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D31

$$a) \dot{N}_A = k_1 N - (k_1 + k_2) N_A + A(t)$$

$$N_A(t) = \tilde{N}_A(t) e^{-(k_1+k_2)t}$$

$$\dot{\tilde{N}}_A(t) = k_1 N e^{-(k_1+k_2)t} + A(t) e^{-(k_1+k_2)t}$$

$$\langle \tilde{N}_A(t) \rangle = k_1 N \int_0^t e^{-(k_1+k_2)t'} dt' = \frac{k_1 N}{k_1+k_2} (e^{-(k_1+k_2)t} - 1)$$

$$\langle N_A \rangle = \frac{k_1}{k_1+k_2} N \quad (t \rightarrow \infty)$$

$$\langle N_A \rangle = \frac{\rho_A}{\rho_A + \rho_B} N \quad \text{so } A \rightleftharpoons B \text{ then } \rho_A$$

$$\langle N_B \rangle = \frac{\rho_B}{\rho_A + \rho_B} N$$

$$\frac{\langle N_A \rangle}{\langle N_B \rangle} = \frac{\rho_A}{\rho_B} = \frac{k_1}{k_2}$$

equilibrium - f

Detailed Balance

$$P(N_A) \cdot \rho_{A \rightarrow B} = P(N_B) \cdot \rho_{B \rightarrow A}$$

$$\frac{dN_A}{dt} = \dot{\delta N_A}$$

$$\delta N_A(t) = e^{-(k_1+k_2)t} \int_0^t (k_1 N_A(t')) e^{(k_1+k_2)t'} dt' - \langle N_A \rangle$$

$$= \frac{-k_1}{k_1+k_2} N e^{-(k_1+k_2)t} + \frac{k_1}{k_1+k_2} N - \langle N_A \rangle + e^{-(k_1+k_2)t} \int_0^t A(t') e^{(k_1+k_2)t'} dt'$$

$$\langle \delta N_A^2(t) \rangle = \left(\frac{k_1 N}{k_1+k_2} e^{-(k_1+k_2)t} \right)^2 + e^{-2(k_1+k_2)t} C \int_0^t e^{2(k_1+k_2)t'} dt'$$

$t \rightarrow \infty$

$$\rightarrow \frac{C}{2(k_1+k_2)} \rightarrow C = 2(k_1+k_2) \langle \delta N_A^2 \rangle$$

$$\langle \delta N_A^2 \rangle = \frac{\langle N_A \rangle \langle N_B \rangle}{N}$$

$$= \frac{N \cdot k_1 k_2}{(k_1+k_2)^2}$$

A24) ad 1/c

$$C = \frac{2k_1 k_2}{k_1+k_2} \cdot N$$

pd

(c) $\mu_B(t) = \mu_B + \delta\mu_B = \mu_B + \delta\mu_B(\omega) e^{-i\omega t}$... μ_B

$\langle N_A(t) \rangle = \int d\omega \delta\mu_B(\omega) e^{-i\omega t} + \langle N_A \rangle_{\text{equilibrium}}$ $\delta(\omega)$

$\delta\mu_B(t) = -kT \frac{\delta k_2(t)}{k_2}$ $\frac{\delta k_2}{k_2}$

$Z_B = \frac{\rho_B^{N_B}}{N_B!} \rightarrow \mu_B = -kT \frac{\partial \ln Z}{\partial N_B} = -kT \ln \frac{\rho_B}{N_B}$ ρ_B

$\frac{k_2 \delta k_2}{k_1} = \frac{\rho_B + \delta \rho_B}{\rho_A} = \frac{\rho_B}{\rho_A} \left(1 + \frac{\delta \rho_B}{\rho_B}\right) = \frac{k_2}{k_1} \left(1 + \frac{\delta k_2}{k_2}\right)$ $\frac{k_2}{k_1} = \frac{\rho_B}{\rho_A}$

$\mu_B = \mu_{B0} + \delta\mu_B = -kT \ln \frac{\rho_{B0} + \delta \rho_B}{N_B} = -kT \ln \left(\frac{\rho_{B0}}{N_B} \right) \left(1 + \frac{\delta \rho_B}{\rho_{B0}} \right)$

