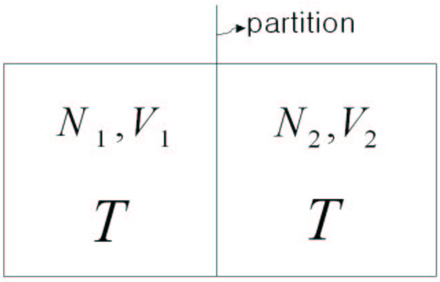
Chapter 3

Applications of Statistical Mechanics

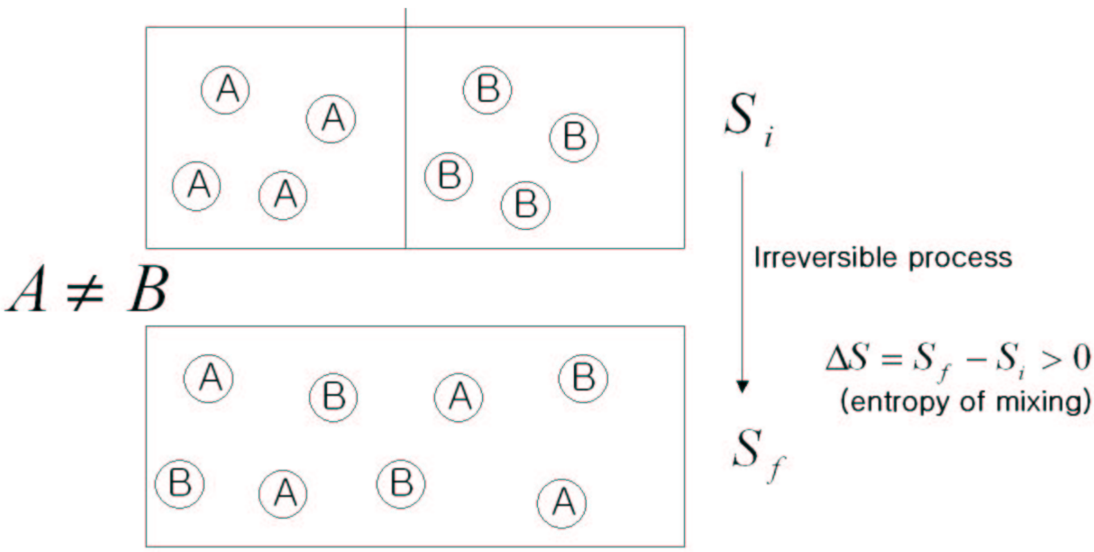
3.1 Gibbs Paradox



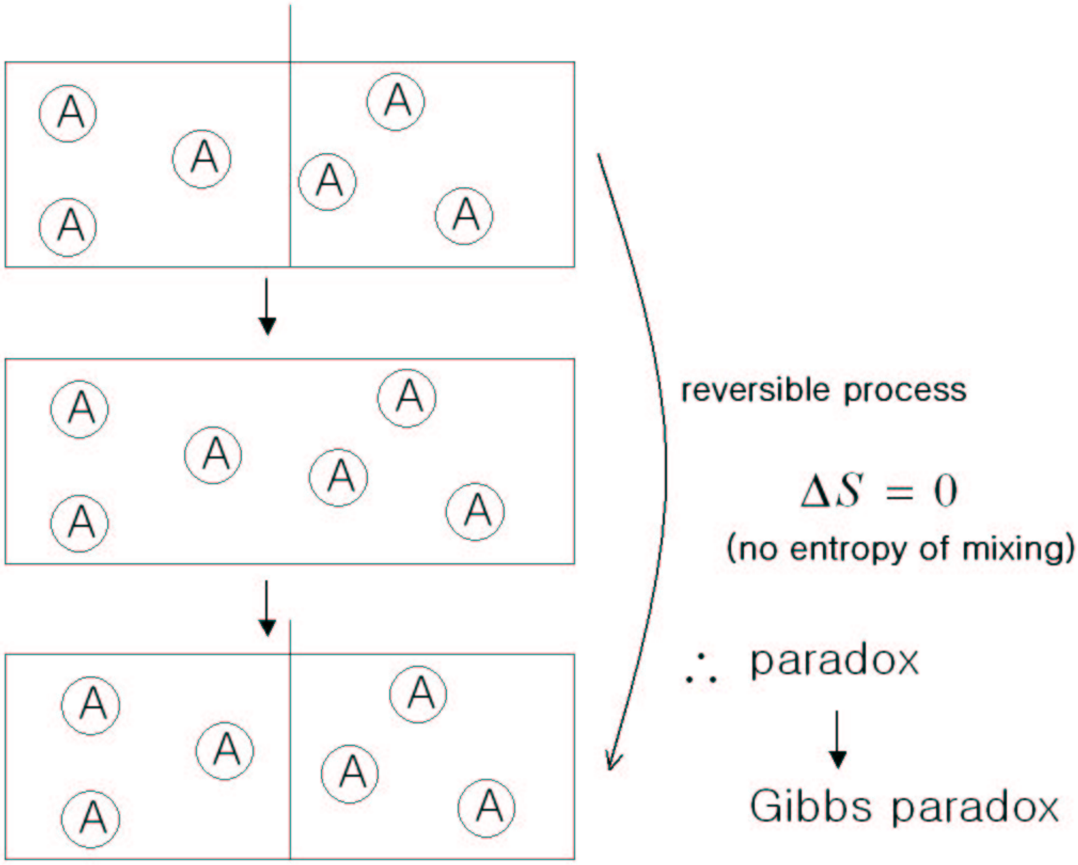
$$S = Nk_B(\ln V + \frac{3}{2}\ln T + S_0) \tag{3.1}$$

