Part IX
Appendix

Appendix A
The Grand Canonical Ensemble

Consider an ensemble of M systems which can exchange energy as well as particles with a reservoir. For large M, the total number of particles $N_{tot} = M\overline{N}$ and the total energy $E_{tot} = M\overline{E}$ have well-defined values since the relative widths decrease as

$$\frac{\sqrt{\overline{N_{tot}^2} - \overline{N_{tot}}^2}}{\overline{N_{tot}}} \sim \frac{1}{\sqrt{M}} \quad \frac{\sqrt{\overline{E_{tot}^2} - \overline{E_{tot}}^2}}{\overline{E_{tot}}} \sim \frac{1}{\sqrt{M}} \tag{A.1}$$

Hence, also the average number and energy can be assumed to have well-defined values (Fig. A.1)

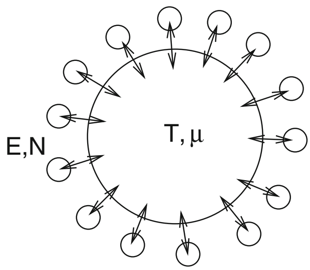

Fig. A.1 Ensemble of systems exchanging energy and particles with a reservoir

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A.1 Grand Canonical Distribution

We distinguish different microstates j which are characterized by the number of particles N_j and the energy E_j. The number of systems in a certain microstate j will be denoted by n_j. The total number of particles and the total energy of the ensemble in a macrostate with n_j systems in the state j are

$$N_{tot} = \sum_j n_j N_j \quad E_{tot} = \sum_j n_j E_j \tag{A.2}$$

and the number of systems is

$$M = \sum_j n_j \tag{A.3}$$

The number of possible representations is given by a multinomial coefficient

$$W(\{n_j\}) = \frac{M!}{\prod_j n_j!}. \tag{A.4}$$

From Stirling's formula, we have

$$\ln W \approx \ln(M!) - \sum_j (n_j \ln n_j - n_j). \tag{A.5}$$

We search for the maximum of (A.5) under the restraints imposed by (A.2), (A.3). To this end, we use the method of undetermined factors (Lagrange method) and consider the variation

$$\begin{aligned} 0 &= \delta \left(\ln W - \alpha \left(\sum_j n_j - M \right) - \beta \left(\sum_j n_j E_j - E_{tot} \right) - \gamma (\sum_j n_j N_j - N_{tot}) \right) \\ &= \sum_j \delta n_j \left(-\ln n_j - \alpha - \beta E_j - \gamma N_j \right). \end{aligned} \tag{A.6}$$

Since the n_j now can be varied independently, we find

$$n_j = \exp(-\alpha - \beta E_j - \gamma N_j). \tag{A.7}$$

The unknown factors α, β, γ have to be determined from the restraints. First, we have

$$\sum_j n_j = \mathrm{e}^{-\alpha} \sum_j \mathrm{e}^{-\beta E_j - \gamma N_j} = M. \tag{A.8}$$

With the grand canonical partition function

$$\Xi = \sum_j \mathrm{e}^{-\beta E_j - \gamma N_j} \tag{A.9}$$

the probability of a certain microstate is given by

$$P(E_j, N_j) = \frac{n_j}{\sum_j n_j} = \frac{\mathrm{e}^{-\beta E_j - \gamma N_j}}{\Xi} \tag{A.10}$$

and further

$$\mathrm{e}^{-\alpha} = \frac{M}{\Xi}. \tag{A.11}$$

From

$$\sum_j n_j E_j = \frac{M}{\Xi} \sum_j E_j \mathrm{e}^{-\beta E_j - \gamma N_j} = E_{tot} \tag{A.12}$$

we find the average energy per system

$$\overline{E} = \frac{\sum n_j E_j}{M} = -\frac{\partial}{\partial \beta} \ln \Xi \tag{A.13}$$

and similarly from

$$\sum_j n_j N_j = \frac{M}{\Xi} \sum_j N_j \mathrm{e}^{-\beta E_j - \gamma N_j} = N_{tot} \tag{A.14}$$

the average particle number of a system

$$\overline{N} = \frac{\sum n_j N_j}{M} = -\frac{\partial}{\partial \gamma} \ln \Xi. \tag{A.15}$$

Equations (A.13), (A.15) determine the parameters β, γ implicitly and then α follows from (A.11).

A.2 Connection to Thermodynamics

Entropy is given by

$$\begin{aligned} S &= -k \sum P(E_j, N_j) \ln P(E_j, N_j) = -k \sum P(E_j, N_j)(-\beta E_j - \gamma N_j - \ln \Xi) \\ &= k\beta \overline{E} + k\gamma \overline{N} + k \ln \Xi. \end{aligned} \tag{A.16}$$

From thermodynamics, the Duhem–Gibbs relation is known which states for the free enthalpy

$$G = U - TS + pV = \mu N \tag{A.17}$$

where $U = \overline{E}$ and S, V, N are the thermodynamic averages. Solving for the entropy, we have

$$S = \frac{U + pV - \mu N}{T} \tag{A.18}$$

and comparison with (A.16) shows that

$$\beta = \frac{1}{k_B T} \quad \gamma = -\frac{\mu}{k_B T} \tag{A.19}$$

$$k_B T \ln \Xi = pV. \tag{A.20}$$

The summation over microstates j with energy E_j and N_j particles can be replaced by a double sum over energies $E_i(N)$ and particle number N to give

$$\Xi = \sum_{E,N} \mathrm{e}^{-\beta(E(N) - \mu N)} \tag{A.21}$$

which can be written as a sum over canonical partition functions with different particle numbers

$$\Xi = \sum_N \mathrm{e}^{\beta\mu N} \sum_E \mathrm{e}^{-\beta E(N)} = \sum_N \mathrm{e}^{\beta\mu N} Q(N). \tag{A.22}$$

Appendix B
Classical Approximation of Quantum Motion

In quantum mechanics, the motion of a particle (which could be a whole molecule) in an external potential is described by the time-dependent Schrödinger equation

$$i\hbar\dot{\psi}(\mathbf{r},t) = H\psi(\mathbf{r},t) = \left[-\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\psi(\mathbf{r},t). \tag{B.1}$$

A special kind of solution is a localized wavepacket, which can be approximated as a classical particle as long as dispersion of the wavepacket is negligible. The classical position and momentum are given by the expectation values

$$< \mathbf{r} >=< \psi(\mathbf{r},t)\mathbf{r}\psi(\mathbf{r},t) >=< \psi(\mathbf{r},t)\mathbf{r}\psi(\mathbf{r},t) > \tag{B.2}$$

$$< \mathbf{r} >=< \psi(\mathbf{r},t)\mathbf{p}\psi(\mathbf{r},t) >=< \psi(\mathbf{r},t)\frac{\hbar}{\mathrm{i}}\nabla\psi(\mathbf{r},t) > \tag{B.3}$$

which obey the equations of motion (Ehrenfest theorem)

$$< \dot{\mathbf{r}} >= \frac{1}{\mathrm{i}\hbar} < \psi(\mathbf{r},t)(\mathbf{r}H - H\mathbf{r})\psi(\mathbf{r},t) >$$

$$= \frac{1}{m} < \psi(\mathbf{r},t)\frac{\hbar}{\mathrm{i}}\nabla\psi(\mathbf{r},t) >= \frac{< \mathbf{p} >}{m} \tag{B.4}$$

$$< \dot{\mathbf{p}} >= \frac{1}{\mathrm{i}\hbar} < \psi(\mathbf{r},t)(\mathbf{p}H - H\mathbf{p})\psi(\mathbf{r},t) >= - < \nabla V(\mathbf{r}) > . \tag{B.5}$$

If the variation of the potential gradient over the width of the wavepacket is negligible[1] these look like Newton's equations with a classical force

$$\mathbf{F} = - < \nabla V(\mathbf{r}) > \approx -\nabla V(< \mathbf{r} >). \tag{B.6}$$

[1]Or in some special cases like the harmonic oscillator.

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For the harmonic oscillator with Hamiltonian

$$\hat{H} = \hbar\omega\left(\hat{a}^\dagger\hat{a} + \frac{1}{2}\right) \tag{B.7}$$

and eigenfunctions $|n>$obeying

$$\begin{aligned}
&\hat{H}|n>= \hbar\omega\left(n + \frac{1}{2}\right)|n> \\
&\hat{a}|n>= \sqrt{n}|n-1> \quad \hat{a}^\dagger|n>= \sqrt{n+1}|n+1>
\end{aligned} \tag{B.8}$$

a dispersionless Gaussian wavepacket is provided by the coherent oscillator state (Glauber state)[2]

$$\varphi_\alpha(x,t) = e^{-|\alpha|^2/2}\sum_{n=0}^{\infty} \mathrm{e}^{-\mathrm{i}(n+1/2)\omega t}\frac{\alpha^n}{\sqrt{n!}}|n> \tag{B.9}$$

which for any complex α solves the time dependent Schrödinger equation since

$$\mathrm{i}\hbar\dot{\varphi}_\alpha(x,t) = \hat{H}\varphi_\alpha(x,t) = e^{-|\alpha|^2/2}\sum \hbar\omega\left(n + \frac{1}{2}\right)\mathrm{e}^{-\mathrm{i}(n+1/2)\omega t}\frac{\alpha^n}{\sqrt{n!}}|n>. \tag{B.10}$$

Furthermore, it is an eigenfunction of $\hat{a}$ as can be seen from

$$\begin{aligned}
&\hat{a}\varphi_\alpha(x,t) = e^{-|\alpha|^2/2}\sum_{n=1}^{\infty} \mathrm{e}^{-\mathrm{i}(n+1/2)\omega t}\frac{\alpha^n}{\sqrt{n!}}\sqrt{n}|n-1> \\
&= \mathrm{e}^{-\mathrm{i}\omega t}\alpha\varphi_\alpha(x,t)
\end{aligned} \tag{B.11}$$

from which we find the expectation values

$$< \varphi_\alpha(x,t)\hat{a}\varphi_\alpha(x,t) >= \mathrm{e}^{-\mathrm{i}\omega t}\alpha \tag{B.12}$$

$$< \varphi_\alpha(x,t)\hat{a}^\dagger\varphi_\alpha(x,t) >= \mathrm{e}^{\mathrm{i}\omega t}\alpha^* \tag{B.13}$$

$$\overline{n} =< \varphi_\alpha(x,t)\hat{a}^\dagger\hat{a}\varphi_\alpha(x,t) >= |\alpha|^2 \tag{B.14}$$

$$\overline{H} = \hbar\omega\left(|\alpha|^2 + \frac{1}{2}\right). \tag{B.15}$$

The coherent state is not an eigenfunction of the Hamiltonian. The number of excitations is not sharp. Its variance is

$$\mathrm{Var}(n) =< \varphi_\alpha(x,t)(\hat{a}^\dagger\hat{a})^2\varphi_\alpha(x,t) > -|\alpha|^4 = |\alpha|^2 \tag{B.16}$$

[2]Coherent states are normalized but not orthogonal.

hence the relative uncertainty decreases as $1/\sqrt{\overline{n}}$. Average position and momentum oscillate

$$\overline{x} = \frac{x_0}{\sqrt{2}} 2\Re(\alpha e^{-i\omega t}) = x_0\sqrt{2}|\alpha| \cos(\omega t - \arg(\alpha)) \tag{B.17}$$

$$\overline{p} = \frac{\hbar}{x_0}\sqrt{2}\Im(\alpha(t)) = -\frac{\hbar}{x_0}\sqrt{2}|\alpha| \sin(\omega t - \arg(\alpha)) \tag{B.18}$$

where the characteristic length is

$$x_0 = \sqrt{\frac{\hbar}{m\omega}}. \tag{B.19}$$

For large $\overline{n}$, the values of position and momentum become well defined and the oscillator behaves classically with an amplitude

$$x_0\sqrt{2}|\alpha| = x_0\sqrt{2\overline{n}} = \sqrt{\frac{\overline{H}}{\frac{m\omega^2}{2}}}. \tag{B.20}$$

The quantized electromagnetic field is a sum of harmonic oscillators. The Fourier component of the vector potential

$$\mathbf{A} = \sum_{\mathbf{k},\lambda} \sqrt{\frac{\hbar\omega_k}{2\varepsilon_0 V}} \frac{1}{\omega k} \left(\hat{a}_{k,\lambda}\mathbf{e}_{k,\lambda}e^{i\mathbf{kr}} + \hat{a}^\dagger_{k,\lambda}\mathbf{e}^*_{\mathbf{k},\lambda}e^{-i\mathbf{kr}}\right) \tag{B.21}$$

therefore has to be replaced in the classical limit (B.12)–(B.14) by

$$\begin{aligned}\mathbf{A} &= \sum_{\mathbf{k},\lambda} \sqrt{\frac{\overline{n}\hbar\omega_k}{2\varepsilon_0 V}} \frac{1}{\omega k} \left(\mathbf{e}_{k,\lambda}e^{i(\mathbf{kr}-\omega_k t)} + \mathbf{e}^*_{\mathbf{k},\lambda}e^{-(i\mathbf{kr}-\omega_k t)}\right) \\ &= \sum_{\mathbf{k},\lambda} A_0(\omega_k, \mathbf{k}) \left(\mathbf{e}_{k,\lambda}e^{i(\mathbf{kr}-\omega_k t)} + \mathbf{e}^*_{\mathbf{k},\lambda}e^{-(i\mathbf{kr}-\omega_k t)}\right)\end{aligned} \tag{B.22}$$

and the amplitude is in classical approximation

$$A_0(\omega_k, \mathbf{k}) = \sqrt{\frac{u(\omega_k, \mathbf{k})}{2\varepsilon_0\omega_k^2}}. \tag{B.23}$$

Appendix C
Time Correlation Function of the Displaced Harmonic Oscillator Model

In the following we evaluate the time correlation function of the displaced harmonic oscillator model (19.14)

$$f_r(t) = \left\langle e^{-it\omega_r b_r^\dagger b_r} e^{it\omega_r (b_r^\dagger + g_r)(b_r + g_r)} \right\rangle.$$

C.1 Evaluation of the Time Correlation Function

To proceed we need some theorems which will be derived afterward.

