Physics III: Final (Solutions)

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(Tuesday July 31, 9 AM)

First and Last Name: _____

Exam Instructions:
This is an open-notebook exam, so feel free to use the notes you have transcribed throughout the summer and problem sets you have completed, but cellphones, laptops, and any notes written by someone else are prohibited. You will have **2 hours** to complete this exam.

Since this is a timed exam, your solutions need not be as "organized" as are your solutions to assignments. Short calculations and succinct explanations are acceptable, and you can state (without derivation) the standard results we derived in class. However, you should also recognize that you cannot receive partial credit for derivations/explanations you do not provide.

Challenge _____

Problem 1 (10 pts): _____

Problem 2 (30 pts): _____

Problem 3 (20 pts): _____

Problem 4 (20 pts): _____

Problem 5 (25 pts): _____

Problem 6 (25 pts): _____

Total (130 pts):

1. **Protein Expression and Probability (20 points)**

For a particular model of a gene in a cell, the probability density that said gene produces a concentration x of proteins during the cell cycle is given by

$$p(x) = A\left(\frac{x}{b}\right)^N e^{-x/b}, \tag{1}$$

where b is a biological constant with units of concentration, N is a physical constant, and A is a normalization parameter.

(a) (5 points) The concentration of proteins that can be produced ranges from zero to infinite. What must A be in order for Eq.(1) to be normalized?

(b) (5 points) What is the mean of the normalized probability density?

(c) **(Removed in Final Version)** For this probability distribution, compute the average

$$\langle e^{x/a} \rangle, \tag{2}$$

and write the result in terms of an infinite sum over a binomial coefficient. *(Note that* $e^x = \sum_{j=0}^{\infty} x^j/j!$*.)*

Solution:

(a) Given the range of possible protein production, x can go from 0 to ∞. Therefore, for $p(x)$ to be normalized, we must obtain 1 when we integrate the function over this entire domain:

$$\int_0^\infty dx\, p(x) = 1. \tag{3}$$

From the definition of the probability density we have

$$\begin{aligned} 1 &= \int_0^\infty dx\, A\left(\frac{x}{b}\right)^N e^{-x/b} \\ &= A\int_0^\infty dx\, \left(\frac{x}{b}\right)^N e^{-x/b} \\ &= A\int_0^\infty du\, b\, u^N e^{-u} \\ &= A\, b\int_0^\infty du\, u^N e^{-u}, \end{aligned} \tag{4}$$

where we changed variables with $u = x/b$ in the third line, and factored the u-independent constant out of the integral in the final line. By the integral definition of factorial, we have

$$N! = \int_0^\infty du\, u^N e^{-u}. \tag{5}$$

Therefore, the final line of Eq.(4) becomes

$$1 = A\, b\, N!, \tag{6}$$

and we can conclude

$$\boxed{A = \frac{1}{bN!}.} \tag{7}$$

The normalized probability density is therefore

$$p(x) = \frac{1}{bN!}\left(\frac{x}{b}\right)^N e^{-x/b}. \tag{8}$$

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(b) The mean of a random variable defined by the probability density $p(x)$ (which has a nonzero domain for $x \in [0, \infty)$) is

$$\langle x \rangle = \int_0^\infty dx\, x\, p(x). \tag{9}$$

Using Eq.(8) to compute this value, we obtain

$$\begin{aligned}
\langle x \rangle &= \int_0^\infty dx\, x\, \frac{1}{bN!}\left(\frac{x}{b}\right)^N e^{-x/b} \\
&= \frac{1}{N!}\int_0^\infty dx\, \left(\frac{x}{b}\right)^{N+1} e^{-x/b} \\
&= \frac{1}{N!}\int_0^\infty du\, b\, u^{N+1} e^{-u} \\
&= b\frac{(N+1)!}{N!},
\end{aligned} \tag{10}$$

where in the third line we performed a change of variables with $u = x/b$ and in the final line we used Eq.(5). By the definition of factorial, we ultimately find

$$\boxed{\langle x \rangle = b(N+1).} \tag{11}$$

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(c) **(Not part of final version of exam)** We now seek to compute the average of $e^{x/a}$. Noting the Taylor series definition of the exponential

$$e^{x/a} = \sum_{j=0}^\infty \frac{(x/a)^j}{j!}, \tag{12}$$

we have

$$\begin{aligned}
\langle e^{x/a} \rangle &= \left\langle \sum_{j=0}^\infty \frac{(x/a)^j}{j!} \right\rangle \\
&= \sum_{j=0}^\infty \frac{1}{j!}\,\frac{1}{a^j}\,\langle x^j \rangle.
\end{aligned} \tag{13}$$