After removal of the partition,

$$\Delta S/k_B = N_1 \ln \frac{V}{V_1} + N_2 \ln \frac{V}{V_2} > 0 \text{ (the entropy of mixing)} \tag{3.2}$$



But, A=B



$$S(T,V) = Nk_B(\ln V + \frac{3}{2}\ln T + S_0) : \text{ right?} \tag{3.3}$$

$$S : \text{ not extensive quantity!} \tag{3.4}$$

$$S = k_B \cdot \ln \Omega(E) \tag{3.5}$$

$$\text{Was } \Omega(E) \text{ counted correctly?} \tag{3.6}$$

$$\text{Gibbs: } (\frac{dq \cdot dp}{h_o^{3N}})/N! : \text{ assumption for identical particles} \tag{3.7}$$

$$\Downarrow \tag{3.8}$$

$$S(T,V) = Nk_B(\ln \frac{V}{N} + \frac{3}{2}\ln T + S_0) \tag{3.9}$$

$$\therefore \text{ By the assumption, Gibbs resolved the paradox} \tag{3.10}$$

$$\text{Is the assumption really right?} \tag{3.11}$$

$$\text{“identical particle”} \tag{3.12}$$

C. M. $\longrightarrow$ distinguishable

Q. M. $\longrightarrow$ indistinguishable

Ψ: N-ptl. waveftn.: symmetric or antisymmetric with respect to any two ptl. exchange

$$\downarrow$$

$\therefore$ A permutation of ptls. can at most change the waveftn. by a sign, and thus it does not produce a new state of the system.

$$\therefore \;\; dq \cdot dp/N! : \text{ reasonable} \tag{3.13}$$

But, the correct Boltzman counting cannot be derived from C. M., because in C. M. identical ptls. are distinguishable.

In the classical limit, Q. S. M. $\longrightarrow$ C. S. M. with “correct Boltzman counting”

3.2 Ideal Gas (validity of the classical approximation)

$$Z = z^N/N!\,, \quad z = \int \frac{d^3r \cdot d^3p}{h_0^3} e^{-\beta \frac{p^2}{2m}} \tag{3.14}$$

$$= V \cdot (2\pi m k_B T/h_0^2)^{3/2} \tag{3.15}$$

$\overline{p}$: mean momentum of a ptl.

$\overline{R}$: mean separation between ptls.

$\therefore \;\; \overline{p} \cdot \overline{R} \gg \hbar \Longrightarrow$ classical approximation is valid.