Theorem 1: A displacement of the oscillator potential energy minimum can be formulated as a canonical transformation

$$\hbar\omega_r (b_r^\dagger + g_r)(b_r + g_r) = e^{-g_r(b_r^\dagger - b_r)} \hbar\omega_r b_r^\dagger b_r e^{g_r(b_r^\dagger - b_r)}. \tag{C.1}$$

With the help of this relation the single-mode correlation function becomes

$$F_r(t) = \left\langle e^{-it\omega_r b_r^\dagger b_r} e^{-g_r(b_r^\dagger - b_r)} e^{it\omega_r b_r^\dagger b_r} e^{g_r(b_r^\dagger - b_r)} \right\rangle. \tag{C.2}$$

The first three factors can be interpreted as another canonical transformation. To this end we apply

Theorem 2: The time dependent boson operators are given by

$$e^{-i\omega_r t b_r^\dagger b_r} b_r^\dagger e^{i\omega_r t b_r^\dagger b_r} = b_r^\dagger e^{-i\omega_r t} \tag{C.3}$$

$$e^{-i\omega_r t b_r^\dagger b_r} b_r e^{i\omega_r t b_r^\dagger b_r} = b_r e^{i\omega_r t} \tag{C.4}$$

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to find

$$F_r(t) = \left\langle \exp\left(-g_r(b_r^\dagger e^{-i\omega_r t} - b_r e^{i\omega_r t})\right) \exp\left(g_r(b_r^\dagger - b_r)\right)\right\rangle. \tag{C.5}$$

The two exponentials can be combined due to

Theorem 3: If the commutator of two operators A and B is a c-number then

$$e^{A+B} = e^A e^B e^{-\frac{1}{2}[A,B]}. \tag{C.6}$$

The commutator is

$$-g_r^2[b_r^\dagger e^{-i\omega_r t} - b_r e^{i\omega_r t}, b_r^\dagger - b_r] = -g_r^2(e^{-i\omega_r t} - e^{i\omega_r t}) \tag{C.7}$$

and we have

$$F_r(t) = \exp\left(-\frac{1}{2}g_r^2(e^{-i\omega_r t} - e^{i\omega_r t})\right)\left\langle \exp\left(-g_r b_r^\dagger(e^{-i\omega_r t} - 1) + g_r b_r(e^{i\omega_{tr}} - 1)\right)\right\rangle. \tag{C.8}$$

The remaining average is easily evaluated due to

Theorem 4: For a linear combination of b_r and $b_r^\dagger$ the second order cumulant expansion is exact

$$\left\langle e^{\mu b^\dagger + \tau b}\right\rangle = e^{\frac{1}{2}\langle(\mu b^\dagger + \tau b)^2\rangle} = e^{\mu\tau\langle b^\dagger b + 1/2\rangle}. \tag{C.9}$$

The average square is

$$\begin{aligned} &\left\langle \left(b_r^\dagger(e^{-i\omega_r t} - 1) - b_r(e^{i\omega_r t} - 1)\right)^2\right\rangle g_r^2 \\ &= -g_r^2(2 - e^{i\omega_r t} - e^{-i\omega_r t})\left\langle b_r^\dagger b_r + b_r b_r^\dagger\right\rangle \\ &= -g_r^2(2 - e^{i\omega_r t} - e^{-i\omega_r t})(2\overline{n}_r + 1) \end{aligned} \tag{C.10}$$

with the average phonon number[3]

$$\overline{n}_r = \frac{1}{e^{\beta\hbar\omega_r} - 1}. \tag{C.11}$$

Finally we have

$$\begin{aligned} F_r(t) &= \exp\left(-\frac{1}{2}g_r^2(2 - e^{i\omega_r t} - e^{-i\omega_r t})(2\overline{n}_r + 1) - \frac{1}{2}g_r^2(e^{-i\omega_r t} - e^{i\omega_r t})\right) \\ &= \exp\left(g_r^2\left[(e^{i\omega_r t} - 1)(\overline{n}_r + 1) + (e^{-i\omega_r t} - 1)\overline{n}_r\right]\right) \end{aligned} \tag{C.12}$$

[3] In the following we use the abbreviation $\beta = 1/k_B T$.

or, using trigonometric functions

$$F_r(t) = \exp\left(g_r^2\left[(\cos\omega_r t - 1 + \mathrm{i}\sin\omega_r t)(\overline{n}_r + 1) + (\cos\omega_r t - 1 - \mathrm{i}\sin\omega_r t)\overline{n}_r\right]\right)$$
$$= \exp\left(g_r^2(\overline{n}_r + 1)(\cos\omega_r t - 1) + \mathrm{i}g_r^2\sin\omega_r t\right). \quad \text{(C.13)}$$

C.2 Boson Algebra

C.2.1 Derivation of Theorem 1

Consider the following unitary transformation

$$A = \mathrm{e}^{-g(b^\dagger - b)}b^\dagger b\mathrm{e}^{g(b^\dagger - b)} \quad \text{(C.14)}$$

and make a series expansion

$$A = A(0) + g\frac{\mathrm{d}A}{\mathrm{d}g} + \frac{1}{2}g^2\frac{\mathrm{d}^2A}{\mathrm{d}g^2}\cdots \quad \text{(C.15)}$$

The derivatives are

$$\frac{\mathrm{d}A}{\mathrm{d}g}|_{g=0} = [b^\dagger b, b^\dagger - b] = b^\dagger[b, b^\dagger] + [b^\dagger, -b]b$$
$$= (b + b^+) \quad \text{(C.16)}$$

$$\frac{\mathrm{d}^2A}{\mathrm{d}g^2}|_{g=0} = [[b^\dagger b, b^\dagger - b], b^\dagger - b]$$
$$= [b + b^\dagger, b^\dagger - b,] = 2 \quad \text{(C.17)}$$

$$\frac{\mathrm{d}^nA}{\mathrm{d}g^n}|_{g=0} = 0 \quad \text{for } n \geq 3 \quad \text{(C.18)}$$

and the series is finite

$$A = b^\dagger b + g(b^\dagger + b) + g^2 = (b^\dagger + g)(b + g). \quad \text{(C.19)}$$

Hence for any of the normal modes

$$\hbar\omega_r(b_r^\dagger + g_r)(b_r + g_r) = \mathrm{e}^{-g_r(b_r^\dagger - b_r)}\hbar\omega_r b_r^\dagger b_r\mathrm{e}^{g_r(b_r^\dagger - b_r)}. \quad \text{(C.20)}$$

C.2.2 Derivation of Theorem 2

Consider

$$A = e^{\tau b^\dagger b} b e^{-\tau b^\dagger b} \quad \text{with } \tau = -i\omega t. \tag{C.21}$$

Make again a series expansion

$$\frac{dA}{d\tau} = [b^+ b, b] = -b \tag{C.22}$$

$$\frac{d^2 A}{d\tau^2} = [b^+ b, -b] = b \quad \text{etc.} \tag{C.23}$$

$$A = b\left(1 - \tau + \frac{\tau^2}{2} - \cdots\right) = b\left(1 + it\omega + \frac{(it\omega)^2}{2} + \cdots\right) = b\, e^{i\omega t}. \tag{C.24}$$

Hermitian conjugation gives

$$e^{-i\omega t b^\dagger b} b^+ e^{i\omega t b^\dagger b} = b^\dagger e^{-i\omega t}. \tag{C.25}$$

C.2.3 Derivation of Theorem 3

Consider the operator

$$f(\tau) = e^{-B\tau} e^{-A\tau} e^{(A+B)\tau} \tag{C.26}$$

as a function of the c-number τ. Differentiation gives

$$\frac{df(\tau)}{d\tau} = e^{-B\tau}(-A - B)e^{-A\tau}e^{(A+B)\tau} + e^{-B\tau}e^{-A\tau}(A + B)e^{(A+B)\tau}$$
$$= e^{-B\tau}[e^{-A\tau}, B]e^{(A+B)\tau}. \tag{C.27}$$

Now if the commutator $[A, B]$ is a c-number then

$$[A^n, B] = A[A^{n-1}, B] + [A, B]A^{n-1} = \cdots n[A, B]A^{n-1} \tag{C.28}$$

and therefore

$$[e^{-A\tau}, B] = \sum_{n=0}^{\infty} \frac{(-\tau)^n}{n!}[A^n, B] = \sum_n \frac{(-\tau)^n}{(n-1)!}A^{n-1}[A, B]$$

$$= -\tau[A, B]e^{-A\tau} \tag{C.29}$$

and (C.27) gives

$$\frac{df(\tau)}{d\tau} = -\tau[A, B]e^{-B\tau}e^{-A\tau}e^{(A+B)\tau} = -\tau[A, B]f(\tau) \tag{C.30}$$

which is for the initial condition $f(0) = 1$ solved by

$$f(\tau) = \exp\left(-\frac{\tau^2}{2}[A, B]\right). \tag{C.31}$$

Substituting $\tau = 1$ finally gives

$$e^{-B}e^{-A}e^{(A+B)} = e^{-\frac{1}{2}[A,B]}. \tag{C.32}$$

C.2.4 Derivation of Theorem 4

This derivation is based on (200). For one single oscillator consider the linear combination

$$\mu b^\dagger + \tau b = A + B \tag{C.33}$$

$$[A, B] = -\mu\tau. \tag{C.34}$$

Application of (C.32) gives

$$\left\langle e^{\mu b^\dagger + \tau b}\right\rangle = \left\langle e^{\mu b^\dagger} e^{\tau b}\right\rangle e^{\mu\tau/2} \tag{C.35}$$

and after exchange of A and B

$$\left\langle e^{\mu b^\dagger + \tau b}\right\rangle = \left\langle e^{\tau b} e^{\mu b^\dagger}\right\rangle e^{-\mu\tau/2}. \tag{C.36}$$

Combination of the last two equations gives

$$\left\langle e^{\tau b} e^{\mu b^\dagger}\right\rangle = \left\langle e^{\mu b^\dagger} e^{\tau b}\right\rangle e^{\mu\tau}. \tag{C.37}$$

Using the explicit form of the averages we find

$$Q^{-1}\,\mathrm{tr}\left(e^{-\beta\hbar\omega b^\dagger b} e^{\tau b} e^{\mu b^\dagger}\right) = Q^{-1}\,\mathrm{tr}\left(e^{-\beta\hbar\omega b^\dagger b} e^{\mu b^\dagger} e^{\tau b}\right) e^{\mu\tau} \tag{C.38}$$

and due to the cyclic invariance of the trace operation the right side becomes

$$= Q^{-1}\mathrm{tr}(e^{\tau b} e^{-\beta\hbar\omega b^\dagger b} e^{\mu b^\dagger})e^{\mu\tau} \tag{C.39}$$

which can be written as

$$= Q^{-1}\mathrm{tr}(\mathrm{e}^{-\beta\hbar\omega b^\dagger b}\mathrm{e}^{+\beta\hbar\omega b^\dagger b}\mathrm{e}^{\tau b}\mathrm{e}^{-\beta\hbar\omega b^\dagger b}\mathrm{e}^{\mu b^\dagger})\mathrm{e}^{\mu\tau}$$

$$= \left\langle \mathrm{e}^{+\beta\hbar\omega b^\dagger b}\mathrm{e}^{\tau b}\mathrm{e}^{-\beta\hbar\omega b^\dagger b}\mathrm{e}^{\mu b^\dagger}\right\rangle \mathrm{e}^{\mu\tau}. \tag{C.40}$$