Computing $\langle x^j \rangle$ yields

$$\begin{aligned}
\langle x^j \rangle &= \int_0^\infty dx\, x^j\, \frac{1}{bN!}\left(\frac{x}{b}\right)^N e^{-x/b} \\
&= \frac{b^j}{bN!}\int_0^\infty dx\, \left(\frac{x}{b}\right)^{N+j} e^{-x/b} \\
&= \frac{b^j}{bN!}\int_0^\infty du\, b\, u^{N+j} e^{-u}
\end{aligned}$$

$$= b^j \frac{(N+j)!}{N!}, \tag{14}$$

where in the second line we multiplied the numerator and the denominator by b^j, in the third line we performed a change of variables $u = x/b$, and in the final line we used Eq.(5). Inserting this result into Eq.(13), we find

$$\langle e^{x/a} \rangle = \sum \sum_{j=0}^{\infty} \frac{1}{j!} \frac{1}{a^j} b^j \frac{(N+j)!}{N!} = \sum_{j=0}^{\infty} \frac{(N+j)!}{j!N!} \left(\frac{b}{a}\right)^j, \tag{15}$$

or

$$\boxed{\langle e^{x/a} \rangle = \sum_{j=0}^{\infty} \binom{N+j}{j} \left(\frac{b}{a}\right)^j.} \tag{16}$$

We note that we could evaluate $\langle e^{x/a} \rangle$ directly using a change of variables in the argument of the exponential of the distribution. The result would be

$$\begin{aligned}
\langle e^{x/a} \rangle &= \frac{1}{bN!} \int_0^{\infty} dx\, e^{x/a} \left(\frac{x}{b}\right)^N e^{-x/b} \\
&= \frac{1}{bN!} \int_0^{\infty} dx\, \left(\frac{x}{b}\right)^N e^{-(1/b - 1/a)x} \\
&= \frac{1}{bN!} \int_0^{\infty} du\, \frac{ab}{a-b} \left(\frac{au}{a-b}\right)^N e^{-u} \\
&= \frac{1}{N!} \left(\frac{a}{a-b}\right)^{N+1} \int_0^{\infty} du\, u^N e^{-u} \\
&= \frac{1}{(1-b/a)^{N+1}},
\end{aligned} \tag{17}$$

where in the second line we made the change of variables $u = x(a-b)/ab$. Considering Eq.(16), the result Eq.(17) implies

$$\sum_{j=0}^{\infty} \binom{N+j}{j} q^j = \frac{1}{(1-q)^{N+1}}. \tag{18}$$

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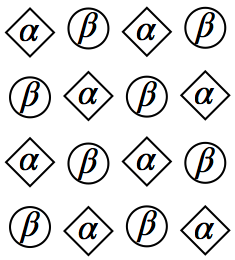
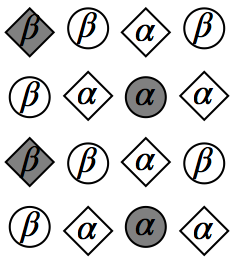
2. **Binary Alloy**[1] **(30 points)**



(a) $N = 8$ and $k = 0$ microstate



(b) Microstate with $N = 8$ and $k = 2$

Figure 2: Two different microstates for an $N = 8$ system. The figure on the left shows the original positions of the α and β atoms (i.e., the positions at temperature zero). The figure on the right shows a microstate in which $k = 2$ atoms (both α and β) have been displaced.

A binary alloy contains N identical atoms of type α and N identical atoms of type β. At low temperatures the system can be modeled as follows. There are N well-defined α-sites which are normally occupied by the α atoms and N well-defined β-sites which are normally occupied by the β atoms. At $T = 0$, the system is completely ordered, and all the α-sites are occupied by α atoms and same thing for β-sites and β atoms. However, at finite temperature, $k \leq N$ of the α atoms are displaced into the β-sites. (An equal number of β atoms is displaced to the α-sites).

The energy of the system is given by $E = \varepsilon k$, where ε is a constant with units of energy. To specify one of the many microstates of the system consistent with a particular value of k, one needs to indicate which α-sites are occupied by the k β atoms and which β-sites are occupied by the k α atoms. For example, if $k = 1$, then one α atom is displaced and there are N possible α atoms to choose from, and there are N possible β-site locations where it could be placed.

(a) (5 points) What is the number of different ways of choosing k of the α-sites to be vacated and occupied by β atoms?

(b) (5 points) What is the number of different ways of choosing k of the β-sites to be vacated and occupied by α atoms?

(c) (5 points) What is the free energy of the system as a function of k? *(Your answer can be written in terms of factorials or binomial coefficients)*

(d) (5 points) Take Stirling's approximation to be $\ln N! \simeq N \ln N - N$. What is the free energy of the system as a function of k after applying Stirling's approximation?

(e) (10 points) The system is in thermal equilibrium at a temperature T, and the number of displaced sites is $\overline{k}(T)$. Using the result from (c), and the properties of free energy at thermal equilibrium, determine $\overline{k}$ as a function of ε, N, and T.

