6.1 N particles, two energy levels. Consider a system consisting of N indistinguishable particles, each capable of being at energy level \(-\varepsilon\) or \(\varepsilon\), where \(\varepsilon > 0\). Do not assume \(N \gg 1\).

(1) Calculate the partition function and find \(\langle E \rangle\).

(2) What is the low-temperature limit of \(\langle E \rangle\)? What is the state of the system in the limit?

(3) What is the high-temperature asymptote of \(\langle E \rangle\)? What is the state of the system in the limit?

(4) Draw a sketch for the plot of \(\langle E \rangle\) as a function of \(T\).

(1) The table below lists all the states with energy and degeneracy.

<table>
<thead>
<tr>
<th>Number of particles at (-\varepsilon)</th>
<th>Number of particles at (\varepsilon)</th>
<th>Energy</th>
<th>Degeneracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(N)</td>
<td>(N\varepsilon)</td>
<td>1</td>
</tr>
<tr>
<td>1</td>
<td>(N-1)</td>
<td>((N-2)\varepsilon)</td>
<td>1</td>
</tr>
<tr>
<td>\vdots</td>
<td>\vdots</td>
<td>\vdots</td>
<td>\vdots</td>
</tr>
<tr>
<td>(N-1)</td>
<td>1</td>
<td>(-(N-2)\varepsilon)</td>
<td>1</td>
</tr>
<tr>
<td>(N)</td>
<td>0</td>
<td>(-N\varepsilon)</td>
<td>1</td>
</tr>
</tbody>
</table>

The partition function is expressed as

\[
Z = e^{\beta N\varepsilon} + e^{\beta(N-2)\varepsilon} + \cdots + e^{-\beta(N-2)\varepsilon} + e^{-\beta N\varepsilon}
\]

which is rewritten to

\[
Z = \frac{e^{\beta N\varepsilon} \left[ 1 - e^{-2(N+1)\beta\varepsilon} \right]}{1 - e^{-2\beta\varepsilon}} = \frac{e^{(N+1)\beta\varepsilon} - e^{-(N+1)\beta\varepsilon}}{e^{\beta\varepsilon} - e^{-\beta\varepsilon}} = \frac{\sinh((N+1)\beta\varepsilon)}{\sinh(\beta\varepsilon)}
\]

The mean of the energy is then calculated as
\[ \langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z = \frac{\varepsilon}{\tanh(\beta \varepsilon)} - \frac{(N+1)\varepsilon}{\tanh((N+1)\beta \varepsilon)} \]

(2) At low temperatures, $\beta \varepsilon \gg 1$. Then, $\tanh(\beta \varepsilon) \approx 1$ and $\tanh((N+1)\beta \varepsilon) = 1$. Therefore,

\[ \langle E \rangle \approx -N\varepsilon \]

All the particles are at energy level $-\varepsilon$.

(3) At high temperatures, $\beta \varepsilon << 1$. Then,

\[ \langle E \rangle \approx \frac{\varepsilon}{\beta \varepsilon - \frac{1}{3} (\beta \varepsilon)^3} - \frac{(N+1)\varepsilon}{(N+1)\beta \varepsilon - \frac{1}{3} [(N+1)\beta \varepsilon]^3} = \frac{1}{\beta} \left[ \frac{1}{1 - \frac{1}{3} (\beta \varepsilon)^2} - \frac{1}{1 - \frac{1}{3} [(N+1)\beta \varepsilon]^2} \right] \]

\[ \approx \frac{1}{\beta} \left\{ 1 + \frac{1}{3} (\beta \varepsilon)^2 - 1 - \frac{1}{3} [(N+1)\beta \varepsilon]^2 \right\} = -\frac{N(N+2)\beta \varepsilon^2}{3} \]

All states (energies are from $-N\varepsilon$ to $N\varepsilon$) are equally populated. The mean of the energy is zero in a crude approximation. How it approaches zero is described by the answer above.

(4)

\[ \langle E \rangle \]

6.2 Five particles, two energy levels. A system consists of five indistinguishable particles, each capable of adopting the energy of 0 and $\varepsilon$ ($\varepsilon > 0$).

