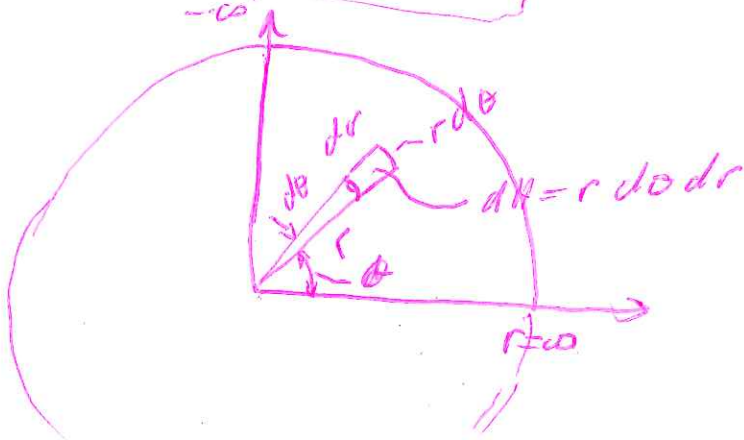
d) evaluation of

$$I = \int_0^\infty e^{-x^2} dx$$

1) trick : $I^2 = \int_{-\infty}^\infty e^{-x^2} dx \int_{-\infty}^\infty e^{-y^2} dy = \iint_{-\infty}^\infty e^{-(x^2+y^2)} dx dy$



Transform
 $e^{-(x^2+y^2)} = e^{-r^2}$
 $dx dy = r dr d\theta$



lec 22
3/19/15 (5)

$$\therefore I^2 = \int_0^{2\pi} \int_0^\infty r e^{-r^2} dr d\theta$$

$$= 2\pi \frac{1}{2} e^{-r^2} \Big|_0^\infty$$

$$= \pi$$

$$\therefore \boxed{I = \sqrt{\pi} \quad \int_{-\infty}^{\infty} e^{-x^2} dx}$$

6th AS100

to get

$\therefore$ product of integrals in (2) is:

$$i) x^2 = \frac{B}{2M} p_j^2 \Rightarrow x = \sqrt{\frac{B}{2M}} p_j \quad j = 1, \dots, 3N$$

$$ii) \therefore dx = \sqrt{\frac{B}{2M}} dp_j \Rightarrow dp_j = \frac{1}{\sqrt{B/2M}} dx$$

$$iii) \therefore Q = \left(\sqrt{\pi} \right)^{3N} \left(\frac{1}{\sqrt{B/2M}} \right)^{3N}$$

$$d) \therefore \boxed{Q = \frac{1}{N! h^{3N}} V^N (\pi M kT)^{3N/2} 2^{3N/2}}$$

THIS IS THE SAME RESULT
OBTAINED IN THE TEXT,
see ex. (3.5.9).