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Statistical Physics and Thermodynamics
Self-Test

Solution to Problem 1

By inspecting all the events

	1	2	3	4	5	6
1	1	2	3	4	5	6
2	2	4	6	8	10	12
3	3	6	9	12	15	18
4	4	8	12	16	20	24
5	5	10	15	20	25	30
6	6	12	18	24	30	36

we obtain $p = \frac{11}{36}$.

Solution to Problem 2

The characteristic function is given by

$$\chi(k) = \int_0^\infty dz\, e^{-ikz}\rho(z) = \frac{1}{1 + i\frac{k}{a}} = \sum_{n=0}^\infty \frac{(-ik)^n}{n!}\left(\frac{1}{a}\right)^n n!, \tag{1}$$

where the expansion converges for $|k|/a < 1$. On the other hand,

$$\chi(k) = \int_0^\infty dz\, e^{-ikz}\rho(z) = \sum_{n=0}^\infty \frac{(-ik)^n}{n!}\langle Z^n\rangle. \tag{2}$$

Therefore $\langle Z\rangle = \frac{1}{a}$, $\langle Z^2\rangle = \frac{2}{a^2}$ and $\langle Z^2\rangle - \langle Z\rangle^2 = \frac{1}{a^2}$.

Solution to Problem 3

Let $\rho(x) = \frac{1}{\sqrt{2\pi}\sigma}e^{-\frac{x^2}{2\sigma^2}}$, $z_\pm = x \pm y$. Then

$$\rho_+(z_+) = \int dxdy\, \delta(z_+ - x - y)\rho(x)\rho(y) = \frac{1}{2\pi\sigma^2}e^{-\frac{z_+^2}{4\sigma^2}} \int dx\, e^{-\frac{(x+\frac{1}{2}z_+)^2}{\sigma^2}} = \frac{1}{\sqrt{2\pi}\sqrt{2}\sigma}e^{-\frac{z_+^2}{4\sigma^2}}, \tag{3}$$

where we integrated over the delta and completed the square in the exponent. By symmetry of $\rho(y)$ we obtain

$$\rho_-(z_-) = \int dxdy\, \delta(z_- - x + y)\rho(x)\rho(y) = \int dxdy\, \delta(z_- - x - y)\rho(x)\rho(y) = \rho_+(z_-). \tag{4}$$

Solution to Problem 4

Note that

$$\langle X\rangle = \int dx\rho(x)x = \frac{5}{8}, \tag{5}$$

$$\langle X^2\rangle = \int dx\rho(x)x^2 = \frac{17}{32}, \tag{6}$$

$$\sigma^2 = \langle X^2\rangle - \langle X\rangle^2 = \frac{9}{64}. \tag{7}$$

The law of large numbers give the following distribution for $Y_N = X_1 + \cdots + X_N$, where X_i statistically independent copies of X,

$$\rho_{Y_N}(y) = \frac{1}{(2\pi N\sigma^2)^{\frac{1}{2}}} e^{-\frac{(y-\langle X\rangle N)^2}{2\sigma^2 N}} \tag{8}$$

in the limit $N \to \infty$ [Schwabl]. Since $Z_N = (\sqrt{N})^{-1} Y_N$ we obtain in this limit

$$\rho_{Z_N}(z) = \int dy\, \delta(z - (\sqrt{N})^{-1} y)\rho_{Y_N}(y) = \frac{1}{(2\pi\sigma^2)^{\frac{1}{2}}} e^{-\frac{(z-\langle X\rangle N^{1/2})^2}{2\sigma^2}}. \tag{9}$$

Solution to Problem 5

By definition of the median M

$$\int_0^M dz\, \rho(z) = \frac{1}{2}. \tag{10}$$

Consequently $M = \frac{\ln 2}{a}$.