Application of (C.3) finally gives the relation

$$\langle \exp(\tau b)\exp(\mu b^\dagger)\rangle = \langle \exp\left(\tau \mathrm{e}^{-\beta\hbar\omega} b\right)\exp\left(\mu b^\dagger\right)\rangle \mathrm{e}^{\mu\tau} \tag{C.41}$$

which can be iterated to give

$$\begin{aligned}\langle \exp(\tau b)\exp(\mu b^\dagger)\rangle &= \langle \exp\left(\tau \mathrm{e}^{-2\beta\hbar\omega} b\right)\exp\left(\mu b^\dagger\right)\rangle \mathrm{e}^{\mu\tau(1+\mathrm{e}^{-\beta\hbar\omega})} = \cdots \\ &= \langle \exp\left(\tau \mathrm{e}^{-(n+1)\beta\hbar\omega} b\right)\exp\left(\mu b^\dagger\right)\rangle \mathrm{e}^{\mu\tau(1+\mathrm{e}^{-\beta\hbar\omega}+\cdots+\mathrm{e}^{-n\beta\hbar\omega})}\end{aligned} \tag{C.42}$$

and in the limit $n \to \infty$

$$\left\langle \exp(\tau b)\exp(\mu b^\dagger)\right\rangle = \left\langle \exp(\mu b^\dagger)\right\rangle \exp\left(\frac{\mu\tau}{1-\mathrm{e}^{-\beta\hbar\omega}}\right) = \exp\left(\frac{\mu\tau}{1-\mathrm{e}^{-\beta\hbar\omega}}\right) \tag{C.43}$$

since only the zero-order term of the expansion of the exponential gives a nonzero contribution to the average. With the average number of vibrations

$$\overline{n} = \frac{1}{\mathrm{e}^{\beta\hbar\omega}-1} \tag{C.44}$$

we have

$$\langle \exp(\tau b)\exp(\mu b^\dagger)\rangle = \exp\left(\mu\tau(\overline{n}+1)\right) \tag{C.45}$$

and finally

$$\left\langle \mathrm{e}^{\mu b^\dagger + \tau b}\right\rangle = \mathrm{e}^{\mu\tau(\overline{n}+1/2)}. \tag{C.46}$$

The average of the square is

$$\langle (\mu b^\dagger + \tau b)^2\rangle = \mu\tau\langle b^\dagger b + b\, b^\dagger\rangle = \mu\tau(2\overline{n}+1) \tag{C.47}$$

which shows the validity of the theorem.

Appendix D
Complex Cotangent Function

The cotangent of an imaginary argument can be written as

$$\cot(iy) = \frac{\cosh y}{i \sinh y} = -i\coth y \tag{D.1}$$

which for large $|y|$ approximates

$$\cot(iy) \rightarrow -i \quad \text{sign}(y). \tag{D.2}$$

For a complex argument we write (Fig. D.1)

$$\cot(x + iy) = \frac{1 + i \coth y \cot x}{i \coth y - \cot x} \tag{D.3}$$

which for large y approximates

$$\frac{1 + i \frac{1+e^{-2y}}{1-e^{-2y}} \cot x}{i \frac{1+e^{-2y}}{1-e^{-2y}} - \cot x} = -i + \frac{2i(\cot x + 1)}{i - \cot x} e^{-2y} + \cdots \tag{D.4}$$

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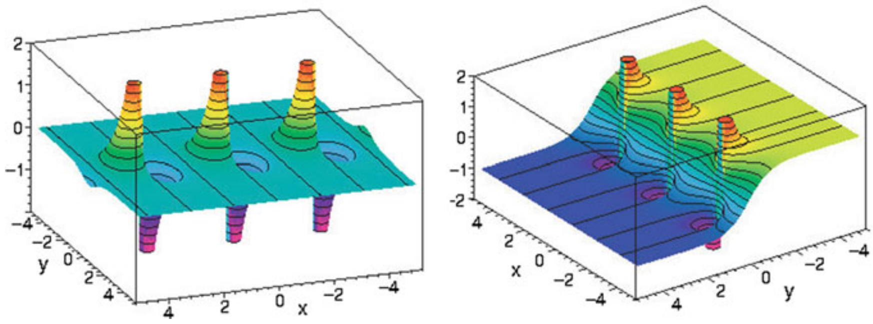

Fig. D.1 Complex cotangent function. Real (*left*) and imaginary (*right*) part of $\cot(x+iy)$ are shown

and for large negative y

$$\frac{1-i\,\frac{1+e^{2y}}{1-e^{2y}}\cot x}{-i\,\frac{1+e^{2y}}{1-e^{2y}}-\cot x}=i+\frac{2i(\cot x-i)}{i+\cot x}e^{2y}+\cdots \tag{D.5}$$

Appendix E
The Saddle Point Method

The saddle point method is an asymptotic method to calculate integrals of the type

$$\int_{-\infty}^{\infty} e^{\phi(x)} dx \tag{E.1}$$

If the function $\phi(x)$ has a maximum at x_0 then the integrand also has a maximum there and the integral can be approximated by expanding the exponent around x_0

$$\phi(x) = \phi(x_0) + \frac{1}{2}\frac{d^2\phi(x)}{dx^2}_{|x_0}(x - x_0)^2 + \cdots \tag{E.2}$$

as a Gaussian integral

$$\int_{-\infty}^{\infty} e^{\phi(x)} dx \approx e^{\phi(x_0)} \sqrt{\frac{2\pi}{|\phi''(x_0)|}}. \tag{E.3}$$

The method can be extended to integrals in the complex plane

$$\int_C e^{\phi(z)} dz = \int_C e^{\Re(\phi(z))} e^{i\Im(\phi(z))} dz. \tag{E.4}$$

If the integration contour is deformed such that the imaginary part is constant (stationary phase), then (Fig. E.1)

$$\int_C e^{\phi(z)} dz = e^{i\Im(\phi(z_0))} \int_{C'} e^{\Re(\phi(z))} dz. \tag{E.5}$$

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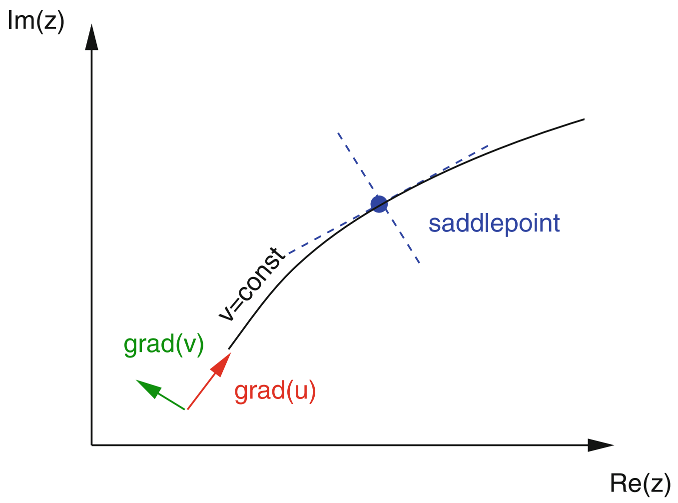

Fig. E.1 Saddle point method

The contour C' and the expansion point are determined from

$$\phi'(z_0) = 0 \tag{E.6}$$

$$\phi(z) = u(z) + iv(z) = u(z) + iv(z_0). \tag{E.7}$$

Now consider the imaginary part as a function of (x, y). The gradient is according to Cauchy and Riemann

$$\nabla v(x, y) = (\frac{\partial v}{\partial x}, \frac{\partial v}{\partial y}) = (-\frac{\partial u}{\partial y}, \frac{\partial u}{\partial x}) \tag{E.8}$$

which is perpendicular to the gradient of the real part

$$\nabla u(x, y) = (\frac{\partial u}{\partial x}, \frac{\partial u}{\partial y}) \tag{E.9}$$

which gives the direction of steepest descent. The method is known as saddle point method since a maximum of the real part always is a saddle point. From the expansion

$$\phi(z) = \phi(z_0) + \frac{1}{2}\phi''(z_0)(z - z_0)^2 + \cdots \tag{E.10}$$

and

$$dz^2 = dx^2 - dy^2 + 2i dx\, dy \tag{E.11}$$

we find

$$\begin{aligned}\Re(\phi(z)) &= \Re(\phi(z_0)) - \frac{1}{2}\left(\Re(\phi''(z_0))(dx^2 - dy^2) - 2\Im(\phi''(z_0))dx\,dy\right)\\ &= \Re(\phi(z_0)) - \frac{1}{2}(dx, dy)\begin{pmatrix} \Re(\phi'') & -\Im(\phi'') \\ -\Im(\phi'') & -\Re(\phi'')\end{pmatrix}\begin{pmatrix} dx \\ dy\end{pmatrix}.\end{aligned} \tag{E.12}$$

The eigenvalues of the matrix are

$$\pm\sqrt{\Re(\phi'')^2 + \Im(\phi'')^2} = \pm|\phi''| \tag{E.13}$$

and the eigenvectors

$$\begin{pmatrix} dx \\ dy\end{pmatrix} \propto \begin{pmatrix} 1 \\ \frac{\Re(\phi'')\pm|\phi''|}{\Im(\phi'')}\end{pmatrix}. \tag{E.14}$$

Similarly, the imaginary part

$$\begin{aligned}\Im(\phi(z)) &= \Im(\phi(z_0)) + \Re(\phi''(z_0))dxdy + \frac{1}{2}\Im(\phi''(z_0))(dx^2 - dy^2)\\ &= \Im(\phi(z_0)) + \frac{1}{2}(dx, dy)\begin{pmatrix} \Im(\phi'') & \Re(\phi'') \\ \Re(\phi'') & -\Im(\phi'')\end{pmatrix}\begin{pmatrix} dx \\ dy\end{pmatrix}.\end{aligned} \tag{E.15}$$

The direction of stationary phase is given by

$$dy = \frac{\Re(\phi'') \pm |\phi''|}{\Im(\phi'')}dx \tag{E.16}$$

hence is along the eigenvectors of the real part.

Solutions

Problems of Chap. 1

1.1 Gaussian Polymer Model

$$\Delta\mathbf{r}_i = \mathbf{r}_i - \mathbf{r}_{i-1} \quad i = 1 \cdots N$$

(a)

$$P(\Delta\mathbf{r}_i) = \frac{1}{b^3}\sqrt{\frac{27}{8\pi^3}} \exp\left\{-\frac{3(\Delta\mathbf{r}_i)^2}{2b^2}\right\}$$

is the normalized probability function with

$$\int_{-\infty}^{\infty} P(\Delta\mathbf{r}_i) d^3\Delta\mathbf{r}_i = 1 \quad \int_{-\infty}^{\infty} \Delta\mathbf{r}_i^2 P(\Delta\mathbf{r}_i) d^3\Delta\mathbf{r}_i = b^2$$

(b)

$$\mathbf{r}_N - \mathbf{r}_0 = \sum_{i=1}^{N} \Delta\mathbf{r}_i$$

$$P\left(\sum_{i=1}^{N} \Delta\mathbf{r}_i = \mathbf{R}\right) = \int_{-\infty}^{\infty} d^3\Delta\mathbf{r}_1 \cdots \int_{-\infty}^{\infty} d^3\Delta\mathbf{r}_N \prod_{i=1}^{N} P(\Delta\mathbf{r}_i)\delta\left(\mathbf{R} - \sum_{i=1}^{N} \Delta\mathbf{r}_i\right)$$

$$= \int \frac{1}{(2\pi)^3} d^3\mathbf{k} e^{\mathbf{ikR}} \int_{-\infty}^{\infty} d^3\Delta\mathbf{r}_1 \cdots \int_{-\infty}^{\infty} d^3\Delta\mathbf{r}_N \left(\frac{1}{b^3}\sqrt{\frac{27}{8\pi^3}}\right)^N$$