S*olution* :

(a) We have N different α-sties and we seek to choose k of them to be vacated. The number of ways to make this choice is a classic result in combinatorics. There are

$$\boxed{\binom{N}{k}} \tag{19}$$

[1]This problem is from an MIT 8.044 Open courseware exam.

ways to choose k alpha sites from N possible sites.

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(b) The answer to this question is identical to the answer of the above question. We have N different β-sites and we seek to choose k of them to be vacated. The number of ways to make this choice is

$$\boxed{\binom{N}{k}.} \tag{20}$$

(c) We denote the free energy of the system as $F_N(k)$. In terms of the energy $E_N(k)$ and the entropy $S_N(k)$ of the system, this free energy is

$$F_N(k) = E_N(k) - TS_N(k). \tag{21}$$

From the problem prompt, we know that the energy of the system is

$$E_N(k) = \varepsilon k. \tag{22}$$

Since we are writing our free energy in terms of the macrostate variable k, the entropy must also be written in terms of the macrostate. Writing the entropy in terms of the macrostate entails using the Boltzmann definition of the entropy, namely,

$$S_N(k) = k_B \ln \Omega_N(k), \tag{23}$$

where $\Omega_N(k)$ is the number of microstates associated with a particular value of k. In parts (a) and (b) we calculated the two factors which contribute to $\Omega_N(k)$. The number of microstates associated with k displaced atoms, is the number of ways to choose k atoms of type-α to be displaced times the number of ways to choose k atoms of type-β to replace them. Namely,

$$\Omega_N(k) = \binom{N}{k}\binom{N}{k} = \binom{N}{k}^2. \tag{24}$$

Assembling the pieces of Eq.(21), we then obtain

$$\boxed{F_N(k) = \varepsilon k - 2k_B T \ln \binom{N}{k},} \tag{25}$$

where we used $\ln a^2 = 2 \ln a$ to simplify the final result.

(d) We want to apply Stirling's approximation to Eq.(25) and obtain an analytic form of the free energy. The only term to which we need to apply Stirling's approximation is the last one. Doing so, we find

$$\begin{aligned} \ln \binom{N}{k} &= \ln N! - \ln k! - \ln(N-k)! \\ &\simeq N \ln N - N - k \ln k + k - (N-k)\ln(N-k) + (N-k) \\ &= N \ln N - k \ln k - (N-k)\ln(N-k). \end{aligned} \tag{26}$$

The free energy Eq.(25) then becomes

$$\boxed{F_N(k) \simeq \varepsilon k - 2k_B T \Big[N \ln N - k \ln k - (N-k)\ln(N-k) \Big].} \tag{27}$$

(e) We now wish to find the value of k which defines the thermal equilibrium of the system. Since

the free energy is at a local minimum at thermal equilibrium we are looking for $\overline{k}$ such that

$$\frac{\partial}{\partial k}F_N(k)\Big|_{k=\overline{k}} = 0, \quad \frac{\partial^2}{\partial k^2}F_N(k)\Big|_{k=\overline{k}} > 0. \tag{28}$$

Applying the first condition in Eq.(28) to Eq.(27), we obtain

$$\begin{aligned} 0 &= \frac{\partial}{\partial k}\Big[\varepsilon k - 2k_BT\big[N\ln N - k\ln k - (N-k)\ln(N-k)\big]\Big]\Big|_{k=\overline{k}} \\ &= \varepsilon - 2k_BT\Big[-\ln\overline{k} - 1 + \ln(N-\overline{k}) + 1\Big] \\ &= \varepsilon + 2k_BT\ln\frac{\overline{k}}{(N-\overline{k})} \end{aligned} \tag{29}$$

Subtracting ε, dividing by $2k_BT$, and taking the exponential of both sides gives us

$$e^{-\varepsilon/2k_BT} = \frac{\overline{k}}{N-\overline{k}}. \tag{30}$$

Solving for $\overline{k}$ leaves us with

$$\boxed{\overline{k}(T) = \frac{N}{e^{\varepsilon/2k_BT}+1}.} \tag{31}$$

which defines the how the average number of displaced atoms varies as a function of the thermal equilibrium temperature T. For completeness, we need to ensure that Eq.(31) corresponds to a local minimum of the free energy and not just a critical point. Checking the inequality in Eq.(28), we have

$$\begin{aligned} \frac{\partial^2}{\partial k^2}F_N(k)\Big|_{k=\overline{k}} &= \frac{\partial^2}{\partial k^2}\Big[\varepsilon k - 2k_BT\big[N\ln N - k\ln k - (N-k)\ln(N-k)\big]\Big]\Big|_{k=\overline{k}} \\ &= \frac{\partial}{\partial k}\Big[-2k_BT\big[-\ln k - 1 + \ln(N-k) + 1\big]\Big]\Big|_{k=\overline{k}} \\ &= \frac{2k_BT}{\overline{k}} + \frac{2k_BT}{N-\overline{k}}, \end{aligned} \tag{32}$$

which is indeed always greater than zero because $\overline{k}$ is less than N and greater than 0. Therefore, Eq.(31) indeed defines a local minimum of the free energy and also the thermal equilibrium of the system.