Solution to Problem 6

The joint probability density for the N statistically independent copies $T_1 \ldots T_N$ is given by

$$\rho_\tau(T_1 \ldots T_N) = \prod_{i=1}^{N} \rho_\tau(T_i) = (\tau)^{-N} e^{-\sum_{i=1}^{N} T_i/\tau}. \tag{11}$$

The likelihood of a given sample $T_1 \ldots T_N$ is defined as

$$L(\tau) = \rho_\tau(T_1 \ldots T_N). \tag{12}$$

To find the maximal likelihood estimate for τ one finds the maximum of $L(\tau)$ for $T_1 \ldots T_N$ fixed. One obtains the arithmetic mean

$$\tau_{\max} = \frac{1}{N} \sum_{i=1}^{N} T_i. \tag{13}$$

Solution to Problem 7

We have $k = 10$, $\chi^2_{1-\alpha} = 0.7$, the problem is to compute α. (See HS1). We have

$$\alpha = \int_{\chi^2_{1-\alpha}}^{\infty} \rho(\chi^2, k-1) d\chi^2 = 0.99987, \tag{14}$$

(from the table) where

$$\rho(\chi^2; k) = \frac{(\chi^2)^{k/2-1}}{2^{k/2}\Gamma(k/2)} e^{-\chi^2/2}. \tag{15}$$

So the probability of an error is 0.00013.

Solution to Problem 8

ρ is not a quantum mechanical density matrix because it is not positive. In fact

$$\det \begin{pmatrix} \frac{1}{2} - \lambda & i \\ -i & \frac{1}{2} - \lambda \end{pmatrix} = (\lambda + \frac{1}{2})(\lambda - \frac{3}{2}), \tag{16}$$

so the eigenvalues are $\lambda_1 = -\frac{1}{2}$ and $\lambda_2 = \frac{3}{2}$.

Solution to Problem 9

The center of mass position of the system is given by

$$X = \frac{x_1 + \cdots + x_N}{N}. \tag{17}$$

The corresponding Langevin equation has the form

$$\dot{X} = \frac{\dot{x}_1 + \cdots + \dot{x}_N}{N} =: \Xi(t). \tag{18}$$

We have

$$\langle \Xi(t) \rangle = 0, \tag{19}$$

$$\langle \Xi(t)\Xi(t') \rangle = \frac{1}{N^2} \sum_{k=1}^{N} \sum_{l=1}^{N} \langle \xi_k(t)\xi_l(t') \rangle = 2\frac{D}{N}\delta(t - t'). \tag{20}$$

So the diffiusion constant of the center of mass equals D/N.

Solution to Problem 10

Let $P(N_E, N_D, t)$ be the probability that at time t there are N_E 'molecules' (DNA chains) of type E and N_D 'molecules' of type D. The system has two reaction channels and we determine the corresponding stochiometric matrix:

$$E + E \to D : \quad \Delta^1_E = -2, \quad \Delta^1_D = 1 \tag{21}$$

$$D \to E + E : \quad \Delta^2_E = 2, \quad \Delta^2_D = -1. \tag{22}$$

From the lecture, the reaction rates have the form

$$\begin{aligned} E + E \to D \quad & r_1(N_E, N_D) = k_+ N_E(N_E - 1), && (23)\\ D \to E + E \quad & r_2(N_E, N_D) = k_- N_D, && (24) \end{aligned}$$

and the Master equation reads

$$\begin{aligned} \dot{P}(N_E, N_D, t) \;&=\; r_1(N_E - \Delta_E^1, N_D - \Delta_D^1) P(N_E - \Delta_E^1, N_D - \Delta_D^1, t)\\ &+\; r_2(N_E - \Delta_E^2, N_D - \Delta_D^2) P(N_E - \Delta_E^2, N_D - \Delta_D^2, t)\\ &-\; r_1(N_E, N_D) P(N_E, N_D) - r_2(N_E, N_D) P(N_E, N_D). \qquad (25) \end{aligned}$$

Solution to Problem 11

For the Langevin equation of the form

$$\dot{z} = -a + \xi(t), \tag{26}$$

where $a \geq 0$ is a constant, $\langle \xi(t) \rangle = 0$, $\langle \xi(t)\xi(t') \rangle = \sigma^2 \delta(t - t')$, the Fokker-Planck equation reads

$$\frac{\partial \rho(x,t)}{\partial t} = a \frac{\partial \rho(x,t)}{\partial x} + \frac{\sigma^2}{2} \frac{\partial^2 \rho(x,t)}{\partial x^2}. \tag{27}$$