$\overline{R} \gg \lambda_T \,(= \frac{h}{\overline{p}})$: Nonoverlap condition between particles $\longrightarrow$ distinguishable

(ptl. 의 wavelike property를 무시 할 수 있다.)

$$\overline{R}^3 \cdot N = V \longrightarrow \overline{R} = (V/N)^{1/3} \tag{3.16}$$

$$\frac{\overline{p^2}}{2m} = \frac{3}{2}k_BT \longrightarrow \overline{p} = \sqrt{\overline{p^2}} = \sqrt{3mk_BT} \tag{3.17}$$

$$\lambda_T = \frac{h}{\overline{p}} = \frac{h}{\sqrt{3mk_BT}} \tag{3.18}$$

$\uparrow$ thermal wavelength

$$\therefore \ (V/N)^{1/3} \gg \lambda_T \tag{3.19}$$

$$\therefore \ \text{high } T \,\&\, \text{low density} \Longrightarrow \text{고전근사를 적용.} \tag{3.20}$$

3.3 Equipartition Theorem

$$H = \sum_{i=1}^{3N}(A_iP_i^2 + B_iQ_i^2), \ \{(P_i, Q_i), \ i = 1, \cdots, 3N\} \tag{3.21}$$

$$Z = \frac{1}{N!} \cdot \int \frac{\prod_i dP_i \, dQ_i}{h_0^{3N}} \cdot e^{-\beta \sum_i (A_iP_i^2 + B_iQ_i^2)} \tag{3.22}$$

$$= \frac{1}{N!} \cdot \prod_{i=1}^{3N}(\sqrt{\frac{\pi}{\beta A_i}} \cdot \sqrt{\frac{\pi}{\beta B_i}}) \cdot \frac{1}{h_0^{3N}} \tag{3.23}$$

$$< A_i \, P_i^2 >= -\frac{A_i}{\beta}\frac{\partial}{\partial A_i}\ln Z = \frac{1}{2\beta} = \frac{1}{2}k_BT \tag{3.24}$$

$$< B_i \, Q_i^2 >= -\frac{B_i}{\beta}\frac{\partial}{\partial B_i}\ln Z = \frac{1}{2\beta} = \frac{1}{2}k_BT \tag{3.25}$$

$\therefore$ the mean value of each indep. quadratic (harmonic) term in the Hamiltonian in C. S. M. $= \frac{1}{2}k_BT$

$$E = < H > = \sum_{i=1}^{3N}(< A_i \, P_i^2 > + < B_i \, Q_i^2 >) \tag{3.26}$$

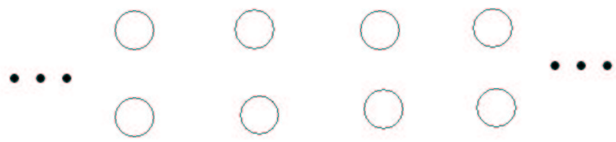
$$= 3N \cdot k_BT \tag{3.27}$$

$$\downarrow$$

$$C_V/3N \;=\; k_B\,(\text{제 3법칙에 위배됨}) \tag{3.28}$$

3.4 Specific Heats

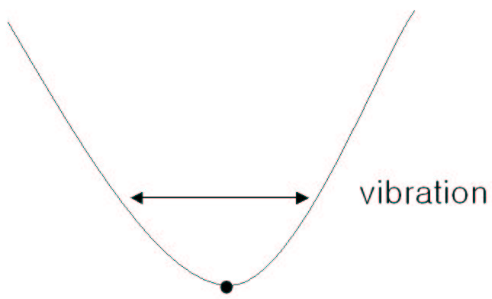
1) Solid (lattice vibrations)



$$H = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{\vec{r_i}}^2 + U\,(\vec{r_1}, \cdots), \quad \vec{r_i} = (x_{i1}, x_{i2}, x_{i3}) \tag{3.29}$$

U가 min. pt. $(\vec{r_1}^{(0)}, \cdots, \vec{r_i}^{(0)}, \cdots)$ 를 갖는 경우를 생각하자

$$\left.\frac{\partial U}{\partial x_{i\alpha}}\right|_{\vec{r_0}} = 0 \;\; (\alpha = 1, 2, 3), \quad \vec{r_0} = (\vec{r_1}^{(0)}, \cdots, \vec{r_i}^{(0)}, \cdots) \tag{3.30}$$