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3. **Model of Receptor Binding (20 points)**
On the cell membranes of cells, there are protein receptors to which extracellular molecules can bind and ultimately induce a signal in the cell. Let us consider a simple model of such receptor-molecule binding and analyze this model from the perspective of statistical physics.

Say we have many molecules each of which can either be free or bound to one of M distinct protein receptors (There are many more molecules than receptors). The molecules are identical to one another and each one has energy 0 when it is free and energy $-E_0$ when it is bound to a receptor. Our system exists at a temperature T. When the particles are free, we assume there is only *one* microstate for the free particles. An example microstate is shown in Fig. 3.

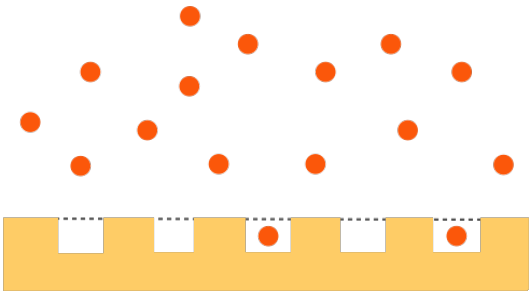

Figure 3: A particular microstate of a system with $M = 5$ receptor sites. There are two molecules bound to receptors so the energy of this microstate is $-2E_0$.

(a) (10 points) What is the partition function of the system written in terms of T, M, and E_0 (and a physical constant)? *(Your result should not have any unevaluated summations)*

(b) (5 points) Compute $\langle k \rangle$, the average number of molecules bound to receptors as a function of T.

(c) (5 points) At what temperature is an average of one molecule bound to the receptors?

Solution:

(a) We seek the partition function of this system. We have a system with many identical molecules, each of which has energy 0 when it is unbound and energy $-E_0$ when it is bound to a receptor site. There are M distinct receptor sites. Therefore, if $k \leq M$ molecules are bound to receptor sites, there are "M choose k" ways to arrange these identical molecules amongst the M sites, and such a microstate has energy $-E_0 k$. Therefore, the probability to have k occupied receptor sites is given by

$$p_k = \frac{1}{Z_M(\beta E_0)} \binom{M}{k} e^{\beta E_0 k}, \tag{33}$$

where Z is the partition function of the system. Given that k can run from 0 to M, we then find the partition function

$$Z_M(\beta E_0) = \sum_{k=0}^{N} \binom{M}{k} e^{\beta E_0 k} = \left(1 + e^{\beta E_0}\right)^M, \tag{34}$$

where we used the Binomial theorem in the final line.

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(b) We can compute $\langle k \rangle$, the average number of occupied receptor sites, by using Eq.(33) in our prob-

ability based definition of average. We have

$$\langle k \rangle = \sum_{k=0}^{M} k\, p_k = \frac{1}{Z_M(\beta E_0)} \sum_{k=0}^{M} k \binom{M}{k} e^{\beta E_0 k}. \tag{35}$$

From Eq.(34), we can write Eq.(35) in terms of the partial derivative of the partition function. We then find

$$\begin{aligned} \langle k \rangle &= \frac{1}{Z_M(\beta E_0)} \frac{\partial}{\partial(\beta E_0)} \sum_{k=0}^{M} \binom{M}{k} e^{\beta E_0 k} \\ &= \frac{1}{Z_M(\beta E_0)} \frac{\partial}{\partial(\beta E_0)} Z_M(\beta E_0) \\ &= \frac{\partial}{\partial(\beta E_0)} \ln Z_M(\beta E_0). \end{aligned} \tag{36}$$

Using Eq.(34) to compute this quantity yields

$$\langle k \rangle = \frac{\partial}{\partial(\beta E_0)} \ln \left(1 + e^{\beta E_0}\right)^M = \frac{M}{1 + e^{-\beta E_0}}. \tag{37}$$

Therefore, the Eq.(37) is bounded above by M (as we expect) and as $T \to 0$ (i.e., $\beta \to \infty$), $\langle k \rangle$ approaches M and all the receptor sites become fully occupied. Conversely, as $T \to \infty$ (i.e., $\beta \to 0$), $\langle k \rangle$ approaches $M/2$ and half of the sites become occupied. Entropically, this makes sense because as $T \to 0$, entropy dominates the free energy and the system seeks the macrostate with the highest entropy.