It can be put in a form of a flow equation

$$\frac{\partial \rho(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(a\rho(x,t) + \frac{\sigma^2}{2} \frac{\partial \rho(x,t)}{\partial x} \right), \tag{28}$$

with the current density $j(x,t) = -\left(a\rho(x,t) + \frac{\sigma^2}{2} \frac{\partial \rho(x,t)}{\partial x} \right)$. The stationary solution with vanishing current density satisfies the equation

$$\frac{\sigma^2}{2} \frac{\partial \rho(x)}{\partial x} = -a\rho(x), \tag{29}$$

which has the solution

$$\rho(x) = \rho(0) e^{-\frac{2a}{\sigma^2} x} = \rho(0) e^{-\frac{|q||E|x}{kT}}, \tag{30}$$

where we set $a = \frac{|q||E|}{\eta}$ and $\sigma^2 = \frac{2kT}{\eta}$.

Solution to Problem 12

The Master equation has the form

$$\partial_t P(n,t) = \sum_m \big(r(n|m) P(m,t) - r(m|n) P(n,t) \big). \tag{31}$$

Note that only $r(n|m)$ with $n \neq m$ enter. The condition that P_{eq} is stationary reads

$$\sum_m \big(r(n|m) P_{eq}(m) - r(m|n) P(n)_{eq} \big) = 0 \tag{32}$$

and it is implied by the detailed balance property

$$r(n|m)P_{eq}(m) = r(m|n)P(n)_{eq}. \tag{33}$$

We construct $r(m|n)$ so as to assure that this last property is satisfied. It can be rewritten as follows

$$\frac{r(n|m)}{r(m|n)} = e^{-\beta(E_n - E_m)}, \tag{34}$$

what is satisfied e.g. for $r(n|m) = e^{-\beta E_n}$. (The solution is not unique.)

Solution to Problem 13

The Itô Lemma says that if

$$\Delta x(t) = f(x(t))dt + dW_t \tag{35}$$

and $z = z(x)$ then

$$\begin{aligned} \langle \Delta z(t) \rangle &= [z'(x(t))f(x(t)) + \frac{\sigma^2}{2} z''(x(t))]dt, & (36) \\ \langle (\Delta z(t))^2 \rangle &= (z'(x(t))^2 \sigma^2 dt. & (37) \end{aligned}$$

In our case $z = x^2$, f is the identity, so

$$\begin{aligned} \langle \Delta z(t) \rangle &= [2z(t) + \sigma^2]dt, & (38) \\ \langle (\Delta z(t))^2 \rangle &= 4z(t)\sigma^2 dt. & (39) \end{aligned}$$

The Fokker-Planck equation for $\rho(z,t)$ has the form

$$\begin{aligned} \frac{\partial}{\partial t}\rho(z,t) &= \lim_{dt\to 0} \left\{ -\frac{\partial}{\partial z}\left[\frac{\langle \Delta z \rangle}{dt}\rho(z,t)\right] + \frac{1}{2}\frac{\partial^2}{\partial z^2}\left[\frac{\langle (\Delta z)^2 \rangle}{dt}\rho(z,t)\right] + \dots \right\}, & (40) \\ \frac{\partial}{\partial t}\rho(z,t) &= -\frac{\partial}{\partial z}\left[(2z+\sigma^2)\rho(z,t)\right] + \frac{1}{2}\frac{\partial^2}{\partial z^2}\left[4z\sigma^2\rho(z,t)\right]. & (41) \end{aligned}$$

Solution to Problem 14

We write the pseudocode for computation of a trajectory $n(t)$, $0 \le t \le T$ for a system jumping between discrete levels, say $n \in \{1, 2, \dots, N\}$. As input we have the initial position n_0, the rates $\Gamma(n)$ for jumping from n to any other level (for absorbing levels $\Gamma(n) = 0$) and the non-overlapping intervals $I_m^{(n)}$ s.t. $\bigcup_m I_m^{(n)} = [0,1]$ which say to which level m the system will jump from n. (See lecture notes attached to solution 5).