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$$\times \prod \exp\left\{-\frac{3\Delta\mathbf{r}_i^2}{2b^2} - \mathrm{i}\mathbf{k}\Delta\mathbf{r}_i\right\}$$

$$= \int \frac{1}{(2\pi)^3} d^3\mathbf{k} e^{\mathrm{i}\mathbf{k}\mathbf{R}} \left[\left(\frac{1}{b^3}\sqrt{\frac{27}{8\pi^3}}\right)\int_{-\infty}^{\infty} d^3\Delta\mathbf{r} \exp\left\{-\frac{3\Delta\mathbf{r}^2}{2b^2} - \mathrm{i}\mathbf{k}\Delta\mathbf{r}\right\}\right]^N$$

$$= \int \frac{1}{(2\pi)^3} d^3\mathbf{k} e^{\mathrm{i}\mathbf{k}\mathbf{R}} \exp(-\frac{Nb^2}{6}\mathbf{k}^2)$$

$$= \frac{1}{b^3}\sqrt{\frac{27}{8\pi^3 N^3}} \exp\left\{-\frac{3\mathbf{R}^2}{2Nb^2}\right\}$$

(c)

$$\exp\left\{-\frac{1}{k_B T}\left(\frac{f}{2}\sum \Delta\mathbf{r}_i^2 - \kappa \sum \Delta\mathbf{r}_i\right)\right\} = \prod_i \exp\left\{-\frac{1}{k_B T}\left(\frac{f}{2}\Delta\mathbf{r}_i^2 - \kappa\Delta\mathbf{r}_i\right)\right\}$$

$$\frac{f}{2k_B T} = \frac{3}{2b^2} \rightarrow f = \frac{3k_B T}{b^2}$$

(d)

$$x_N - x_0 = \frac{N\kappa}{f} \quad y_N - y_0 = z_N - z_0 = 0$$

$$L = x_N - x_0 = \frac{N\kappa b^2}{3k_B T}$$

1.2 Three-dimensional Polymer Model

(a)

$$Nb^2$$

(b)

$$b^2\left(N\frac{1+x}{1-x} + \frac{2x(x^2-1)}{(1-x)^2}\right) \quad \text{with } x = \cos\theta$$

$$\approx Nb^2\frac{1+\cos x}{1-\cos x}$$

(c)

$$Nb^2 \frac{(1+\cos\theta_1)(1+\cos\theta_2)}{1-\cos\theta_1\cos\theta_2}$$

(d) $N \gg a/b$ with the coherence length

$$a = b\frac{1+\cos x}{(1-\cos x)\cos\frac{x}{2}}$$

(e)

$$Nb^2\left(\frac{4}{\theta^2}-1\right) - b^2\left(\frac{4}{\theta^2}-\frac{8}{\theta^4}\right)$$

1.3 Two-Component Model

(a)

$$\kappa = -k_B T\frac{1}{l_\alpha - l_\beta}\ln\left(\frac{Ml_\alpha - L}{L - Ml_\beta}\right)$$

$$-k_B T\left(\frac{1}{2Ml_\alpha - 2L} + \frac{1}{2Ml_\beta - L} + \frac{l_\alpha - l_\beta}{12(L-Ml_\beta)^2} - \frac{l_\alpha - l_\beta}{12(Ml_\alpha - L)^2}\right)$$

The exact solution can be written with the digamma function Ψ which is well known by algebra programs as

$$\kappa = -k_B T\frac{1}{l_\alpha - l_\beta}\left(-\Psi(\frac{L-Ml_\beta}{l_\alpha - l_\beta}+1) + \Psi(\frac{Ml_\alpha - L}{l_\alpha - l_\beta})\right)$$

The error of the asymptotic expansion is largest for $L \approx Ml_\alpha$ or $L \approx Ml_\beta$. The following table compares the relative errors of the Stirling approximation and the higher order asymptotic expansion for $M = 1000$ and $l_\beta/l_\alpha = 2$

L/l_α	Stirling	asympt. expansion
1000.2	0.18	0.13
1000.5	0.11	0.009
1001	0.065	0.00094
1005	0.019	$2.5{*}10^{-6}$

(b)

$$Z(\kappa, M, T) = \left(\mathrm{e}^{\frac{\kappa l_\alpha}{k_B T}} + \mathrm{e}^{\frac{\kappa l_\beta}{k_B T}}\right)^M$$

$$\overline{L} = M \frac{l_\alpha e^{\frac{\kappa l_\alpha}{k_B T}} + l_\beta e^{\frac{\kappa l_\beta}{k_B T}}}{e^{\frac{\kappa l_\alpha}{k_B T}} + e^{\frac{\kappa l_\beta}{k_B T}}}$$

$$\overline{L^2} = \overline{L}^2 + M e^{\kappa(l_\alpha + l_\beta)/k_B T} \left(\frac{l_\alpha - l_\beta}{e^{\kappa l_\alpha / k_B T} + e^{\kappa l_\beta / k_B T}} \right)^2$$

$$\sigma^2 = M e^{\kappa(l_\alpha + l_\beta)/k_B T} \left(\frac{l_\alpha - l_\beta}{e^{\kappa l_\alpha / k_B T} + e^{\kappa l_\beta / k_B T}} \right)^2$$

$$\frac{\sigma}{\overline{\overline{L}}} \sim \frac{1}{\sqrt{N}}$$

$$\frac{\partial \sigma}{\partial \kappa} = 0 \text{ for } (l_\alpha + l_\beta) = 2 \frac{l_\alpha e^{\kappa l_\alpha / k_B T} + l_\beta e^{\kappa l_\beta / k_B T}}{e^{\kappa l_\alpha / k_B T} + e^{\kappa l_\beta / k_B T}}$$

hence for

$$\kappa = 0$$

$$\frac{\partial^2 \sigma^2}{\partial \kappa^2}(\kappa = 0) = -\frac{M}{k (k_B T)^2} (l_\alpha - l_\beta)^2 < 0 \rightarrow \text{ maximum}$$

also a maximum of σ since the square root is monotonous.

Problems of Chap. 2

2.1 Osmotic Pressure of a Polymer Solution

$$\mu_\alpha(P,T) - \mu_\alpha^0(P,T) = k_B T \left(\ln(1 - \phi_\beta) + (1 - \frac{1}{M})\phi_\beta + \chi \phi_\beta^2 \right)$$

$$\mu_\alpha^0(P',T) - \mu_\alpha^0(P,T) = \mu_\alpha(P,T) - \mu_\alpha^0(P,T) = -\Pi \frac{\partial \mu_\alpha^0(P,T)}{\partial P}$$

$$\Pi = -\left(\frac{\partial \mu_\alpha^0(P,T)}{\partial P} \right)^{-1} k_B T \left(\ln(1 - \phi_\beta) + (1 - \frac{1}{M})\phi_\beta + \chi \phi_\beta^2 \right)$$

For the pure solvent

$$\mu_\alpha^0 = \frac{G}{N_\alpha}$$

$$dG = -SdT + VdP + \mu_\alpha^0(P,T)dN$$

$$\frac{\partial \mu_\alpha^0}{\partial P}\Big|_{T,N_\alpha} = \frac{V}{N_\alpha}$$

$$\Pi = -\frac{N_\alpha}{V}k_BT\left(-\phi_\beta - \frac{1}{2}\phi_\beta^2 - \frac{1}{3}\phi_\beta^3 + \cdots + (1-\frac{1}{M})\phi_\beta + \chi\phi_\beta^2\right)$$

$$= \frac{N_\alpha k_BT}{V}\left(\frac{1}{M}\phi_\beta + (\frac{1}{2}-\chi)\phi_\beta^2 + \cdots\right)$$

$$\chi = \frac{\chi_0 T_0}{T}$$

high T:

$$\frac{1}{2} - \chi > 0 \quad \Pi > 0 \text{ good solvent}$$

low T:

$$\Pi < 0 \text{ bad solvent, possibly phase separation}$$

2.2 Polymer Mixture

$$\Delta F = Nk_BT\left(\frac{\phi_1}{M_1}\ln\phi_1 + \frac{\phi_2}{M_2}\ln\phi_2 + \chi\phi_1\phi_2\right)$$

$$\phi_{2,c} = \frac{1}{1+\sqrt{\frac{M_2}{M_1}}}$$

$$\chi_c = \frac{1}{2}(\sqrt{M_1}+\sqrt{M_2})(\frac{1}{M_2\sqrt{M_1}} + \frac{1}{M_1\sqrt{M_2}})$$

symmetric case

$$\phi_c = \frac{1}{2}$$

$$\chi_c = \frac{2}{M} \text{ can be small, demixing possible}$$

Problems of Chap. 4

4.1 Membrane Potential

$$\Phi_I = B\mathrm{e}^{\kappa x} \quad \Phi_{II} = B\left(1 + \frac{\epsilon_W}{\epsilon_M}\kappa x\right) \quad \Phi_{III} = V - B\mathrm{e}^{-\kappa(x-L)}$$

$$B = \frac{V}{2 + \frac{\epsilon_w}{\epsilon_M}\kappa L}$$

$$Q/A = \epsilon_W \kappa B \quad \text{per area } A$$

$$C/A = \frac{Q/A}{V} = \frac{\epsilon_W \kappa}{2 + \frac{\epsilon_W}{\epsilon_M}\kappa L} = \frac{1}{\frac{2}{\epsilon_w \kappa} + \frac{L}{\epsilon_M}}$$

4.2 Ion Activity

$$k_B T \ln \gamma^c = k_B T \ln \frac{a}{c} = -\frac{Z^2 \mathrm{e}^2}{8\pi\epsilon} \frac{\kappa}{1 + \kappa R}$$

$$\ln \gamma_+^c = \ln \gamma_-^c = -\frac{1}{k_B T} \frac{Z^2 \mathrm{e}^2}{8\pi\epsilon} \frac{\kappa}{1 + \kappa R}$$

$$\ln \gamma_\pm^c = -\frac{1}{k_B T} \frac{Z^2 \mathrm{e}^2}{16\pi\epsilon} \left(\frac{\kappa}{1 + \kappa R_+} + \frac{\kappa}{1 + \kappa R_-}\right)$$

$\kappa \rightarrow 0$ for dilute solution

$$\ln \gamma_\pm^c \rightarrow -\frac{1}{k_B T} \frac{Z^2 \mathrm{e}^2 \kappa}{8\pi\epsilon}$$

Problems of Chap. 5

5.1 Abnormal Titration Curve

$$\Delta G(B, B) = 0$$

$$\Delta G(BH^+, B) = \Delta G_{1,int}$$

$$\Delta G(B, BH^+) = \Delta G_{2,int}$$

$$\Delta G(BH^+, BH^+) = \Delta G_{1,int} + \Delta G_{2,int} + W_{1,2}$$

$$\Xi = 1 + \mathrm{e}^{-\beta(\Delta G_{1,int}-\mu)} + \mathrm{e}^{-\beta(\Delta G_{2,int}-\mu)} + \mathrm{e}^{-\beta(\Delta G_{1,int}+\Delta G_{2,int}-W+2\mu)}$$

$$\overline{s_1} = \frac{\mathrm{e}^{-\beta(\Delta G_{1,int}-\mu)} + \mathrm{e}^{-\beta(\Delta G_{1,int}+\Delta G_{2,int}-W+2\mu)}}{\Xi}$$

$$\overline{s_2} = \frac{\mathrm{e}^{-\beta(\Delta G_{2,int}-\mu)} + \mathrm{e}^{-\beta(\Delta G_{1,int}+\Delta G_{2,int}-W+2\mu)}}{\Xi}$$

Problems of Chap. 6

6.1 pH-Dependence of Enzyme Activity

$$\frac{r}{r_{max}} = \frac{1}{1 + (1 + \frac{c_{H+}}{K})\frac{K_M}{c_S}}$$

$$K = \frac{c_{H+}c_{S-}}{c_{HS}} \quad c_s = c_{S-} + c_{HS}$$

6.2 Polymerization at the End of a Polymer

$$c_{iM} = Kc_M c_{(i-1)M} = \cdots = \frac{(Kc_M)^i}{K}$$

$$< i >= \frac{\sum_{i=1}^{\infty} i(Kc_M)^i}{\sum_{i=1}^{\infty}(Kc_M)^i} = \frac{1}{1 - Kc_M} \text{ for } Kc_M < 1$$

6.3 Primary Salt Effect

$$r = k_1 c_X$$

$$K = \frac{c_X}{c_A c_B} \exp\left\{-\frac{Z_A Z_B e^2 \kappa}{4\pi\epsilon k_B T}\right\}$$

$$c_X = K c_A c_B \exp\left\{\frac{Z_A Z_B e^2 \kappa}{4\pi\epsilon k_B T}\right\}$$