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(c) To find the temperature at which the average number of bound molecules is 1, we set Eq.(37) to 1 and solve for T. Doing so we find

$$\begin{aligned} 1 &= \frac{M}{1 + e^{-E_0/k_B T}} \\ 1 + e^{-E_0/k_B T} &= M \\ e^{-E_0/k_B T} &= M - 1, \end{aligned} \tag{38}$$

which upon solving for T yields the temperature

$$\boxed{T = -\frac{E_0}{k_B \ln(M-1)}.} \tag{39}$$

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4. **Ideal Gas of Distinguishable Particles (20 points)**
The partition function for an ideal gas of N distinguishable particles where particle k has mass m_k can be written as

$$Z = \frac{1}{h^{3N}} \int_V d^3\mathbf{q}_1 \int_{\text{all } \mathbf{p}} d^3\mathbf{p}_1 \cdots \int_V d^3\mathbf{q}_N \int_{\text{all } \mathbf{p}} d^3\mathbf{p}_N \, \exp\left(-\frac{1}{k_B T} \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m_k} \right)., \tag{40}$$

where V is the volume of the system.

(a) (10 points) Evaluate all the integrals in Eq.(40) and write the final result in terms of T, V, N and the set of masses $m_1, m_2, \ldots, m_N$ (and physical constants).

(b) (5 points) What is the free energy of this system written in terms of T, V, N and the set of masses $m_1, m_2, \ldots, m_N$ (and physical constants).

(c) (5 points) Given that pressure is the negative of the volume partial derivative of the free energy, derive the relationship between pressure P, number of particles N, volume V and temperature T for this system.

Solution:

(a) We can evaluate the integral Eq.(40) by using the fact that the integrand is independent of position and by using the formula

$$\int_{-\infty}^{\infty} dx \, e^{-ax^2} = \sqrt{\frac{\pi}{a}}. \tag{41}$$

Working through the calculation, we have

$$\begin{aligned}
Z &= \frac{1}{h^{3N}} \int_V d^3\mathbf{q}_1 \int_{\text{all } \mathbf{p}} d^3\mathbf{p}_1 \cdots \int_V d^3\mathbf{q}_N \int_{\text{all } \mathbf{p}} d^3\mathbf{p}_N \, \exp\left(-\frac{1}{k_B T} \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m_k} \right) \\
&= \frac{V^N}{h^{3N}} \int_{\text{all } \mathbf{p}} d^3\mathbf{p}_1 \cdots \int_{\text{all } \mathbf{p}} d^3\mathbf{p}_N \exp\left(-\frac{1}{k_B T} \sum_{k=1}^{N} \frac{\mathbf{p}_k^2}{2m_k} \right) \\
&= \frac{V^N}{h^{3N}} \prod_{k=1}^{N} \int_{\text{all}\mathbf{p}} d^3\mathbf{p}_k \, \exp\left(-\frac{1}{k_B T} \frac{\mathbf{p}_k^2}{2m_k} \right) \\
&= \frac{V^N}{h^{3N}} \prod_{k=1}^{N} \left(\int_{-\infty}^{\infty} dp_k \, e^{-p_k^2/2m_k k_B T} \right)^3 \\
&= \frac{V^N}{h^{3N}} \prod_{k=1}^{N} \left(\sqrt{2\pi m_k k_B T} \right)^3 .
\end{aligned} \tag{42}$$

In the second equality, we evaluated all of the position integrals. In the third equality we used the fact that the momentum integrals had identical forms to condense them into product notation. In the fourth equality, we multiplied the gaussian integrals for the three coordinate directions and in the final line we used Eq.(41). Further simplifying Eq.(42) by factoring out $\sqrt{2\pi k_B T}$ from the product, we obtain

$$\boxed{Z = \frac{V^N}{h^{3N}} (2\pi k_B T)^{3N/2} \prod_{k=1}^{N} \sqrt{m_k^3}.} \tag{43}$$

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(b) Given the partition function Z of a system, the free energy is

$$F = -k_B T \ln Z. \tag{44}$$

Therefore, the free energy of this ideal gas system is

$$\begin{aligned} F &= -k_B T \ln \left[\frac{V^N}{h^{3N}} (2\pi k_B T)^{3N/2} \prod_{k=1}^{N} \sqrt{m_k^3} \right] \\ &= -k_B T \ln \left[V^N \left(\frac{2\pi k_B T}{h^2} \right)^{3N/2} \prod_{k=1}^{N} m_k^{3/2} \right] \\ &= \boxed{-k_B T \left[N \ln V + \frac{3N}{2} \ln \frac{2\pi k_B T}{h^2} + \frac{3}{2} \sum_{k=1}^{N} \ln m_k \right].} \end{aligned} \tag{45}$$

