E8490

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Consider molecules A and B in a box. The molecules are subjected to weak electric field $\mathcal{E}$ that modifies the binding energy of the B molecules such that $\varepsilon_B = \varepsilon_B^{(0)} + \alpha\mathcal{E}$, where α is a constant. In the lack of electric field the molecules reach chemical equilibrium A$\leftrightarrow$B, such that their fractions are $f_A = \langle N_A \rangle / N$ and $f_B = \langle N_A \rangle / N$. In item (c) it is assumed that the system can be described by the rate equation

$$\frac{dN_A}{dt} = k_B N_B - k_A N_A + A(t)$$

Where $A(t)$ is a stochastic term with zero average and correlation function $\langle A(t)A(t')\rangle = C\delta(t-t')$. In item (e) assume that only k_B is affected by the weak electric field.

(a) Express $\langle N_A \rangle, \langle N_B \rangle$ by f_A and f_B and $\alpha\mathcal{E}$.

(b) Express $\text{Var}(N_A)$ by $\langle N_A \rangle$ and $\langle N_B \rangle$.

(c) Determine the constants k_A and k_B and D in the stochastic rate equation such that $\langle N_A \rangle$ and $\text{Var}(N_A)$ will agree with the canonical expectation of items (a) and (b).

(d) Determine how k_B is modified by the weak electric field. In other words find the coefficient in $\delta k_B \propto \mathcal{E}$.

(e) Find the generalized susceptibility $\chi(\omega)$ that relates the variation δN_A to $\mathcal{E}$.

(f) Find the power spectrum of δN_A in steady state.

The solution:
(a) In chemical equilibrium (without electric field) we have:

$$\frac{f_A}{f_B} = \frac{Z_A^1}{Z_B^1}$$

Where $Z_{A/B}^1$ is the single partition function.
In the present of an electric field the Hamiltonian for a single type B molecule becomes:

$$H_B = \frac{p^2}{2m} + \epsilon$$

Therefore the single partition function change:

$$Z_B^1 \to e^{-\beta\epsilon} Z_B^1 \implies \frac{\tilde{f}_A}{\tilde{f}_B} = \frac{Z_A^1}{Z_B^1} e^{\beta\epsilon} = \frac{f_A}{f_B} e^{\beta\epsilon}$$

Using $\tilde{f}_A + \tilde{f}_B = 1$ and after a some algebra we get:

$$\langle N_A \rangle = \frac{f_A}{f_A + e^{-\beta\epsilon} f_B} N, \langle N_B \rangle = \frac{f_B}{f_B + e^{\beta\epsilon} f_A} N$$

(b) The full partition function Z is:

$$Z = \sum_{N_A, N_B = N - N_A} \frac{(Z_A^1)^{N_A} (Z_B^1)^{N_B}}{N_A! N_B!} = \frac{(Z_A^1 + Z_B^1)^N}{N!}$$

$$\langle N_A^2\rangle = \frac{1}{Z}\sum_{N_A,N_B=N-N_A}\frac{(Z_A^1)^{N_A}(Z_B^1)^{N_B}}{N_A!N_B!}N_A^2$$

$$= \frac{1}{Z}Z_A^1\frac{\partial}{\partial Z_A^1}(Z_A^1\frac{\partial Z}{\partial Z_A^1}) = \frac{1}{Z}Z_A^1\frac{\partial}{\partial Z_A^1}(\frac{Z_A^1 N(Z_A^1+Z_B^1)^N}{N!})$$

$$= \frac{1}{Z}[Z_A^1(Z_A^1+Z_B^1)^{N-1}/N! + (Z_A^1)^2(Z_A^1+Z_B^1)^{N-2}N(N-1)/N!]$$

$$= \frac{Z_A^1}{Z_A^1+f_B}N + \frac{(Z_A^1)^2 N(N-1)}{(Z_A^1+Z_B^1)^2}$$

$$\implies Var(N_A) = \frac{Z_A^1}{Z_A^1+Z_B^1}N + \frac{(Z_A^1)^2 N}{(Z_A^1+Z_B^1)^2} = \frac{Z_A^1 Z_B^1}{(Z_A^1+Z_B^1)^2} = \frac{\langle N_A\rangle\langle N_B\rangle}{N}$$