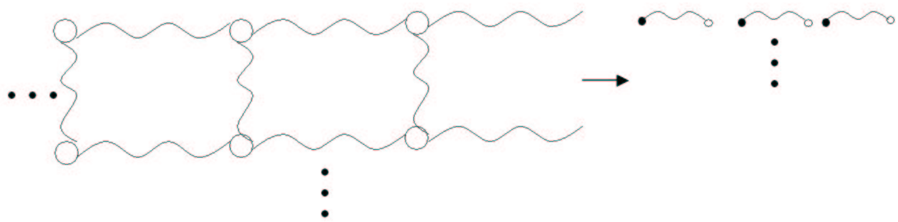
U를 min. pt. 에 대해서 Taylor 전개를 하고 2차항까지 취하자. (harmonic approximation)

$$\eta_{i\alpha} = x_{i\alpha} - x_{i,\alpha}^{(0)} \tag{3.31}$$

$$U \;=\; U_0 + \sum_{i,\alpha} \left[\frac{\partial U}{\partial x_{i,\alpha}}\right]_0 \cdot \eta_{i\alpha} + \frac{1}{2} \sum_{i,\alpha\; j,\beta} \left[\frac{\partial^2 U}{\partial x_{i\alpha} \partial x_{j\beta}}\right]_0 \cdot \eta_{i\alpha}\, \eta_{j\beta} + O(\eta^3) \tag{3.32}$$

$$\approx \quad U_0 + \frac{1}{2}\sum_{i,\alpha\, j,\beta} A_{i\alpha,j\beta}\,\eta_{i\alpha}\,\eta_{j\beta}, \quad A_{i\alpha,j\beta} = \left[\frac{\partial^2 U}{\partial x_{i\alpha}\partial x_{j\beta}}\right]_0 \tag{3.33}$$

$$H \quad = \quad U_0 + \frac{1}{2}\sum_{i,\alpha} m_i \cdot \dot{\eta}_{i\alpha}^2 + \frac{1}{2}\sum_{i,\alpha\, j,\beta} A_{i\alpha,j\beta}\,\eta_{i\alpha}\,\eta_{j\beta} : \text{ lattice vibrations near the min. pt.}$$



$$\text{대각선화: } \eta_{i\alpha} \quad = \quad \sum_{r=1}^{3N} B_{i\alpha,r}\cdot q_r; \quad \{q_r\} : \text{ normal coordinates} \tag{3.34}$$

$$H \quad = \quad U_0 + \frac{1}{2}\sum_{r=1}^{3N}(\dot{q}_r^2 + \omega_r^2 q_r^2) \tag{3.35}$$

$$\quad = \quad \sum_{r=1}^{3N}(\frac{p_r^2}{2} + \frac{1}{2}\omega_r^2 q_r^2) \tag{3.36}$$

C. S. M. $\longrightarrow$ by the equipartition theorem,

$$\overline{E} \quad = \quad 3N(\frac{1}{2}k_B T + \frac{1}{2}k_B T) = 3Nk_B T \tag{3.37}$$

$$\downarrow \; N = N_a \text{ (Avogadro No.)}$$

$$\overline{E} \quad = \quad 3RT \longrightarrow C_V = \left(\frac{\partial \overline{E}}{\partial T}\right)_V = 3R \tag{3.38}$$

But, the 3rd law: $\lim_{T\to 0} C_V \longrightarrow 0.$

Q. S. M. $\longrightarrow$ Einstein model

가정: 3N개 S. H. O. 가 모두 똑같은 각진동수 ω를 갖는다고 하자:

$\omega_r = \omega, r = 1, \cdots, 3N.$

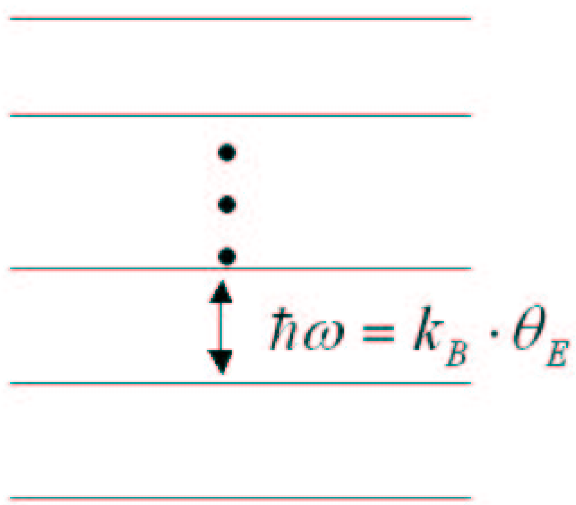
$$Z \quad = \quad z^{3N} \tag{3.39}$$

$$e_n = (n+\frac{1}{2})\hbar\omega, \quad n = 0, 1, 2, \cdots \tag{3.40}$$

$$z = \sum_{n=0}^{\infty} e^{-\beta\cdot e_n} = e^{-\beta\hbar\omega/2}\cdot\frac{1}{1-e^{-\beta\hbar\omega}} = \frac{1}{2}\cdot(\sinh\beta\hbar\omega/2)^{-1} \tag{3.41}$$