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(c) The pressure of an ideal gas system is given by

$$P = -\frac{\partial F}{\partial V}. \tag{46}$$

Computing the pressure from Eq.(45), we find

$$\begin{aligned} P &= -\frac{\partial}{\partial V} \left\{ -k_B T \left[N \ln V + \frac{3N}{2} \ln \frac{2\pi k_B T}{h^2} + \frac{3}{2} \sum_{k=1}^{N} \ln m_k \right] \right\} \\ &= k_B T \frac{\partial}{\partial V} N \ln V = k_B T N \frac{1}{V}, \end{aligned} \tag{47}$$

where in the second line we dropped all terms which were independent of V. Therefore, we have

$$\boxed{P = \frac{N k_B T}{V},} \tag{48}$$

which is the standard ideal gas law for identical particles. Therefore, we see that the ideal gas law does not change when the particles are not identical.

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5. **Statistical Physics of Permutations (25 points)**
We have $2N$ objects consisting of N objects of type-B denoted $B_1, B_2, \ldots, B_N$ and N objects of type-W denoted $W_1, W_2, \ldots, W_N$. The objects can only exist in (B_k, W_ℓ) pairs, and the mircostates of our system are defined by a particular collection of pairings between the Bs and Ws. Fig. 4 depicts one such microstate for $N = 15$.

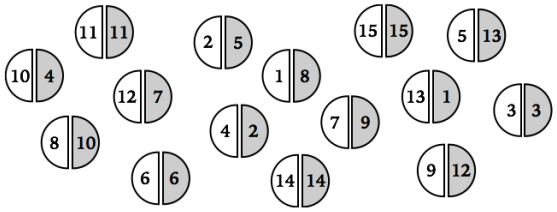

Figure 4: A particular microstate of a $N = 15$ system.

The energy of a microstate is the sum of the energies of all the pairs. The energy of a particular pair (consisting of (B_k, W_ℓ)) is

$$\mathcal{E}(B_k, W_\ell) = \begin{cases} 0 & \text{if } k = \ell, \\ \lambda & \text{if } k \neq \ell, \end{cases} \tag{49}$$

where $\lambda > 0$ is a parameter with units of energy. Namely, from Eq.(49), if a pair consists of (B_k, W_k), for any k, then the energy of the pair is zero, and if a pair consists of (B_ℓ, W_k), for $\ell \neq k$, then the energy of the pair is λ. We call the former a "matched pair" and the latter a "mismatched pair".

The partition function for this system can be written as

$$Z_N(\beta\lambda) = \sum_{j=0}^{N} g_N(j) e^{-\beta\lambda j} = \int_0^\infty dx\, e^{-x} \left[1 + (x-1)e^{-\beta\lambda}\right]^N, \tag{50}$$

where $\beta = 1/k_B T$ and where j is the number of mismatched pairs for a macrostate, and $g_N(j)$ is the number of microstates for a particular j. *You do not need to know the value of $g_N(j)$ to solve this problem*

(a) (5 points) Derive an expression for $\langle j \rangle$ in terms of the partition function and a partial derivative.

(b) (15 points) Use Laplace's method to evaluate the integral in Eq.(50)

(c) (5 points) Combining (a) and (b), what is $\langle j \rangle$ as a function of T?

Solution:

(a) We want to find an expression for $\langle j \rangle$, the average number of mismatched pairs, in terms of the partition function and its derivative. From the definition of the partition function as a finite sum, we have

$$Z_N(\beta\lambda) = \sum_{j=0}^{N} g_N(j) e^{-\beta\lambda j}. \tag{51}$$

From this expression, we can infer that $\langle j \rangle$ is

$$\begin{aligned} \langle j \rangle &= \frac{1}{Z_N(\beta\lambda)} \sum_{j=0}^{N} j\, g_N(j) e^{-\beta\lambda j} \\ &= -\frac{1}{Z_N(\beta\lambda)} \frac{\partial}{\partial(\beta\lambda)} Z_N(\beta\lambda). \end{aligned} \tag{52}$$

From the properties of chain rule, we then find

$$\boxed{\langle j \rangle = -\frac{\partial}{\partial(\beta\lambda)} \ln Z_N(\beta\lambda),} \tag{53}$$

which is the desired expression. ■

(b) We now seek to use Laplace's method to evaluate the integral in Eq.(50). First we write the partition function as

$$Z_N(\beta\lambda) = \int_0^\infty dx\, e^{-x} \left[1 + (x-1)e^{-\beta\lambda}\right]^N = \int_0^\infty dx\, e^{-N f(x,\beta\lambda)}, \tag{54}$$

where we defined

$$f(x, \beta\lambda) = \frac{x}{N} - \ln(1 + (x-1)e^{-\beta\lambda}). \tag{55}$$

Then, by Laplace's method, we have

$$Z_N(\beta\lambda) \simeq \sqrt{\frac{2\pi}{N f''(x_1, \beta\lambda)}} \exp\left[-N f(x_1, \beta\lambda)\right], \tag{56}$$

