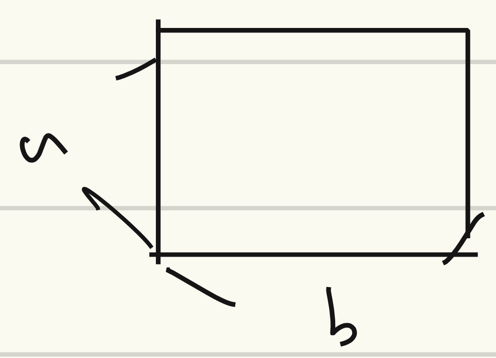
HW2 임오중

1. 넓이가 A인 2차원의 네모꼴 내부에 속박된 이상기체의 상태 방정식 및 내부 에너지를 구하시오.

Suppose that there's rectangle like below, which satisfy $a \times b = A$



(partition function) $Z = \sum e^{-\varepsilon_i / kT}$,

apply $\varepsilon_i = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$

$\rightarrow Z = \sum \exp\left\{\left(\frac{-h^2}{8mkT}\right)\left(\frac{n_x^2}{a^2}\right)\right\} \sum \exp\left\{\left(\frac{-h^2}{8mkT}\right)\left(\frac{n_y^2}{b^2}\right)\right\}$

$\sum \exp — \Rightarrow \int_0^\infty \exp — dn_x$, dn_y

apply $\int_0^\infty e^{-ax^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}$

$\rightarrow Z = \frac{a}{2}\sqrt{\frac{8mkT\cdot\pi}{h^2}} \times \frac{b}{2}\sqrt{\frac{8mkT\cdot\pi}{h^2}}$

$= \frac{8mkT}{h^2} \times \frac{ab}{4}$ $(ab = A)$

$= \frac{2AmkT}{h^2}\cdot\pi$

$\ln Z = \ln A + \ln T + \ln\left(\frac{2mk\cdot\pi}{h^2}\right)$

$p = -\left(\frac{\partial F}{\partial V}\right)_T$

$= NkT\left(\frac{\partial \ln Z}{\partial V}\right)_T = \frac{NkT}{A} \Rightarrow P\cdot A = NkT = nRT$

(since 2-D $V \rightarrow A$).

$\rightarrow$ in 2-D, $p = \tau$, which means surface tension at region A.

$\Rightarrow \tau A = NkT = nRT$

$U = NkT^2\left(\frac{\partial \ln Z}{\partial T}\right)_V = NkT^2 \times \frac{1}{T} = NkT$

2. 모든 결정은 원자가 일정한 격자 자리에 위치하고 있다. 원자가 있어야 할 격자 자리가 비어 있는 경우 원자공공 (vacancy)이 발생했다고 한다. Vacancy formation energy는 vacancy가 하나 생겼을 때 증가하는 system의 에너지를 말하며 ΔH_v로 표시한다. N 개의 격자 자리로 이루어진 순수 결정에서 평형 vacancy 수 (n) 또는 vacancy와 총 격자 자리 개수 비율 (n/N)의 표현 식을, 통계열역학적 접근 방식으로 유도하시오.

$$Z = \sum e^{-\varepsilon_i/kT}.$$

let $\begin{cases} \Delta H_A : \Delta H \text{ of atom} = 0 \\ \Delta H_v : \text{ " vacancy} \end{cases}$

$$\rightarrow Z = e^{-\Delta H_A/kT} + e^{-\Delta H_v/kT}$$

$$= 1 + e^{-\Delta H_v/kT}$$

$$\Rightarrow \frac{n}{N} = \exp\left(-\frac{\Delta H_v}{kT}\right) / Z$$

$$= \frac{1}{1 + e^{\Delta H_v/kT}}$$

(1) (2)

3. "Microscopically reversible, macroscopically irreversible"이라는 표현이 전달하고자 하는 의미가 무엇일지 각자 이해한 대로 의미를 설명하시오.

First of all, reversible means state that is able to be turned the other way around.
Macroscopically means a point of view which focus on total particle, just like checking pressure, temperature, volume ... of the total system.
Microscopically means a point of view which focus on each particle, just like checking velocity, position, size, and so on.. of each particle at each time. Moreover, since it aims to very small moment, we consider every change as change of very small time (δt).

(1) Microscopically reversible means, as I think, a state where every individual process has reverse process, and every process and its reverse has same average rate in equilibrium state. Plus, the state is time reversible — the microscopic motions is symmetric (in case of equations of motion) with respect to inversion in time.

(2) Macroscopically reversible means 'reversible' state which we are familiar. Plus, macroscopic is sum of microstate.

4. A rigid container is divided into two compartments of equal volume by a partition. One compartment contains 1 mole of ideal gas A at 1 atm, and the other compartment contains 1 mole of ideal gas B at 1 atm.

(a) Calculate the entropy increase in the container if the partition between the two compartments is removed.

(b) If the first compartment had contained 2 moles of ideal gas A, what would have been the entropy increase due to gas mixing when the partition was removed?

(c) Calculate the corresponding entropy changes in each of the above two situations if both compartments had contained ideal gas A.

(a) let

n_A	n_B

removed →

	P	V
A	$1 \to \frac{1}{2}$	$v_i \to 2v_i$
B	$1 \to \frac{1}{2}$	$v_i \to 2v_i$

$\Delta U = 0 : TdS - PdV$

$\Rightarrow dS = \frac{P}{T} dV = \frac{nR}{V} dV$

$\to \Delta S = \int_i^f dS = nR \ln(V_f/V_i) = nR\ln(P_i/P_f)$

$\Rightarrow \Delta S_A = 1 \cdot R \cdot \ln 2$
$\Delta S_B = 1 \cdot R \cdot \ln 2$ $\Big) \Rightarrow \Delta S = \Delta S_A + \Delta S_B = 2R\ln 2$

(b) same with above, $\Delta S = nR\ln(P_i/P_f)$

$\Delta S_A = 2 \cdot R \cdot \ln 2$
$\Delta S_B = 1 \cdot R \cdot \ln 2$ $\Big) \Rightarrow \Delta S = 3R\ln 2$.

(c) case (a) $P_{left} : \frac{RT}{V_i} \to \frac{2RT}{2V_i} = \frac{RT}{V_i}$

P_{right} : "

$\to \ln(P_i/P_f) = 0$ at both side

$\therefore \Delta S = 0$

case (b) $P_{left} = \frac{2RT}{V_i} \to \frac{3RT}{2V_i}$

$P_{right} : \frac{RT}{V_i} \to \frac{3RT}{2V_i}$

$\Delta S_{left} : 2 \cdot R \cdot \ln \frac{4}{3}$
$\Delta S_{right} = 1 \cdot R \cdot \ln \frac{2}{3}$ $\Big) \Rightarrow \Delta S = R\ln\frac{32}{27}$