Problems of Chap. 7

7.1 Smoluchowski Equation

$$P(t+\Delta t, x) = e^{\Delta t \frac{\partial}{\partial t}} P(t,x)$$

$$w^{\pm}(x \pm \Delta x) P(t, x \pm \Delta x) = e^{\pm \Delta x \frac{\partial}{\partial x}} w^{\pm}(x) P(t,x)$$

$$e^{\Delta t \frac{\partial}{\partial t}} P(t,x) = e^{\Delta x \frac{\partial}{\partial x}} w^{+}(x) P(t,x) + e^{-\Delta x \frac{\partial}{\partial x}} w^{-}(x) P(t,x)$$

$$P(t,x) + \Delta t \frac{\partial}{\partial t} P(t,x) + \cdots = (w^{+}(x) + w^{-}(x)) P(x,t)$$

$$+\Delta x \frac{\partial}{\partial x}(w^{+}(x) - w^{-}(x)) P(x,t) + \frac{\Delta x^2}{2} \frac{\partial^2}{\partial x^2}(w^{+}(x) + w^{-}(x)) P(x,t) + \cdots$$

$$\frac{\partial}{\partial t} P(t,x) = \frac{\Delta x}{\Delta t} \frac{\partial}{\partial x}(w^{+}(x) - w^{-}(x)) P(x,t) + \frac{\Delta x^2}{\Delta t} \frac{\partial^2}{\partial x^2} P(x,t) + \cdots$$

$$D = \frac{\Delta x^2}{\Delta t} \quad K(x) = -\frac{k_B T}{\Delta x}(w^{+}(x) - w^{-}(x))$$

7.2 Eigenvalue Solution to the Smoluchowski Equation

$$-\frac{k_B T}{m\gamma} e^{-U/k_B T} \left(\frac{\partial}{\partial x} e^{U/k_B T} W\right)$$

$$= -\frac{k_B T}{m\gamma} e^{-U/k_B T} \left(e^{U/k_B T} \frac{\partial W}{\partial x} + e^{U/k_B T} W \frac{1}{k_B T} \frac{\partial U}{\partial x} \right)$$

$$= -\frac{k_B T}{m\gamma} \frac{\partial W}{\partial x} - \frac{1}{m\gamma} \frac{\partial U}{\partial x} W = S$$

$$\mathfrak{L}_{FP} W = -\frac{\partial}{\partial x} S = \frac{\partial}{\partial x} \frac{k_B T}{m\gamma} e^{-U/k_B T} \left(\frac{\partial}{\partial x} e^{U/k_B T} W \right)$$

$$\mathfrak{L}_{FP} = \frac{k_B T}{m\gamma} \frac{\partial}{\partial x} e^{-U/k_B T} \frac{\partial}{\partial x} e^{U/k_B T}$$

$$\mathfrak{L} = e^{U/2k_B T} \mathfrak{L}_{FP} e^{-U/2k_B T} = e^{U/2k_B T} \frac{k_B T}{m\gamma} \frac{\partial}{\partial x} e^{-U/k_B T} \frac{\partial}{\partial x} e^{U/2k_B T}$$

$$\mathfrak{L}^H = e^{U/2k_B T} \left(-\frac{\partial}{\partial x} \right) e^{-U/k_B T} \left(-\frac{\partial}{\partial x} \right) \frac{k_B T}{m\gamma} e^{U/2k_B T} = \mathfrak{L}$$

since

$$\frac{k_B T}{m\gamma} = \text{ const}$$

For an eigenfunction ψ of $\mathfrak{L}$ we have

$$\lambda\psi = \mathfrak{L}\psi = e^{U/2k_B T} \mathfrak{L}_{FP} e^{-U/2k_B T} \psi$$

hence

$$\mathfrak{L}_{FP} \left(e^{-U/2k_B T} \psi \right) = \lambda \left(e^{-U/2k_B T} \psi \right)$$

gives an Eigenfunction of the Focker-Planck operator to the same eigenvalue λ. A solution of the Smoluchowski equation is then given by

$$W(x, t) = e^{\lambda t} e^{-U/2k_B T} \psi(x)$$

The Hermitian operator is very similar to the harmonic oscillator in second quantization

$$\mathfrak{L} = \frac{k_B T}{m\gamma} \left(e^{U/2k_B T} \frac{\partial}{\partial x} e^{-U/2k_B T} \right) \left(e^{-U/2k_B T} \frac{\partial}{\partial x} e^{U/2k_B T} \right)$$

$$= \frac{k_B T}{m\gamma}\left(\frac{\partial}{\partial x} - \frac{1}{2k_B T}\frac{\partial U}{\partial x}\right)\left(\frac{\partial}{\partial x} + \frac{1}{2k_B T}\frac{\partial U}{\partial x}\right)$$

$$= \frac{k_B T}{m\gamma}\left(\frac{\partial}{\partial x} - \frac{m\omega^2}{2k_B T}x\right)\left(\frac{\partial}{\partial x} + \frac{m\omega^2}{2k_B T}x\right)$$

$$= -\frac{\omega^2}{\gamma}\left(\sqrt{\frac{k_B T}{m\omega^2}}\frac{\partial}{\partial x} - \frac{1}{2}\sqrt{\frac{m\omega^2}{k_B T}}x\right)\left(\sqrt{\frac{k_B T}{m\omega^2}}\frac{\partial}{\partial x} + \frac{1}{2}\sqrt{\frac{m\omega^2}{k_B T}}x\right)$$

$$= -\frac{\omega^2}{\gamma}\left(\frac{\partial}{\partial \xi} - \frac{1}{2}\xi\right)\left(\frac{\partial}{\partial \xi} + \frac{1}{2}\xi\right) = -\frac{\omega^2}{\gamma}b^+ b$$

with boson operators

$$b^+ b - b b^+ = 1.$$

From comparison with the harmonic oscillator we know the eigenvalues

$$\lambda_n = -\frac{\omega^2}{\gamma}n \quad n = 0, 1, 2, \cdots$$

The ground state obeys

$$a\psi_0 = \left(\frac{\partial}{\partial x} + \frac{1}{2k_B T}\frac{\partial U}{\partial x}\right)\psi_0 = 0$$

with the solution

$$\psi_0 = \mathrm{e}^{-U(x)/2k_B T}.$$

This corresponds to the stationary solution of the Smoluchowski equation

$$W = \sqrt{\frac{m\omega^2}{2\pi k_B T}}\mathrm{e}^{-U(x)/k_B T}.$$

7.3 Diffusion Through a Membrane

$$k_{AB} = k_A + k_B$$

$$0 = \frac{\mathrm{d}\overline{N}}{\mathrm{d}t} = \sum_{N=}^{M} \frac{\mathrm{d}P_N}{\mathrm{d}t} N = -\sum_{N=1}^{M} k_{AB} M N P_N + \sum_{N=1}^{N} (k_{AB} - 2k_m) N^2 P_N$$

$$+\sum_{N=2}^{M} k_{AB} M N P_{N-1} - \sum_{N=2}^{M} k_{AB}(N-1) N P_{N-1}$$

$$+\sum_{N=1}^{M-1} 2k_m N(N+1) P_{N+1}$$

$$\approx -k_{AB} M\overline{N} + (k_{AB} - 2k_m)\overline{N^2} + k_{AB} M(1+\overline{N}) - k_{AB}(\overline{N^2}+\overline{N}) + 2k_m(\overline{N^2}-\overline{N})$$

$$= k_{AB} M - k_{AB}\overline{N} - 2k_m\overline{N}$$

$$\overline{N} = M\frac{k_A + k_B}{k_A + k_B + 2k_m}$$

$$0 = \frac{\mathrm{d}\overline{N^2}}{\mathrm{d}t} = \sum N^2 \frac{\mathrm{d}P_N}{\mathrm{d}t} = -\sum_{N=1}^{M} k_{AB} M N^2 P_N + \sum_{N=1}^{N} (k_{AB} - 2k_m) N^3 P_N$$

$$+\sum_{N=2}^{M} k_{AB} M N^2 P_{N-1} - \sum_{N=2}^{M} k_{AB}(N-1) N^2 P_{N-1}$$

$$+\sum_{N=1}^{M-1} 2k_m N^2(N+1) P_{N+1}$$

$$\approx -k_{AB} M\overline{N^2} + (k_{AB} - 2k_m)\overline{N^3} + k_{AB} M(\overline{N^2} + 2\overline{N} + 1)$$

$$-k_{AB}(\overline{N^3} + 2\overline{N^2} + \overline{N}) + 2k_m(\overline{N^3} - 2\overline{N^2} + \overline{N})$$

$$= +k_{AB} M(2\overline{N} + 1) - k_{AB}(2\overline{N^2} + \overline{N}) + 2k_m(-2\overline{N^2} + \overline{N})$$

$$= k_{AB} M + \overline{N}(2k_{AB} M - k_{AB} + 2k_m) - \overline{N^2}(2k_{AB} + 4k_m)$$

$$\overline{N^2} = \frac{k_{AB} M + (2k_{AB} M - k_{AB} + 2k_m) M \frac{k_{AB}}{k_{AB}+2k_m}}{2k_{AB} + 4k_m}$$

$$= \frac{2k_{AB} k_m}{(k_{AB} + 2k_m)^2} M + \frac{k_{AB}^2}{(k_{AB} + 2k_m)^2} M^2$$

and the variance is

$$\overline{N^2} - \overline{N}^2 = \frac{2k_m k_{AB}}{(k_{AB}+2k_m)^2} M = \frac{2k_m}{k_{AB} M} \overline{N}^2.$$

The diffusion current from $A \to B$ is

$$J = \frac{\mathrm{d}N_A}{\mathrm{d}t} - \frac{\mathrm{d}N_B}{\mathrm{d}t} = \sum_N (-k_A(M-N)P_N + k_m N P_N) - \sum_N (-k_B(M-N)P_N + k_m N P_N)$$

$$= \sum_N (k_B - k_A)(M-N)P_N = (k_B - k_A)(M - \overline{N}).$$

Problems of Chap. 9

9.1 Dichotomous Model

$$\lambda_1 = 0$$

$$\mathbf{L}_1 = (\,1\;1\;1\;1\,) \quad \mathbf{R}_1 = \begin{pmatrix} 0 \\ 0 \\ \beta \\ \alpha \end{pmatrix} \quad \frac{(\mathbf{L}_1\mathbf{P}_0)}{(\mathbf{L}_1\mathbf{R}_1)} = \frac{1}{\alpha+\beta}$$

$$\lambda_2 = -(\alpha+\beta)$$

$$\mathbf{L}_2 = (\,\alpha\; -\beta\; \alpha\; -\beta\,)\, \mathbf{R}_2 = \begin{pmatrix} 0 \\ 0 \\ -1 \\ 1 \end{pmatrix} \quad \frac{(\mathbf{L}_2\mathbf{P}_0)}{(\mathbf{L}_2\mathbf{R}_2)} = 0$$

$$\lambda_{3,4} = -\frac{k_- + k_+ + \alpha + \beta}{2} \pm \frac{1}{2}\sqrt{(\alpha+\beta)^2 + (k_+ - k_-)^2 + 2(\beta-\alpha)(k_- - k_+)}$$

fast fluctuations:

$$\lambda_3 = -\frac{\alpha}{\alpha+\beta}k_- - \frac{\beta}{\alpha+\beta}k_+ + O(k^2)$$

$$\mathbf{L}_3 \approx (1, 1, 0, 0) \quad \mathbf{R}_3 \approx \begin{pmatrix} \beta \\ \alpha \\ -\beta \\ -\alpha \end{pmatrix} \quad \frac{(\mathbf{L}_3\mathbf{P}_0)}{(\mathbf{L}_3\mathbf{R}_3)} \approx \frac{1}{\alpha+\beta}$$

$$\lambda_4 = -(\alpha+\beta) - \frac{\alpha}{\alpha+\beta}k_+ - \frac{\beta}{\alpha+\beta}k_- + O(k^2)$$

$$\mathbf{L}_4 \approx (-\alpha, \beta, 0, 0) \quad \mathbf{R}_4 \approx \begin{pmatrix} 1 \\ -1 \\ 1 \\ -1 \end{pmatrix} \quad \frac{(\mathbf{L}_4\mathbf{P}_0)}{(\mathbf{L}_4\mathbf{R}_1)} \approx 0$$

$$\mathbf{P}(t) \approx \begin{pmatrix} 0 \\ 0 \\ \frac{\beta}{\alpha+\beta} \\ \frac{\alpha}{\alpha+\beta} \end{pmatrix} + \begin{pmatrix} \frac{\beta}{\alpha+\beta} \\ \frac{\alpha}{\alpha+\beta} \\ -\frac{\beta}{\alpha+\beta} \\ -\frac{\alpha}{\alpha+\beta} \end{pmatrix} \mathrm{e}^{\lambda_3 t} \quad \rightarrow P(D^*) = \mathrm{e}^{\lambda_3 t}$$