where x_1 is the value of x at which $f(x, \beta\lambda)$ is at a local minimum. To find this value of x we calculate $f'(x, \beta\lambda)$ and set it to zero for when $x = x_1$. Doing so we have

$$\begin{aligned} 0 &= f'(x, \beta\lambda)|_{x=x_1} \\ &= \frac{1}{N} - \frac{e^{-\beta\lambda}}{1 + (x_1 - 1)e^{-\beta\lambda}} \\ \frac{1}{N} &= \frac{e^{-\beta\lambda}}{1 + (x_1 - 1)e^{-\beta\lambda}} \\ &= \frac{1}{e^{\beta\lambda} + x_1 - 1}. \end{aligned} \tag{57}$$

Calculating the inverse of the final line and adding $1 - e^{\beta\lambda}$ to both sides gives us

$$x_1 = N - e^{\beta\lambda} + 1. \tag{58}$$

Eq.(58) defines the value at which the first x derivative of Eq.(55) is zero. To apply Laplace's method, we need to ensure that Eq.(55) is at a local minimum at Eq.(58). Computing the second derivative of $f(x, \beta\lambda)$ at x_1, we have

$$\begin{aligned} f''(x, \beta\lambda)\Big|_{x=x_1} &= \frac{e^{-\beta\lambda} e^{-\beta\lambda}}{\left(1 + (x_1 - 1)e^{-\beta\lambda}\right)^2} \\ &= \left(\frac{e^{-\beta\lambda}}{1 + (x_1 - 1)e^{-\beta\lambda}}\right)^2 \\ &= \frac{1}{N^2}, \end{aligned} \tag{59}$$

where in the final line we used the equality above Eq.(57). We thus see that x_1 indeed defines a local minimum because $f''(x, \beta\lambda)$ is always positive at x_1. To complete our evaluation of Eq.(56),

we need to compute $f(x, \beta\lambda)$ at x_1. Doing so (using Eq.(55) and Eq.(58)) we have

$$\begin{aligned} f(x, \beta\lambda)|_{x=x_1} &= \frac{N - e^{\beta\lambda} + 1}{N} - \ln(Ne^{\beta\lambda}) \\ &= \frac{N - e^{\beta\lambda} + 1}{N} - \ln N - \beta\lambda. \end{aligned} \tag{60}$$

Finally, with Eq.(60) and Eq.(59), we find that Eq.(56) becomes

$$Z_N(\beta\lambda) \simeq \sqrt{\frac{2\pi}{N\frac{1}{N^2}}} \exp\left[-N\left(\frac{N - e^{\beta\lambda} + 1}{N} - \ln N - \beta\lambda\right)\right], \tag{61}$$

or, more simply,

$$\boxed{Z_N(\beta\lambda) \simeq \sqrt{2\pi N} \exp\Big[-\big(N - e^{\beta\lambda} + 1 - N\ln N - N\beta\lambda\big)\Big],} \tag{62}$$

■

(c) Combining the results from (b) and (c), we can find an approximate expression for the average number of mismatched pairs as a function of temperature. We have

$$\begin{aligned} \langle j\rangle &= -\frac{\partial}{\partial(\beta\lambda)} \ln Z_N(\beta\lambda) \\ &\simeq -\frac{\partial}{\partial(\beta\lambda)} \left[\frac{1}{2}\ln(2\pi N) - \big(N - e^{\beta\lambda} + 1 - N\ln N - N\beta\lambda\big)\right] \\ &= -e^{\beta\lambda} + N, \end{aligned} \tag{63}$$

which yields the temperature dependent function

$$\boxed{\langle j\rangle \simeq N - e^{\lambda/k_B T}.} \tag{64}$$

■

6. **Transition Probabilities (25 points)**
We abstractly represent the connections between various states of a system with the picture below. In the picture, each filled circle represents a "node", and each line represents an "edge." When two nodes are linked by an edge, we say that they are "connected."

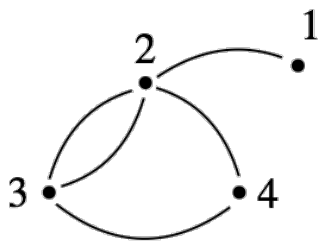

Figure 5

If at time t, we are at a node that is connected to M edges, then, in the next time step $t + \Delta t$, there is a probability of $1/M$ of traveling down any *one* of the connecting edges. There is a probability of zero of remaining at the same node.