$$\ln Z = 3N\cdot\ln z = -3N\cdot\ln(\sinh\beta\hbar\omega/2) - 3N\cdot\ln 2 \tag{3.42}$$

$$\overline{E} = -\frac{\partial\ln Z}{\partial\beta} = 3N\hbar\omega\cdot(\frac{1}{2}+\frac{1}{e^{\beta\hbar\omega}-1}) \tag{3.43}$$



$$C_V = \left(\frac{\partial\overline{E}}{\partial T}\right)_V = -\frac{1}{k_B T^2}\cdot\left(\frac{\partial\overline{E}}{\partial\beta}\right)_V \tag{3.44}$$

$$= -\frac{3N\hbar\omega}{k_B T^2}\cdot\frac{e^{\beta\hbar\omega}\cdot\hbar\omega}{(e^{\beta\hbar\omega}-1)^2} \tag{3.45}$$

$\downarrow N = N_a,\ R = N_a\cdot k_B,\ \theta_E$ (Einstein temperature) $\equiv \frac{\hbar\omega}{k_B} \longrightarrow \beta\hbar\omega = \theta_E/T$

$$C_V = 3R(\theta_E/T)^2\cdot\frac{e^{\theta_E/T}}{(e^{\theta_E/T}-1)^2} \tag{3.46}$$

1) high temperature: $T \gg \theta_E$,

$$e^x - 1 = (1+x+\frac{x^2}{2}+\cdots)-1 = x(1+\frac{x}{2}+\cdots) \tag{3.47}$$

$$C_V \longrightarrow 3R \tag{3.48}$$

$\hbar\omega$: energy spacing

$k_B T \gg \hbar\omega \longrightarrow$ continuous energy dist. 으로 볼 수 있다.

$\therefore$ classical 근사가 가능.

2) low temperature: $T \ll \theta_E$

$$C_V \longrightarrow 3R \cdot (\theta_E/T)^2 \cdot e^{-\theta_E/T} \xrightarrow[(T\to 0)]{} 0 \tag{3.49}$$

$\therefore$ 열역학 제 3법칙과 일치.

그런데, 실험: $C_V \xrightarrow[(T\to 0)]{} T^3$

$\therefore$ T가 0으로 갈때 C_V는 0으로 가지만, 실험과는 불일치. (Einstein 모형에선 실험보다 훨신 빨리 C_V가 0으로 접근)

Einstein 모형에선 $3N$개의 S. H. O.가 똑같은 freq. ω를 갖는다고 가정했는데, 일반적으로는 서로 다른 freq. 갖게된다. 이점을 고려한 모형을 Debye 모형이라고 하고, 실험과 잘 일치.

3.5 Paramagnetism

N개의 noninteracting atoms

μ: magnetic moment of the atom

H: magnetic field

$$e = -\overrightarrow{\mu} \cdot \overrightarrow{H} \tag{3.50}$$

$\hbar J$: total ang. mom. of the atom

$\overrightarrow{\mu} = g\mu_0 \overrightarrow{J}$, $\mu_0 = \frac{e\hbar}{2mc}$: Bohr magneton,

m : e^-의 mass.

g: g-factor of the atom.