slow fluctuations:

$$\lambda_3 \approx -k_+ - \alpha$$

$$\mathbf{L}_3 \approx (k_+ - k_-, -\beta, 0, 0) \quad \mathbf{R}_3 \approx \begin{pmatrix} k_+ - k_- \\ -\alpha \\ -(k_+ - k_-) \\ \alpha \end{pmatrix} \quad \frac{\mathbf{L}_3\mathbf{P}_0}{\mathbf{L}_3\mathbf{R}_3} \approx \frac{\beta}{\alpha+\beta}\frac{1}{k_+ - k_-}$$

$$\lambda_4 \approx -k_- - \beta$$

$$\mathbf{L}_4 \approx (\alpha, k_+ - k_-, 0, 0)\mathbf{R}_4 \approx \begin{pmatrix} \beta \\ k_+ - k_- \\ -\beta \\ -(k_+ - k_-) \end{pmatrix} \quad \frac{\mathbf{L}_4\mathbf{P}_0}{\mathbf{L}_4\mathbf{R}_4} \approx \frac{\alpha}{\alpha+\beta}\frac{1}{k_+ - k_-}$$

$$\mathbf{P}(t) \approx \begin{pmatrix} 0 \\ 0 \\ \frac{\beta}{\alpha+\beta} \\ \frac{\alpha}{\alpha+\beta} \end{pmatrix} + \frac{\beta}{\alpha+\beta}\begin{pmatrix} 1 \\ 0 \\ -1 \\ 0 \end{pmatrix} \mathrm{e}^{-(k_+ + \alpha)t} + \frac{\alpha}{\alpha+\beta}\begin{pmatrix} 0 \\ 1 \\ 0 \\ -1 \end{pmatrix} \mathrm{e}^{-(k_- + \beta)t}$$

$$P(D^*) \approx \frac{\beta}{\alpha+\beta}\mathrm{e}^{-(k_+ +\alpha)t} + \frac{\alpha}{\alpha+\beta}\mathrm{e}^{-(k_- +\beta)t}$$

Problems of Chap. 10

10.1 Entropy Production

$$0 = dH = TdS + Vdp + \sum_k \mu_k dN_k$$

$$TdS = -\sum_k \mu_k dN_k = -\sum_j \sum_k \mu_k \nu_{kj} d\xi_j = \sum_j A_j d\xi_j$$

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \sum_j \frac{A_j}{T} r_j$$

Problems of Chap. 11

11.1 ATP Synthesis

At chemical equilibrium

$$0 = A = -\sum \nu_k \mu_k$$

$$= \mu^0(ADP) + k_B T \ln c(ADP) + \mu^0(POH) + k_B T \ln c(POH) + 2k_B T \ln c(H^+_{out}) + 2e\Phi_{out}$$

$$-\mu^0(ATP) - k_B T \ln c(ATP) - \mu^0(H_2O) - k_B T \ln c(H_2O) - 2k_B T \ln c(H^+_{in}) - 2e\Phi_{in}$$

$$k_B T \ln K = -\Delta G^0 = \mu^0(ADP) - \mu^0(ATP) + \mu^0(POH) - \mu^0(H_2O)$$

$$= k_B T \ln \frac{c(ATP)c(H_2O)c^2(H^+_{in})}{c(ADP)c(POH)c^2(H^+_{out})} + 2e(\Phi_{in} - \Phi_{out})$$

$$= k_B T \ln \frac{c(ATP)c(H_2O)}{c(ADP)c(POH)} + 2k_B T \ln \frac{c(H^+_{in})}{c(H^+_{out})} + 2e(\Phi_{in} - \Phi_{out})$$

Problems of Chap. 15

15.1 Transition State Theory

$$\mathrm{A+B} \overset{K^\ddagger}{\leftrightharpoons} [\mathrm{AB}]^\ddagger \overset{k^\ddagger}{\rightarrow} \mathrm{P}$$

$$k = k^\ddagger c_{[AB]^\ddagger} = k^\ddagger K^\ddagger c_A c_B$$

$$K^\ddagger = \frac{c_{[AB]^\ddagger}}{c_A c_B} = \frac{q_{[AB]^\ddagger}}{q_A q_B}\mathrm{e}^{-\Delta H^\ddagger/k_B T} = q_x \frac{q^\ddagger_{[AB]^\ddagger}}{q_A q_B}\mathrm{e}^{-\Delta H^\ddagger/k_B T}$$

$$q_x = \frac{\sqrt{2\pi m k_B T}}{h}\delta x$$

$$k^\ddagger = \frac{v^\ddagger}{\delta x} = \frac{1}{\delta x}\sqrt{\frac{k_B T}{2\pi m}}$$

$$k = \frac{1}{\delta x}\sqrt{\frac{k_B T}{2\pi m}}\frac{\sqrt{2\pi m k_B T}}{h}\delta x \frac{q^\ddagger_{[AB]^\ddagger}}{q_A q_B}\mathrm{e}^{-\Delta H^\ddagger/k_B T} c_A c_B$$

$$= \frac{k_B T}{h}\frac{q^\ddagger_{[AB]^\ddagger}}{q_A q_B}\mathrm{e}^{-\Delta H^\ddagger/k_B T} c_A c_B$$

15.2 Harmonic Transition State Theory

$$k = v < \delta(x - x^\ddagger) >= \sqrt{\frac{k_B T}{2\pi m}}\frac{\int_{-\infty}^{\infty}\mathrm{e}^{-m\omega^2 x^2/2k_B T}\delta(x - x^\ddagger)}{\int_{-\infty}^{\infty}\mathrm{e}^{-m\omega^2 x^2/2k_B T}}$$

$$= \sqrt{\frac{k_B T}{2\pi m}}\frac{\mathrm{e}^{-m\omega^2 x^{\ddagger 2}/2k_B T}}{\sqrt{\frac{2\pi k_B T}{m\omega^2}}}$$

$$= \frac{\omega}{2\pi}\mathrm{e}^{-\Delta E/k_B T}$$

Problems of Chap. 16

16.1 Marcus Cross Relation

$$\begin{array}{lll} \mathrm{A+A^- \rightarrow A^-+A} & & \lambda_A = 2\Delta E(A_{eq} \rightarrow A^-_{eq} \\ \mathrm{D+D^+ \rightarrow D^++D} & & \lambda_D = 2\Delta E(D_{eq} \rightarrow D^+_{eq}) \\ \mathrm{A+D \rightarrow A^-+D^+} & & \lambda_{AD} = \Delta E(A_{eq} \rightarrow A^-_{eq}) + \Delta E(D_{eq} \rightarrow D^+_{eq}) = \frac{\lambda_A+\lambda_D}{2} \end{array}$$

$$k_A = \frac{\omega_A}{2\pi} \mathrm{e}^{-\lambda_A/4k_BT}$$

$$k_B = \frac{\omega_B}{2\pi} \mathrm{e}^{-\lambda_B/4k_BT}$$

$$K_{AD} = \mathrm{e}^{-\Delta G/k_BT}$$

$$k_{AD} = \frac{\omega_{AD}}{2\pi} \exp\left\{-\frac{(\lambda_{AD}+\Delta G)^2}{4\lambda_{AD}k_BT}\right\}$$

$$= \frac{\omega_{AD}}{2\pi} \exp\left\{-\frac{\lambda_A+\lambda_D}{8k_BT} - \frac{\Delta G}{2k_BT} - \frac{\Delta G^2}{4\lambda_{AD}k_BT}\right\}$$

$$= \sqrt{k_A k_B K_{AD}} \quad \sqrt{\frac{\omega_{AD}^2}{\omega_A\omega_D}} \exp\left\{-\frac{\Delta G^2}{4\lambda_{AD}k_BT}\right\}$$

Problems of Chap. 18

18.1 Absorption Spectrum

$$\alpha = \frac{1}{2\pi\hbar} \int dt \sum_{i,f} \mathrm{e}^{\mathrm{i}\omega t} < i| \sum \frac{\mathrm{e}^{-\beta H}}{Q} \mathrm{e}^{-\mathrm{i}\omega_i t} \mu f > \mathrm{e}^{\mathrm{i}\omega_f t} < f \mu i >$$

$$= \frac{1}{2\pi\hbar} \int dt \mathrm{e}^{\mathrm{i}\omega t} < \mathrm{e}^{-\mathrm{i}Ht/\hbar} \mu \mathrm{e}^{\mathrm{i}Ht/\hbar} \mu >$$

$$= \frac{1}{2\pi\hbar} \int dt \mathrm{e}^{\mathrm{i}\omega t} < \mu(0)\mu(t) >$$

$$\approx \frac{|\mu_{eg}|^2}{2\pi\hbar} \int dt e^{i\omega t} < e^{-iH_g t/\hbar} e^{iH_e t/\hbar} >_g$$

Problems of Chap. 20

20.1 Motional Narrowing

$$(s + i\omega_1)(s + i\omega_2) + (\alpha + \beta)(s + i\overline{\omega})$$

$$= -\left(\Omega + \frac{\Delta\omega}{2}\right)\left(\Omega - \frac{\Delta\omega}{2}\right) - i\omega_c \Omega$$

$$\Omega = \omega - \overline{\omega}$$

$$\Omega^2 - \frac{\Delta\omega^2}{4} + i\omega_c \Omega = 0$$

$$\left(\Omega + \frac{i\omega_c}{2}\right)^2 = \frac{\Delta\omega^2}{4} - \frac{\omega_c^2}{4}$$

For $\omega_c \ll \Delta\omega$ the poles are approximately at

$$\Omega_p = -\frac{i\omega_c}{2} \pm \frac{\Delta\omega}{2}$$

and two lines are observed centered at the unperturbed frequencies $\overline{\omega} \pm \Delta\omega/2$ and with their width determined by ω_c. For $\omega_c = \Delta\omega$ the two poles coincide at

$$\Omega_p = -\frac{i\omega_c}{2}$$

and a single line at the average frequency $\overline{\omega}$ appears. For $\omega_c \gg \Delta\omega$ one pole approaches zero according to

$$\Omega_p = -i\frac{\Delta\omega^2}{4\omega_c}$$

which corresponds to a sharp line at the average frequency $\overline{\omega}$. The other pole approaches infinity as

$$\Omega_p = -i\omega_c.$$

It contributes a broad line at $\overline{\omega}$ which vanishes in the limit of large ω_c (Fig. 1).

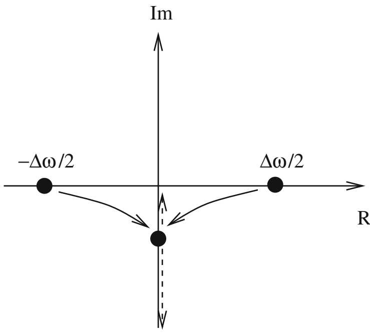


Fig. 1 Poles of the lineshape function

Problems of Chap. 21

21.1 Crude Adiabatic Model

$$\frac{\partial C}{\partial Q}=\begin{pmatrix}-s & c\\ -c & -s\end{pmatrix}\frac{\partial \zeta}{\partial Q}\quad C^{\dagger}\frac{\partial C}{\partial Q}=\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}\frac{\partial \zeta}{\partial Q}$$

$$\frac{\partial^2 C}{\partial Q^2}=\begin{pmatrix}-s & c\\ -c & -s\end{pmatrix}\frac{\partial^2 \zeta}{\partial Q^2}-C\left(\frac{\partial \zeta}{\partial Q}\right)^2$$

$$C^{\dagger}\frac{\partial^2 C}{\partial Q^2}=\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}\frac{\partial^2 \zeta}{\partial Q^2}-\left(\frac{\partial \zeta}{\partial Q}\right)^2$$

$$\int dr\, C^{\dagger}\Phi^{\dagger}\frac{\partial^2}{\partial Q^2}\Phi C=C^{\dagger}\frac{\partial^2 C}{\partial Q^2}+2C^{\dagger}\frac{\partial C}{\partial Q}\frac{\partial}{\partial Q}+\frac{\partial^2}{\partial Q^2}$$

$$=\frac{\partial^2}{\partial Q^2}+\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}\frac{\partial^2 \zeta}{\partial Q^2}-\left(\frac{\partial \zeta}{\partial Q}\right)^2+2\begin{pmatrix}0 & 1\\ -1 & 0\end{pmatrix}\frac{\partial \zeta}{\partial Q}\frac{\partial}{\partial Q}$$