In the pseudocode below $n(t')$ is an array (output), n, m are auxiliary integer variables, t, ξ, η, τ are auxiliary real variables.

1 Set $n := n_0$, $t := 0$.

2 If n absorbing, set $n(t') := n$ for $t \leq t' \leq T$. Go to 4.
Else
Pick ξ, uniformly distributed, from $[0, 1]$.
Calculate $\tau = -\frac{1}{\Gamma(n)} \ln(\xi)$.
Set $t := t + \tau$, $n(t') := n$ for $t \leq t' \leq \min(t + \tau, T)$.
If $t + \tau \geq T$ Go to 4.
Else continue.

3 Pick η, uniformly distributed from $[0, 1]$.
If $\eta \in I_m^{(n)}$, set $n := m$. Go to 2.

4 End.

Solution to Problem 15

Let $\Gamma = (p_1, r_1, \dots p_N, r_N)$, $d\Gamma = \frac{d^{3N} p d^{3N} r}{N! h^{3N}}$. The probability density for a system in contact with infinite heat and volume reservoirs is given by (lecture)

$$\rho(\Gamma, V) = \frac{1}{\Psi(T, p, N)} e^{-\beta(H(\Gamma, V) + pV)}, \tag{42}$$

where

$$\Psi(T, p, N) = \int_0^\infty dV \int d\Gamma e^{-\beta(H(\Gamma, V) + pV)}. \tag{43}$$

The average volume of the system is given by

$$\langle V \rangle = \frac{1}{\Psi(T, p, N)} \int_0^\infty dV \int d\Gamma \, V e^{-\beta(H(\Gamma, V) + pV)}. \tag{44}$$

Note that

$$\left(\frac{\partial \langle V \rangle}{\partial p} \right)_T = -\beta(\langle V^2 \rangle - \langle V \rangle^2) = -\beta(\Delta V)^2. \tag{45}$$

For the ideal gas $\langle V \rangle = \frac{N k_B T}{p}$ so

$$(\Delta V)^2 = \frac{N}{p^2 \beta^2}. \tag{46}$$

Solution to Problem 16

The canonical partition sum for the one dimensional system confined in the interval of length L is given by

$$Z(T, L, N) = \int \frac{d^N p d^N x}{N! h^N} e^{-\beta c \sum_{i=1}^N |p_i|} = \frac{1}{N!} \frac{L^N}{h^N} \left(2 \int_0^\infty dp e^{-\beta c p} \right)^N \tag{47}$$

$$= \frac{1}{N!} \left(\frac{2L}{h \beta c} \right)^N. \tag{48}$$

Consequently

$$F(T,L,N) = -\beta^{-1}\ln Z(T,L,N) = -Nk_BT\ln\left(\frac{2Lk_BT}{hc}\right) + k_BT\ln N!. \tag{49}$$

Recalling that $S(T,L,N) = -\left(\frac{\partial F}{\partial T}\right)_{L,N}$ we get the specific heat

$$c_V = T\left(\frac{\partial S}{\partial T}\right)_{L,N} = T\left(\frac{\partial^2 F}{\partial T^2}\right)_{L,N} = Nk_B. \tag{50}$$

From the equipartition law one would expect $c_V = \frac{1}{2}Nk_B$. However, this law is valid only for quadratic Hamiltonians.

Solution to Problem 17

Making use of the Stirling formula $\ln N! = N\ln N - N + o(N)$ we get

$$\frac{S}{N} = \frac{k_B}{N}\ln\omega_E = k_B\big(\ln(\varepsilon\alpha^\gamma(1-\alpha)^{1-\gamma}\frac{V}{N}) + 1 + \frac{o(N)}{N}\big). \tag{51}$$

Proceeding to the thermodynamic limit we denote $s = \lim_\infty \frac{S}{N}$, $v = \lim_\infty \frac{V}{N}$. We obtain

$$s(\alpha) = k_B\big(\ln(\varepsilon v) + \gamma\ln\alpha + (1-\gamma)\ln(1-\alpha) + 1\big). \tag{52}$$

From the derivative

$$\frac{\partial s(\alpha)}{\partial\alpha} = k_B\left(\frac{\gamma}{\alpha} - \frac{1-\gamma}{1-\alpha}\right) \tag{53}$$

we obtain that the maximum of $s(\alpha)$ is at $\alpha = \gamma$.