$$\therefore \quad e = -g\mu_0 \overrightarrow{J}\,\overrightarrow{H} \tag{3.51}$$

$$\downarrow \overrightarrow{H} = H \cdot \hat{z}$$

$$e = -g\mu_0 H J_z, \quad J_z = m \longrightarrow m = -J, -J+1, \cdots, J \tag{3.52}$$

$$e_m = -g\mu_0 H m \tag{3.53}$$

$$\begin{aligned} z &= \sum_{m=-J}^{J} e^{\eta\, m}, \quad \eta = \beta g \mu_0 H && (3.54)\\ &= \frac{e^{-\eta J}\cdot(1-e^{\eta(2J+1)})}{1-e^{\eta}} = \frac{e^{-\eta J} - e^{\eta(J+1)}}{1-e^{\eta}} && (3.55)\\ &= \frac{e^{-\eta(J+\frac{1}{2})} - e^{\eta(J+\frac{1}{2})}}{e^{-\eta/2} - e^{\eta/2}} && (3.56)\\ &= \frac{\sinh(J+\frac{1}{2})\eta}{\sinh \eta/2} && (3.57) \end{aligned}$$

$$\begin{aligned} f &= -k_B T \cdot \ln z && (3.58)\\ \overline{\mu_z} &= -\left(\frac{\partial f}{\partial H}\right)_T = \frac{1}{\beta}\,\frac{\partial \ln z}{\partial H} = \frac{1}{\beta}\,\frac{\partial \ln z}{\partial \eta}\frac{\partial \eta}{\partial H} && (3.59)\\ &= g\mu_0 \frac{\partial \ln z}{\partial \eta} && (3.60)\\ &= g\mu_0 \left[\frac{(J+\frac{1}{2})\cdot\cosh(J+\frac{1}{2})\eta}{\sinh(J+\frac{1}{2})\eta} - \frac{\frac{1}{2}\cosh\frac{\eta}{2}}{\sinh\frac{\eta}{2}}\right] && (3.61)\\ &= g\mu_0 J B_J(\eta), && (3.62) \end{aligned}$$

$$B_J(\eta) = \frac{1}{J}\left[(J+\frac{1}{2})\coth(J+\frac{1}{2})\eta - \frac{1}{2}\coth\frac{\eta}{2}\right] : \text{ Brillouin function} \tag{3.63}$$

$$\coth y = \frac{e^{y} + e^{-y}}{e^{y} - e^{-y}} \tag{3.64}$$

$$y \gg 1, \quad \coth y \;\approx\; 1 \tag{3.65}$$

$$y \ll 1, \quad \coth y = \frac{1+\frac{1}{2}y^2+\cdots}{y+\frac{1}{6}y^3+\cdots} \tag{3.66}$$

$$\cong (1+\frac{y^2}{2})\cdot\frac{1}{y}\cdot(1+\frac{1}{6}y^2)^{-1} \tag{3.67}$$

$$= \frac{1}{y}(1+\frac{y^2}{2})(1-\frac{y^2}{6}) \tag{3.68}$$

$$= \frac{1}{y}(1+\frac{y^2}{3}) = \frac{1}{y}+\frac{y}{3} \tag{3.69}$$

$$\therefore \quad \eta \gg 1, \quad B_J(\eta) \approx \frac{1}{J}\left[(J+\frac{1}{2})-\frac{1}{2}\right] = 1 \tag{3.70}$$

$$\eta \ll 1, \quad B_J(\eta) = \frac{1}{J}\left\{(J+\frac{1}{2})[\frac{1}{(J+\frac{1}{2})\eta}+\frac{1}{3}(J+\frac{1}{2})\cdot\eta]-\frac{1}{2}[\frac{2}{\eta}+\frac{\eta}{6}]\right\} \tag{3.71}$$

$$= \frac{1}{J}\left\{\frac{1}{3}(J+\frac{1}{2})^2\cdot\eta-\frac{\eta}{12}\right\} \tag{3.72}$$

$$= \frac{(J+1)}{3}\cdot\eta \tag{3.73}$$

$\overline{M_z} = N\cdot\overline{\mu_z} = Ng\mu_0 J B_J(\eta)$

$\eta \ll 1 \longrightarrow g\mu_0 H$ (energy spacing) $/k_B T \ll 1$

$\longrightarrow$ high temperature $\longrightarrow$ energy disk: continuous

$\longrightarrow$ 고전근사가 가능

$$\overline{M_z} \propto \eta \propto H/T \tag{3.74}$$

$$\therefore \chi_T = \frac{\partial M}{\partial H} \propto 1/T : \text{ Curie's law} \tag{3.75}$$

$\eta \gg 1 \longrightarrow g\mu_0 H/k_B T \gg 1$ (low temperature)

$$\overline{M_Z} \longrightarrow N\, g\, \mu_0\, J \tag{3.76}$$