(c) For the average $\langle N_A(t)\rangle$ eq(*) becomes:

$$\frac{< dN_A(t) >}{dt} = k_B N - (k_A+k_B) < N_A(t) >$$

With the general solution:

$$< N_A >= De^{-(k_A+k_B)t} + \frac{k_A N}{k_A+k_B}$$

And for long times $t\to\infty$

$$< N_A >= \frac{k_A}{k_A+k_B}N$$

Comparing with the canonical expectation $< N_A >= \frac{f_A}{f_A+f_B}N$, $< N_B >= \frac{f_B}{f_A+f_B}N$ we get the relation

$$k_A/k_B = f_A/f_B$$

In order to determine C we first need to solve Eq(*)

$$N_{A,h} = D(t)e^{-(k_A+k_B)t}$$

$$\dot{D} = (k_1 N + A(t))e^{(k_A+k_B)t}$$

$$D = \frac{k_A N}{k_A+k_B}e^{(k_A+k_B)t} + \int_0^t A(t')e^{(k_A+k_B)t'}dt'$$

$$N_A = -\frac{k_A N}{k_A+k_B}e^{-(k_A+k_B)t} + \frac{k_A N}{k_A+k_B} + e^{-(k_A+k_B)t}\int_0^t A(t')e^{(k_A+k_B)t'}dt'$$

$$\implies N_A(t) - < N_A >= \delta N_A(t) = -\frac{k_1 N}{k_A+k_B}e^{-(k_A+k_B)t} + e^{-(k_A+k_B)t}\int_0^t A(t')e^{(k_A+k_B)t'}dt'$$

$$[\delta N_A(t)]^2 = (\frac{k_A N}{k_A+k_B}e^{-(k_A+k_B)t})^2 - 2\frac{k_A N}{k_A+k_B}e^{-2(k_A+k_B)t}\int_0^t A(t')e^{(k_A+k_B)t'}dt' +$$

$$e^{-2(k_A+k_B)t}\int_0^t dt''\int_0^t dt' A(t')A(t'')e^{(k_A+k_B)(t'+t'')}$$

Taking $t \to \infty$ and using $\langle A(t)A(t')\rangle = C\delta(t-t')$ we get:

$$\langle[\delta N_A(t)]^2\rangle = e^{-2(k_A+k_B)t}\int_0^t dt''\int_0^t dt' e^{(k_A+k_B)(t'+t'')}C\delta(t'-t'') = \frac{C}{2(k_A+k_B)}$$

From (b) we know that :

$$\langle[\delta N_A(t)]^2\rangle = \frac{<N_A><N_B>}{N} \implies C = \frac{2k_Ak_B}{(k_A+k_B)^2}N$$

(d) If the electric field is modified $\mathcal{E} \to \mathcal{E} + \delta\mathcal{E}$ the single partition function becomes:

$$Z_B^1 e^{-\beta\epsilon} \to Z_B^1 e^{-\beta\epsilon-\beta\delta\epsilon} \approx Z_B^1 e^{-\beta\epsilon}(1-\delta\beta\epsilon) \implies f_B \to f_B(1-\delta\beta\epsilon)$$

Keeping in mind that k_A stays unaffected by the electric field we get:

$$\implies k_B \to k_B - \beta\delta\epsilon k_B$$

(e) The rate eq(*):

$$\dot{N_A} = k_BN - (k_A+k_B)N_A$$

Setting $\tilde{N_A} = N_A - \langle N_A\rangle$ and adding the variation $\mathcal{E} \to \mathcal{E} + \delta\mathcal{E}$ we get:

$$\dot{\tilde{N_A}} = -(k_A+k_B)\tilde{N_A} + \beta\delta k_B\tilde{N_A}\mathcal{E}$$

Taking into account that the field is weak we get:

$$\dot{\tilde{N_A}} \approx -(k_A+k_B)\tilde{N_A} + \beta\delta k_B N_A^{(0)}\mathcal{E}$$

Fourier transform the eq gives:

$$\tilde{N_A}(\omega) = \frac{\beta\delta k_B N_A^{(0)}}{(k_A+k_B)-i\omega}\mathcal{E}(\omega)$$

$$\implies \chi(\omega) = \frac{\beta\delta k_B N_A^{(0)}}{(k_A+k_B)-i\omega}$$

(f) We calculate the power spectrum $\tilde{C}(\omega)$ using the FD relations:

$$\tilde{C}(\omega) = coth(\frac{\omega}{2T})Im[\chi(\omega)] = coth(\frac{\omega}{2T})\frac{\beta\delta k_B N_A^{(0)}\omega}{(k_A+k_B)^2+\omega^2}$$