Solution to Problem 18

From the formula

$$dF = -SdT - pdV \tag{54}$$

there follows the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = \frac{\partial\phi(V,T)}{\partial T}. \tag{55}$$

Solution to Problem 19

The differential of the free enthalpy is given by

$$dG(p.T) = -S(p,T)dT + V(p,T)dp = -\chi(\phi^{-1}(p,T),T)dT + \phi^{-1}(p,T)dp. \tag{56}$$

Solution to Problem 20

The Hamiltonian is $H = \sum_{i=1}^{N}(\frac{p_i^2}{2m} + fx_i)$. The canonical partition sum has the form

$$\begin{aligned} Z(T,L,N) &= \int \frac{d^N p d^N x}{N! h^N} e^{-\beta H(p,x)} = \frac{1}{N! h^N}\left(\frac{2m\pi L^2}{\beta}\right)^{\frac{N}{2}}\left(\frac{1}{\beta f L}(1-e^{-\beta f L})\right)^N \\ &= Z_{\mathrm{ig}}\left(\frac{1}{\beta f L}(1-e^{-\beta f L})\right)^N . \end{aligned} \tag{57}$$

The free energy is given by

$$F = -\frac{1}{\beta}\ln Z = F_{\mathrm{ig}} - \frac{N}{\beta}\ln\left(\frac{1}{\beta f L}(1-e^{-\beta f L})\right). \tag{58}$$

Next, we compute the entropy

$$S = -\left(\frac{\partial F}{\partial T}\right)_{L,N} = S_{\mathrm{ig}} + N k_B \left\{ \ln(1-e^{-\beta f L}) - \ln(\beta f L) + 1 - \frac{\beta f L}{e^{\beta f L}-1}\right\} \tag{59}$$

and the heat transfer in the process.

$$\delta Q = T dS = T\left(\frac{\partial S}{\partial f}\right)_{T,L,N} df = NL(\beta f L)\left\{ -\frac{1}{\beta f L} + \frac{1}{e^{\beta f L}-1} + \frac{1}{(e^{\beta f L}-1)^2}\right\} df. \tag{60}$$

Finally we calculate the energy

$$E = F + TS = E_{\mathrm{ig}} + N k_B T \left(1 - \frac{\beta f L}{e^{\beta f L}-1}\right), \tag{61}$$

and its change in the process

$$dE = NL\left\{\frac{1 - e^{\beta f L}(1-\beta f L)}{(e^{\beta f L}-1)^2}\right\} df. \tag{62}$$

Consequently

$$\delta W = dE - \delta Q = NL\left\{\frac{1}{\beta f L} - \frac{1}{e^{\beta f L}-1}\right\} df. \tag{63}$$

Alternative solution 1: There is a short-cut possible in the above solution which makes use of the 'principle of maximal work' which says (in our context) that the work performed by the system in contact with thermal reservoir in a reversible process is given by the change of the free energy in this process. Therefore we can obtain δW directly from (58)

$$\delta W = dF = \left(\frac{\partial F}{\partial f}\right)_{T,L,N} df = NL\left\{\frac{1}{\beta f L} - \frac{1}{e^{\beta f L}-1}\right\} df. \tag{64}$$