(a) (5 points) Letting $\pi_{i\to j}$ represent the probability of transitioning from node i to node j in a single time step, fill in the elements below

$$\begin{array}{llll} \pi_{1\to1} = & \pi_{1\to2} = & \pi_{1\to3} = & \pi_{1\to4} = \\ \pi_{2\to1} = & \pi_{2\to2} = & \pi_{2\to3} = & \pi_{2\to4} = \\ \pi_{3\to1} = & \pi_{3\to2} = & \pi_{3\to3} = & \pi_{3\to4} = \\ \pi_{4\to1} = & \pi_{4\to2} = & \pi_{4\to3} = & \pi_{4\to4} = \end{array} \tag{65}$$

(b) (10 points) Say that at time t, the probability $p_j(t)$ to be at node j is given by

$$p_1(t) = \frac{1}{3}, \quad p_2(t) = \frac{1}{6}, \quad p_3(t) = \frac{1}{6}, \quad p_4(t) = \frac{1}{3}. \tag{66}$$

What is the probability to be at node 3 at time $t + \Delta t$?

(c) (10 points) We take $t \to \infty$. What is the probability to be at the various nodes?

Solution:

(a) In the problem prompt, we are told that the probability to move from a node and along a particular edge is $1/M$ when a node is connected to M edges. Therefore, by the figure in Fig. 5, we find the transition probabilities

$$\begin{array}{llll} \pi_{1\to1} = 0 & \pi_{1\to2} = 1 & \pi_{1\to3} = 0 & \pi_{1\to4} = 0 \\ \pi_{2\to1} = \frac{1}{4} & \pi_{2\to2} = 0 & \pi_{2\to3} = \frac{1}{2} & \pi_{2\to4} = \frac{1}{4} \\ \pi_{3\to1} = 0 & \pi_{3\to2} = \frac{2}{3} & \pi_{3\to3} = 0 & \pi_{3\to4} = \frac{1}{3} \\ \pi_{4\to1} = 0 & \pi_{4\to2} = \frac{1}{2} & \pi_{4\to3} = \frac{1}{2} & \pi_{4\to4} = 0 \end{array} \tag{67}$$

■

(b) Given the probabilities to be at various nodes at time t, the probability to be at node 3 at $t + \Delta t$ is

$$\begin{aligned} p_3(t+\Delta t) &= p_1(t)\pi_{1\to 3} + p_2(t)\pi_{2\to 3} + p_3(t)\pi_{3\to 3} + p_4(t)\pi_{4\to 3} \\ &= \frac{1}{3}\times 0 + \frac{1}{6}\times\frac{1}{2} + \frac{1}{6}\times 0 + \frac{1}{3}\times\frac{1}{2} \\ &= \frac{1}{12} + \frac{1}{6} = \boxed{\frac{1}{4}.} \end{aligned} \tag{68}$$

■

(c) To find the equilibrium probabilities for this system, we will make use of the detailed balance equation

$$\frac{p_i^{\text{eq}}}{p_j^{\text{eq}}} = \frac{\pi_{j\to i}}{\pi_{i\to j}}. \tag{69}$$

Computing the non-trivial equilibrium probability ratios from Eq.(67), we have

$$\begin{aligned} \frac{p_1^{\text{eq}}}{p_2^{\text{eq}}} &= \frac{1/4}{1} \\ &= \frac{1}{4} \quad\longrightarrow\quad p_2^{\text{eq}} = 4p_1^{\text{eq}} \end{aligned} \tag{70}$$

$$\begin{aligned} \frac{p_2^{\text{eq}}}{p_3^{\text{eq}}} &= \frac{2/3}{1/2} \\ &= \frac{4}{3} \quad\longrightarrow\quad p_3^{\text{eq}} = \frac{3}{4}p_2^{\text{eq}} = 3p_1^{\text{eq}} \end{aligned} \tag{71}$$

$$\begin{aligned} \frac{p_3^{\text{eq}}}{p_4^{\text{eq}}} &= \frac{1/2}{1/3} \\ &= \frac{3}{2} \quad\longrightarrow\quad p_4^{\text{eq}} = \frac{2}{3}p_3^{\text{eq}} = 2p_1^{\text{eq}}. \end{aligned} \tag{72}$$

In the above calculation, for each new result, we used the previous result to write the equilibrium probability in terms of p_1^{eq}. Assembling these results and noting that the probabilities must be normalized, we have the condition

$$1 = p_1^{\text{eq}} + p_2^{\text{eq}} + p_3^{\text{eq}} + p_4^{\text{eq}} = (1+4+3+2)\,p_1^{\text{eq}} = 10p_1^{\text{eq}} \tag{73}$$

which implies that

$$\boxed{p_1^{\text{eq}} = \frac{1}{10}.} \tag{74}$$

Given Eq.(70), Eq.(71), and Eq.(72), we find that the other equilibrium probabilities are

$$\boxed{p_2^{\text{eq}} = \frac{2}{5}, \quad p_3^{\text{eq}} = \frac{3}{10}, \quad p_4^{\text{eq}} = \frac{1}{5}.} \tag{75}$$

■