$= -kT \ln \frac{\rho_{B0}}{N_B} - kT \ln \left(1 + \frac{\delta \rho_B}{\rho_{B0}} \right) \approx \mu_{B0} - kT \frac{\delta \rho_B}{\rho_{B0}}$

$\delta\mu_B \approx -kT \frac{\delta \rho_B}{\rho_B} = -kT \frac{\delta k_2}{k_2}$

$(\gamma = k_1 + k_2)$ $\frac{d\tilde{N}_A}{dt} = k_1 N e^{\gamma t} + A e^{-\gamma t} - \rho_{A0} e^{-i\omega t}$

$\frac{d\tilde{N}_A}{dt} = k_1 N e^{\gamma t} + A e^{-\gamma t} - \rho_{A0} e^{-i\omega t}$

$\langle \tilde{N}_A \rangle = \frac{k_1 N}{k_1 + k_2} (e^{\gamma t} - 1)$ $\frac{k_1 N}{\gamma}$

$\langle N_A \rangle = e^{-(k_1+k_2)t} \left[\langle \tilde{N}_A \rangle - \delta k_2 e^{-\gamma t} \int_0^t e^{-i\omega t'} \frac{k_1 N}{\gamma} (e^{\gamma t'} - 1) dt' \right]$

$= \langle N_A \rangle_{\text{equ}} - \delta k_2 \frac{k_1 N}{\gamma} \frac{e^{-i\omega t}}{-i\omega}$ $t \rightarrow \infty$

$$\delta N_B = -dk_2 \frac{k_1 N}{\gamma} \frac{e^{-i\omega t}}{-i\omega + \gamma}$$

ולא δN_B

$$dN_B = d(\omega) \delta \mu_B e^{-i\omega t}$$

ההפרש של δN_B

$$\delta \mu_B = \frac{-kT \delta k_2}{k_2}$$

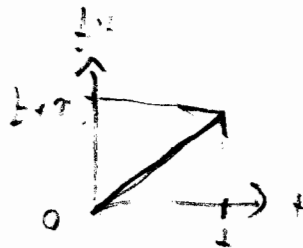
הפרש N_B כולו

$$d(\omega) = \frac{k_1 k_2 N}{kT \gamma (-i\omega + \gamma)}$$

כך

אם $\delta N_B(t) \delta N_B(t+\tau)$ פור $\delta N_B(t)$ ו $\delta N_B(t+\tau)$ הם שני הפרשים (3)

$$\begin{aligned} \langle \delta N_B(t) \delta N_B(t+\tau) \rangle &= \left\langle \left(-\frac{k_1 N}{\gamma} e^{-\gamma t} + e^{-\gamma t} \int_0^t A(t') e^{\gamma t'} dt' \right) \left(-\frac{k_1 N}{\gamma} e^{-\gamma(t+\tau)} + e^{-\gamma(t+\tau)} \int_0^{t+\tau} A(t'') e^{\gamma t''} dt'' \right) \right\rangle \\ &= \left(\frac{k_1 N}{\gamma} \right)^2 e^{-\gamma t - \gamma(t+\tau)} + e^{-\gamma t - \gamma(t+\tau)} \int_0^t \int_0^{t+\tau} e^{\gamma t'} e^{\gamma t''} C(t''-t') dt' dt'' \end{aligned}$$



$$\xrightarrow{t \rightarrow \infty} \frac{C}{2\gamma} e^{-\gamma|\tau|}$$

בין $t \rightarrow \infty$ ו $t \rightarrow \infty$

$$C_{N_B}(\omega) = \frac{C}{2\gamma} \int_{-\infty}^{\infty} e^{-\gamma|t| + i\omega t} dt = \frac{C}{\omega^2 + \gamma^2}$$

כך

$$= \frac{2k_1 k_2 N}{\gamma} \frac{1}{\gamma^2 + \omega^2}$$

בין (2) פור C ו γ

$$\frac{2k_B T}{\omega} \text{Im} d_\omega = \frac{2k_B T}{\omega} \frac{k_1 k_2 N}{kT \gamma} \frac{\omega}{\gamma^2 + \omega^2} = C_{N_B}(\omega)$$

הפרש δN_B

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