Alternative solution 2: One can also obtain work and heat directly from their microscopic definitions: Let ρ be the canonical state (probability density)

$$\rho(\Gamma) = \frac{1}{Z} e^{-\beta H(\Gamma)}, \tag{65}$$

where $\Gamma = (p_1, x_1 \ldots p_N, x_N)$, $d\Gamma = \frac{d^N x d^N p}{N! h^N}$. The average energy is given by

$$E = \langle H \rangle =: (\rho, H) = \frac{1}{Z}\int e^{-\beta H(\Gamma)} H(\Gamma) d\Gamma, \tag{66}$$

and its change equals

$$dE = (d\rho, H) + (\rho, dH). \tag{67}$$

We define $\delta W = (\rho, dH)$ and $\delta Q = (d\rho, H)$. Let us compute the work first

$$\begin{aligned}
\delta W &= \langle \frac{\partial H}{\partial f} \rangle df = \left\{ \frac{1}{Z} \int e^{-\beta H(\Gamma)} \sum_{i=1}^{N} x_i d\Gamma \right\} df = \left\{ \frac{N}{Z_1} \int e^{-\beta H_1(p,x)} x \, dp dx \right\} df &(68)\\
&= \left(\frac{N}{Z_f} \int_0^L e^{-\beta f x} x dx \right) df = NL\{ \frac{1}{\beta f L} - \frac{1}{e^{\beta f L} - 1} \} df, &(69)
\end{aligned}$$

where $H_1(p,x) = \frac{p^2}{2m} + fx$, $Z_0 = \sqrt{\frac{2\pi m}{\beta}}$, $Z_f = \frac{1}{\beta f}(1 - e^{-\beta f L})$, $Z_1 = Z_o Z_f$ and we made use of the fact that

$$\int_0^L e^{-\beta f x} x \, dx = \frac{1}{(\beta f)^2}(1 - e^{-\beta f L}) - \frac{L}{\beta f} e^{-\beta f L}. \tag{70}$$

Next, we compute the heat transfer. Making use of (66) we get

$$\begin{aligned}
\delta Q &= -\left(\frac{1}{Z} \frac{\partial Z}{\partial f} \langle H \rangle + \beta \langle \frac{\partial H}{\partial f} H \rangle \right) df &(71)\\
&= \beta \left(\frac{\partial F}{\partial f} - \langle \frac{\partial H}{\partial f} \rangle \right) \langle H \rangle df - \beta \left(\langle \frac{\partial H}{\partial f} H \rangle - \langle \frac{\partial H}{\partial f} \rangle \langle H \rangle \right) df. &(72)
\end{aligned}$$

The first bracket on the r.h.s of the above equation is equal to zero, by comparing the last equality in (64) with (69), or simply making use of the maximal work principle. Since $H = \sum_{i=1}^{N} H_i$, where H_i are uncorrelated random variables and each H_i is a sum of two uncorrelated random variables $\frac{p_i^2}{2m}$ and $f x_i$, we obtain

$$\begin{aligned}
\delta Q &= -\beta \left(\langle \frac{\partial H}{\partial f} H \rangle - \langle \frac{\partial H}{\partial f} \rangle \langle H \rangle \right) df = -\beta N \left(\langle \frac{\partial H_1}{\partial f} H_1 \rangle - \langle \frac{\partial H_1}{\partial f} \rangle \langle H_1 \rangle \right) df &(73)\\
&= -\beta N f (\langle x^2 \rangle - \langle x \rangle^2) df. &(74)
\end{aligned}$$

We obtain, as in the computation of work,

$$\langle x \rangle = \frac{1}{Z_f} \int_0^L e^{-\beta f x} x dx = L\{ \frac{1}{\beta f L} - \frac{1}{e^{\beta f L} - 1} \}, \tag{75}$$

and

$$\begin{aligned}
\langle x^2 \rangle &= \frac{1}{Z_f} \int_0^L e^{-\beta f x} x^2 dx = -\frac{1}{Z_f} \frac{d}{d(\beta f)} \int_0^L e^{-\beta f x} x dx \\
&= L^2 \left(\frac{2}{(\beta f L)^2} - \frac{1}{e^{\beta f L} - 1} - \left(\frac{2}{\beta f L} \right) \frac{1}{e^{\beta f L} - 1} \right), &(76)
\end{aligned}$$

where we made use of (70). Finally we get

$$\delta Q = NL(\beta f L) \left\{ -\frac{1}{\beta f L} + \frac{1}{e^{\beta f L} - 1} + \frac{1}{(e^{\beta f L} - 1)^2} \right\} df. \tag{77}$$