$$\int dr\, C^{\dagger}\Phi^{\dagger}(T_{el}+V_0+\Delta V)\Phi C=$$

$$C^{\dagger}EC+C^{\dagger}\int dr\Phi^{\dagger}\Delta V\Phi\quad C=C^{\dagger}\begin{pmatrix}\overline{E}(Q)-\frac{\Delta E(Q)}{2} & V(Q)\\ V(Q) & \overline{E}(Q)+\frac{\Delta E(Q)}{2}\end{pmatrix}C$$

$$\int dr\, C^{\dagger}\Phi^{\dagger}H\,\Phi\, C=$$

$$=-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial Q^2}+C^{\dagger}\begin{pmatrix}\overline{E}(Q)-\frac{\Delta E(Q)}{2} & V(Q)\\ V(Q) & \overline{E}(Q)+\frac{\Delta E(Q)}{2}\end{pmatrix}C+\frac{\hbar^2}{2m}\left(\frac{\partial \zeta}{\partial Q}\right)^2$$

$$-\frac{\hbar^2}{2m}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}(\frac{\partial^2\zeta}{\partial Q^2}+2\frac{\partial\zeta}{\partial Q}\frac{\partial}{\partial Q})$$

$$\cos\zeta\sin\zeta=\frac{V(Q)}{\sqrt{4V(Q)^2+\Delta E(Q)^2}} \quad \cos\zeta^2-\sin\zeta^2=\frac{\Delta E(Q)}{\sqrt{4V(Q)^2+\Delta E(Q)^2}}$$

$$\frac{\partial}{\partial Q}(cs)^2=2cs(c^2-s^2)\frac{\partial\zeta}{\partial Q}=\frac{2V\Delta E}{4V^2+\Delta E^2}\frac{\partial\zeta}{\partial Q}$$

$$\frac{\partial}{\partial Q}(cs)^2=\frac{\partial}{\partial Q}\frac{V^2}{4V^2+\Delta E^2}$$

$$=\frac{2V}{4V^2+\Delta E^2}\frac{\partial V}{\partial Q}-\frac{V^2}{(4V^2+\Delta E^2)^2}\left(2\Delta E\frac{\partial\Delta E}{\partial Q}+8V\frac{\partial V}{\partial Q}\right)$$

$$\frac{\partial\zeta}{\partial Q}=\frac{\Delta E}{4V^2+\Delta E^2}\frac{\partial V}{\partial Q}-\frac{V}{4V^2+\Delta E^2}\frac{\partial\Delta E}{\partial Q}\approx\frac{1}{\Delta E}\frac{\partial V}{\partial Q}$$

$$\frac{\partial^2\zeta}{\partial Q^2}=\frac{\Delta E\frac{\partial^2 V}{\partial Q^2}-V\frac{\partial^2\Delta E}{\partial Q^2}}{4V^2+\Delta E^2}-\left(\Delta E\frac{\partial V}{\partial Q}-V\frac{\partial\Delta E}{\partial Q}\right)\frac{2\Delta E\frac{\partial\Delta E}{\partial Q}+8V\frac{\partial V}{\partial Q}}{(4V^2+\Delta\mathrm{e}^2)^2}$$

$$\approx\frac{1}{\Delta E}\frac{\partial^2 V}{\partial Q^2}-\frac{2}{\Delta E^2}\frac{\partial\Delta E}{\partial Q}\frac{\partial V}{\partial Q}$$

$$\widetilde{H}\approx-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial Q^2}+\begin{pmatrix}\overline{E}-\sqrt{4V^2+\Delta E^2} & \\ & \overline{E}+\sqrt{4V^2+\Delta E^2}\end{pmatrix}$$

$$+\frac{\hbar^2}{2m}\frac{1}{\Delta E^2}\left(\frac{\partial V}{\partial Q}\right)^2-\frac{\hbar^2}{2m}\begin{pmatrix} 0 & 1 \\ -1 & 0 \end{pmatrix}\left(\frac{1}{\Delta E}\frac{\partial^2 V}{\partial Q^2}-\frac{2}{\Delta E^2}\frac{\partial\Delta E}{\partial Q}\frac{\partial V}{\partial Q}+\frac{2}{\Delta E}\frac{\partial V}{\partial Q}\frac{\partial}{\partial Q}\right)$$

Problems of Chap. 22

22.1 Ladder Model

$$\mathrm{i}\hbar\dot{C}_0=V\sum_{j=1}^{n}C_j$$

$$\mathrm{i}\hbar\dot{C}_j=E_jC_j+VC_0$$

$$C_j = u_j \mathrm{e}^{\frac{E_j}{\mathrm{i}\hbar}t}$$

$$\mathrm{i}\hbar \dot{u}_j \mathrm{e}^{\frac{E_j}{\mathrm{i}\hbar}t} = VC_0$$

$$u_j = \frac{V}{\mathrm{i}\hbar}\int^t \mathrm{e}^{-\frac{E_j}{\mathrm{i}\hbar}t'} C_0(t')dt'$$

$$C_j = \frac{V}{\mathrm{i}\hbar}\int^t \mathrm{e}^{\mathrm{i}\frac{E_j}{\hbar}(t-t')} C_0(t')dt'$$

$$E_j = \alpha + j * \hbar\Delta\omega$$

$$\dot{C}_0 = \frac{V}{\mathrm{i}\hbar}\sum_{j=1}^{n} C_j = -\frac{V^2}{\hbar^2}\sum \int^t \mathrm{e}^{\mathrm{i}(j\Delta\omega+\alpha/\hbar)(t-t')} C_0(t')dt'$$

$$\omega = j\Delta\omega + \frac{\alpha}{\hbar}$$

$$\sum_{j=-\infty}^{\infty} \mathrm{e}^{\mathrm{i}(j\Delta\omega+\alpha/\hbar)(t-t')}\Delta j \ \rightarrow \ \int_{-\infty}^{\infty} \mathrm{e}^{i\omega(t-t')}\frac{d\omega}{\Delta\omega} = \frac{2\pi}{\Delta\omega}\delta(t-t')$$

$$\dot{C}_0 = -\frac{2\pi V^2}{\Delta\omega}C_0 = -\frac{2\pi V^2}{\hbar}\rho(E)C_0$$

$$\rho(E) = \frac{1}{\hbar\Delta\omega} = \frac{1}{\Delta E}$$

Problems of Chap. 23

23.1 Hückel Model with Alternating Bonds

(a)

$$\alpha \mathrm{e}^{\mathrm{i}kn} + \beta \mathrm{e}^{\mathrm{i}(kn+\chi)} + \beta' \mathrm{e}^{\mathrm{i}(kn+k+\chi)} = \mathrm{e}^{\mathrm{i}kn}\left(\alpha + \beta \mathrm{e}^{\mathrm{i}\chi} + \beta' \mathrm{e}^{\mathrm{i}(k+\chi)}\right)$$

$$\alpha \mathrm{e}^{\mathrm{i}(kn+\chi)} + \beta' \mathrm{e}^{\mathrm{i}(kn-k)} + \beta \mathrm{e}^{\mathrm{i}kn} = \mathrm{e}^{\mathrm{i}(kn+\chi)}\left(\alpha + \beta' \mathrm{e}^{-\mathrm{i}(k+\chi)} + \beta \mathrm{e}^{-\mathrm{i}\chi}\right)$$

(b)

$$\beta \mathrm{e}^{\mathrm{i}\chi} + \beta' \mathrm{e}^{\mathrm{i}(k+\chi)} = \beta' \mathrm{e}^{-\mathrm{i}(k+\chi)} + \beta \mathrm{e}^{-\mathrm{i}\chi}$$

$$e^{2i\chi} = \frac{\beta' e^{-ik} + \beta}{\beta' e^{ik} + \beta} = e^{-ik} \frac{\beta' e^{-ik/2} + \beta e^{ik/2}}{\beta' e^{ik/2} + \beta e^{-ik/2}} = e^{-ik} \frac{\left(\beta' e^{-ik/2} + \beta e^{ik/2}\right)^2}{\beta'^2 + \beta^2 + 2\beta\beta' \cos k}$$

$$e^{i\chi} = \pm e^{-ik/2} \frac{\beta' e^{-ik/2} + \beta e^{ik/2}}{\sqrt{\beta'^2 + \beta^2 + 2\beta\beta' \cos k}}$$

$$\lambda = \alpha + \beta e^{i\chi} + \beta' e^{i(k+\chi)} = \alpha \pm \frac{\beta\beta' e^{-ik} + \beta^2 + \beta'^2 + \beta\beta' e^{ik}}{\sqrt{\beta'^2 + \beta^2 + 2\beta\beta' \cos k}}$$

$$= \alpha \pm \sqrt{\beta'^2 + \beta^2 + 2\beta\beta' \cos k}$$

(c)

$$0 = \Im\left(e^{i\chi + i(N+1)k}\right) = \Im\left(\pm e^{-ik/2} \frac{\beta' e^{-ik/2} + \beta e^{ik/2}}{\sqrt{\beta'^2 + \beta^2 + 2\beta\beta' \cos k}} e^{i(N+1)k}\right)$$

$$= \pm\Im\left(\frac{\beta' e^{iNk} + \beta e^{i(N+1)k}}{\sqrt{\beta'^2 + \beta^2 + 2\beta\beta' \cos k}}\right)$$

$$0 = \beta' \sin(Nk) + \beta \sin(N+1)k)$$

(d) For a linear polyene with 2N-1 carbon atoms use again eigenfunctions

$$c_{2n} = \sin(kn) = \Im(e^{ikn})$$

$$c_{2n-1} = \sin(kn + \chi) = \Im(e^{i(kn+\chi)})$$

and chose the k-values such that

$$\Im(e^{iNk}) = \sin(Nk) = 0$$

Problems of Chap. 25

25.1 Special Pair Dimer

$$\begin{pmatrix} c & -s \\ s & c \end{pmatrix} \begin{pmatrix} -\Delta/2 & V \\ V & \Delta/2 \end{pmatrix} \begin{pmatrix} c & s \\ -s & c \end{pmatrix}$$

is diagonalized if

$$(c^2 - s^2)V = cs\Delta$$

or with $c = \cos\chi$, $s = \sin\chi$

$$\tan(2\chi) = \frac{2V}{\Delta}$$

$$c^2 - s^2 = \cos 2\chi = \frac{1}{\sqrt{1 + \frac{4V^2}{\Delta^2}}} \geq 0$$

$$2cs = \sin(2\chi) = \frac{1}{\sqrt{1 + \frac{\Delta^2}{4V^2}}} \geq 0.$$

The eigenvalues are (Fig. 2)

$$E_\pm = \pm\left(\frac{\Delta}{2}(c^2 - s^2) + 2csV\right)$$

$$= \pm\left(\frac{\Delta}{2}\frac{1}{\sqrt{1 + \frac{4V^2}{\Delta^2}}} + V\frac{1}{\sqrt{1 + \frac{\Delta^2}{4V^2}}}\right) = \pm\frac{1}{2}\sqrt{\Delta^2 + 4V^2}.$$

The transition dipoles are

$$\mu_+ = s\mu_a + c\mu_b$$

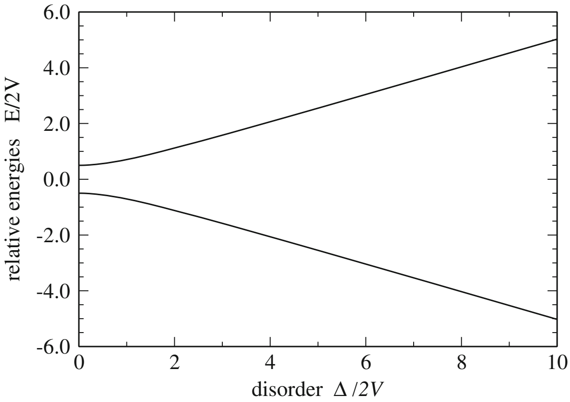


Fig. 2 Energy splitting of the two dimer bands

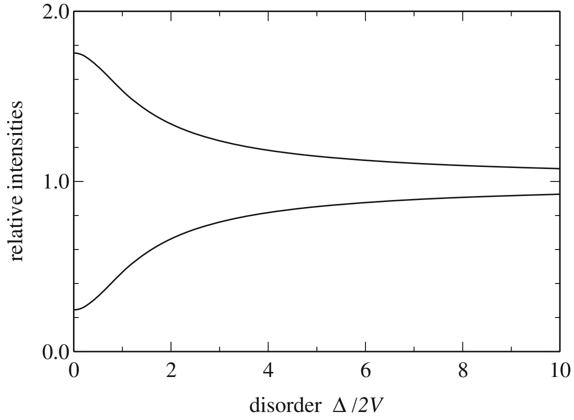


Fig. 3 Intensities of the two dimer bands

$$\mu_- = c\mu_a - s\mu_b$$

and the intensities (for $|\mu_a| = |\mu_b| = \mu$)

$$|\mu_\pm|^2 = \mu^2(1 \pm 2cs\cos\alpha) = \mu^2(1 \pm \frac{\cos\alpha}{\sqrt{1+\frac{\Delta^2}{4V^2}}})$$

with (Fig. 3)

$$\cos\alpha = -0.755.$$

25.2 LHC II

$$|n;\alpha> = \frac{1}{3}\sum_k \mathrm{e}^{-\mathrm{i}kn}|k;\alpha>$$

$$\sum_{n=1}^{9} E_\alpha |n;\alpha><n;\alpha| = \sum_{n=1}^{9} E_\alpha \frac{1}{9}\sum_{k,k'} \mathrm{e}^{-i(k-k')n}|k;\alpha><k';\alpha|$$

$$= \delta_{k,k'} E_\alpha |k;\alpha><k;\alpha|$$

$$\sum_{n=1}^{9} E_\alpha |n;\beta><n;\beta| \sum_{n=1}^{9} E_\alpha \frac{1}{9}\sum_{k,k'} \mathrm{e}^{-i(k-k')n}|k;\beta><k';\beta|$$

$$= \delta_{k,k'} E_\alpha |k;\beta><k;\beta|$$

$$\sum_{n=1}^{9} V_{dim}|n;\alpha><n;\beta| = \sum_{n=1}^{9} V_{dim}\frac{1}{9}\sum_{k,k'} \mathrm{e}^{-i(k-k')n}|k;\alpha><k';\beta|$$

$$= \delta_{k,k'}V_{dim}|k;\alpha><k;\beta|$$

$$\sum_{n=1}^{9} V_{\beta\alpha,1}|n;\alpha><n-1;\beta| = \sum_{n=1}^{9} V_{\beta\alpha,1}\mathrm{e}^{-\mathrm{i}k}\frac{1}{9}\sum_{k,k'} \mathrm{e}^{-i(k-k')n}|k;\alpha><k';\beta|$$

$$= \delta_{k,k'}V_{\beta\alpha,1}\mathrm{e}^{-\mathrm{i}k}|k;\alpha><k;\beta|$$

$$\sum_{n=1}^{9} V_{\beta\alpha,1}|n;\beta><n+1;\alpha| = \sum_{n=1}^{9} V_{\beta\alpha,1}\mathrm{e}^{\mathrm{i}k}\frac{1}{9}\sum_{k,k'} \mathrm{e}^{-i(k-k')n}|k;\beta><k';\alpha|$$

$$= \delta_{k,k'}V_{\beta\alpha,1}\mathrm{e}^{\mathrm{i}k}|k;\beta><k;\alpha|$$

$$\sum_{n=1}^{9} V_{\alpha\alpha,1}(|n;\alpha><n+1;\alpha| + h.c.) = \sum_{n=1}^{9} V_{\alpha\alpha,1}\mathrm{e}^{\mathrm{i}k}\frac{1}{9}\sum_{k,k'} \mathrm{e}^{-i(k-k')n}|k;\alpha><k';\alpha| + h.c.$$

$$= \delta_{k,k'}2V_{\alpha\alpha,1}\cos k|k;\alpha><k;\alpha|$$

$$H_{\alpha\alpha}(k) = E_\alpha + 2V_{\alpha\alpha 1}\cos k$$

$$H_{\beta\beta}(k) = E_\beta + 2V_{\beta\beta 1}\cos k$$

$$H_{\alpha\beta}(k) = V_{dim} + \mathrm{e}^{-\mathrm{i}k}V_{\beta\alpha,1}$$

$$H_{\beta\alpha}(k) = V_{dim} + \mathrm{e}^{\mathrm{i}k}V_{\beta\alpha,1}$$

$$H(k) = \begin{pmatrix} E_\alpha + 2V_{\alpha\alpha 1}\cos k & V + \mathrm{e}^{-\mathrm{i}k}W \\ V + \mathrm{e}^{\mathrm{i}k}W & E_\beta + 2V_{\beta\beta 1}\cos k \end{pmatrix} = \overline{E}_k + \begin{pmatrix} -\Delta_k/2 & V + \mathrm{e}^{-\mathrm{i}k}W \\ V + \mathrm{e}^{\mathrm{i}k}W & \Delta_k/2 \end{pmatrix}$$

Perform a canonical transformation with

$$S = \begin{pmatrix} c & -s\mathrm{e}^{-\mathrm{i}\chi} \\ s\mathrm{e}^{\mathrm{i}\chi} & c \end{pmatrix}.$$

$S^\dagger\ H\ S$ becomes diagonal if

$$c^2(V + \mathrm{e}^{\mathrm{i}k}W) - s^2\mathrm{e}^{2\mathrm{i}\chi}(V + \mathrm{e}^{-\mathrm{i}k}W) + cs\mathrm{e}^{\mathrm{i}\chi}\Delta_k = 0.$$

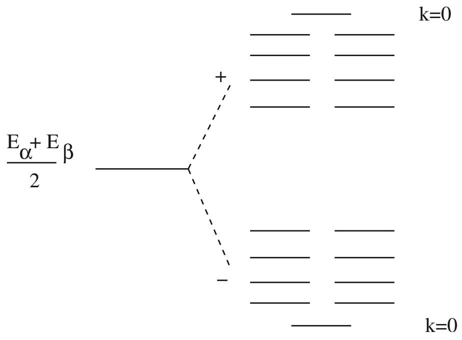


Fig. 4 Energy levels of LHII

Chose χ such that

$$V + e^{ik}W = \operatorname{sign}V|V + e^{ik}W|e^{i\chi} = U(k)e^{i\chi}$$

and solve

$$(c^2 - s^2)U + cs\Delta_k = 0$$

by[4]

$$c^2 - s^2 = -\operatorname{sign}\left(\frac{U}{\Delta}\right)\frac{1}{\sqrt{1+\frac{4U^2}{\Delta^2}}} \quad cs = \frac{\left|\frac{U}{\Delta}\right|}{\sqrt{1+\frac{4U^2}{\Delta^2}}}.$$

The eigenvalues are (Fig. 4)

$$E_\pm(k) = \overline{E}_k \pm \operatorname{sign}V\frac{1}{2}\sqrt{\Delta^2 + 4U^2}$$

$$= \frac{E_\alpha + E_\beta}{2} + (V_{\alpha\alpha1} + V_{\beta\beta1})\cos k$$

$$\pm \operatorname{sign}V\sqrt{\left(\frac{E_\alpha - E_\beta + 2(V_{\alpha\alpha1} - V_{\beta\beta1})\cos k}{2}\right)^2 + V^2 + W^2 + 2VW\cos k}$$

$$\mu_{k,+} = c\frac{1}{3}\sum_n e^{ikn}\mu_{n\alpha} + se^{i\chi}\frac{1}{3}\sum_n e^{ikn}\mu_{n\beta}$$

[4]The sign is chosen such that for $|\Delta| \ll |U|$ the solution becomes $c = s = 1/\sqrt{2}$.

$$= c\frac{1}{3}\sum_n \mathrm{e}^{\mathrm{i}kn} S_9^n \mu_{0\alpha} + s\mathrm{e}^{\mathrm{i}\chi}\frac{1}{3}\sum_n \mathrm{e}^{\mathrm{i}kn} S_9^n R_z(2\nu + \phi_\beta - \phi_\alpha)\mu_{0,\alpha}$$

$$= \frac{1}{3}\sum_n \mathrm{e}^{\mathrm{i}kn} \begin{pmatrix} \cos\frac{2\pi}{9}n & -\sin\frac{2\pi}{9}n & \\ \sin\frac{2\pi}{9}n & \cos\frac{2\pi}{9}n & \\ & & 1 \end{pmatrix} \left(c + s\mathrm{e}^{\mathrm{i}\chi} \begin{pmatrix} \cos\epsilon & -\sin\epsilon & \\ \sin\epsilon & \cos\epsilon & \\ & & 1 \end{pmatrix}\right) \mu_0 \begin{pmatrix} \sin\theta \\ 0 \\ \cos\theta \end{pmatrix}.$$

The sum over n again gives the selection rules

$k = 0$ z-polarisation

$k = \pm\frac{2\pi}{9}$ circular xy-polarisation.

The second factor gives for z-polarization

$$\mu = 3\mu_0(c + s\mathrm{e}^{\mathrm{i}\chi})\cos\theta$$

$$|\mu|^2 = 9\mu_0^2(1 + 2cs\ \cos\chi)\cos^2\theta$$

with

$$\cos^2\theta \approx 0.008$$

and for polarization in the xy plane

$$\mu = 3\mu_0 \sin\theta \begin{pmatrix} c + s\mathrm{e}^{\mathrm{i}\chi}\cos\epsilon \\ s\mathrm{e}^{\mathrm{i}\chi}\sin\epsilon \end{pmatrix}$$

$$|\mu|^2 = 9\mu_0^2 \sin^2\theta(1 + 2\cos\epsilon\, cs\cos\chi)$$

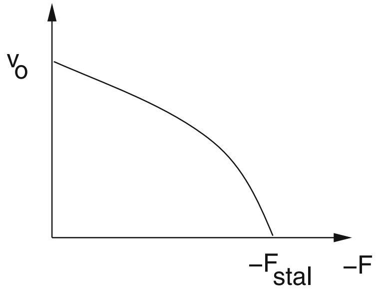
with

$$\sin^2\theta \approx 0.99 \quad \cos\epsilon \approx -0.952.$$

The intensities of the (k,-) states are

$$|\mu_z|^2 = 9\mu_0^2(1 - 2cs\ \cos\chi)\cos^2\theta$$

$$|\mu_\perp|^2 = 9\mu_0^2 \sin^2\theta(1 - 2\cos\epsilon\, cs\cos\chi).$$



25.3 Exchange Narrowing

$$P(\delta E_k = X) = \int d\delta E_1 d\delta E_2 \cdots P(\delta E_1) P(\delta E_2) \cdots \delta(X - \frac{\sum \delta E_n}{N})$$

$$P(\delta E_k = X) = \frac{1}{2\pi} \int dt \int \delta E_1 d\delta E_2 \cdots \frac{1}{\Delta\sqrt{\pi}} \mathrm{e}^{-\delta E_1^2/\Delta^2} \cdots \mathrm{e}^{\mathrm{i}t(X - \sum \delta E_n/N)}$$

$$= \frac{1}{2\pi} \int dt\, \mathrm{e}^{\mathrm{i}tX} \left(\frac{1}{\Delta\sqrt{\pi}} \int \delta E_1 \mathrm{e}^{-\delta E_1^2/\Delta^2 - it\delta E_1/N} \right)^N$$

$$= \frac{1}{2\pi} \int dt\, \mathrm{e}^{\mathrm{i}tX} \mathrm{e}^{-\Delta^2 t^2/4N}$$

$$= \frac{\sqrt{N}}{\sqrt{\pi}\Delta} \mathrm{e}^{-X^2 N/\Delta^2}.$$

Problems of Chap. 29

29.1 Deviation from Equilibrium

$$\Omega = \mathrm{e}^{-\Delta U/k_B T} (1 - \mathrm{e}^{\Delta\mu/k_B T}) \frac{\alpha_2}{\alpha_2 + \beta_2}$$

$$\Omega(x) = \mathrm{e}^{(\Delta\mu^0 - \Delta U(x))/k_B T} \frac{\alpha_2(x)}{\alpha_2(x) + \beta_2(x)} \left(K_{eq} - \frac{C(ATP)}{C(ADP)C(P)} \right).$$

For $\Delta\mu \neq 0$ but $\Delta\mu \ll k_B T$ Ω becomes a linear function of $\Delta\mu$

$$\Omega(x) \to -e^{-\Delta U(x)/k_B T} \frac{\alpha_2(x)}{\alpha_2(x) + \beta_2(x)} \frac{\Delta\mu}{k_B T}$$

whereas in the opposite limit $\Delta\mu \gg k_B T$ it becomes proportional to the concentration ratio

$$\Omega(x) \to -e^{-\Delta U(x)/k_B T} \frac{\alpha_2(x)}{\alpha_2(x) + \beta_2(x)} e^{\Delta\mu^0/k_B T} \frac{C(ATP)}{C(ADP)C(P)}.$$

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