(1) What is the partition function?

(2) Find the heat capacity $C_v$.

(3) What is the low-temperature limit of $C_v$?

(4) What is the high-temperature asymptote of $C_v$?

(5) Draw a sketch of $C_v/k_b$ as a function of $k_b T/\varepsilon$. 
(6) What is the state of the system in the low-temperature limit?

(7) What is the state of the system at high temperatures?

(8) The way the equation in (2) was derived allows us to write an expression of \( C_v \) for \( N \) indistinguishable particles in place of five. Write the expression.

(9) If \( N \gg 1 \) in (8), the expression can be simplified. Write that expression.

---

(1) The following diagram shows all possible states and the energy.

\[
\begin{array}{cccccc}
\varepsilon & \bullet & \bullet & \bullet & \bullet & \bullet \\
0 & \bullet & \bullet & \bullet & \bullet & \bullet \\
E & 0 & \varepsilon & 2\varepsilon & 3\varepsilon & 4\varepsilon & 5\varepsilon \\
\end{array}
\]

The partition function is

\[
Z = 1 + e^{-\varepsilon \beta} + e^{-2\varepsilon \beta} + e^{-3\varepsilon \beta} + e^{-4\varepsilon \beta} = \frac{1-e^{-5\varepsilon \beta}}{1-e^{-\varepsilon \beta}}
\]

(2)

\[
\ln Z = \ln \left(1-e^{-5\varepsilon \beta}\right) - \ln \left(1-e^{-\varepsilon \beta}\right)
\]

\[
\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = -\frac{5\varepsilon e^{-5\varepsilon \beta}}{1-e^{-5\varepsilon \beta}} + \frac{\varepsilon e^{-\varepsilon \beta}}{1-e^{-\varepsilon \beta}} = \frac{\varepsilon}{e^{\beta \varepsilon} - 1} - \frac{5\varepsilon}{e^{5\beta \varepsilon} - 1}
\]

\[
\frac{\partial \langle E \rangle}{\partial \beta} = -\frac{\varepsilon^2 e^{\beta \varepsilon}}{(e^{\beta \varepsilon} - 1)^2} + \frac{25\varepsilon^2 e^{5\beta \varepsilon}}{(e^{5\beta \varepsilon} - 1)^2} = -\frac{\varepsilon^2}{2} \left[ \frac{1}{\cosh(\beta \varepsilon) - 1} - \frac{25}{\cosh(5\beta \varepsilon) - 1} \right]
\]

\[
C_v = \frac{\partial \langle E \rangle}{\partial T} = -\frac{1}{k_B T^2} \frac{\partial \langle E \rangle}{\partial \beta} = \frac{\varepsilon^2}{2k_B T^2} \left[ \frac{1}{\cosh(\beta \varepsilon) - 1} - \frac{25}{\cosh(5\beta \varepsilon) - 1} \right]
\]

(3) \( \cosh(\beta \varepsilon) \to \infty \). Therefore, \( C_v \to 0 \).

(4)
6.3 Two particles, infinite number of energy levels. Consider a system of two indistinguishable particles, each capable of adopting one of energy levels $(0, \varepsilon, 2\varepsilon, \ldots, \text{with } \varepsilon > 0)$.

(1) What is the exact partition function $Z$?

(2) Confirm that $Z_i^2/2$ is a good approximation to $Z$ when the non-degeneracy
condition is met.

(1) The two particles are either at an identical energy level or at different energy levels.

\[ Z = \sum_{i=0}^{\infty} e^{-\beta 2i\epsilon} + \frac{1}{2} \sum_{i,j=0, i \neq j}^{\infty} e^{-\beta (i+j)\epsilon} = \frac{1}{2} \sum_{i=0}^{\infty} e^{-\beta 2i\epsilon} + \frac{1}{2} \sum_{i,j=0}^{\infty} e^{-\beta (i+j)\epsilon} \]

\[ = \frac{1}{2} \sum_{i=0}^{\infty} e^{-\beta 2i\epsilon} + \frac{1}{2} \left( \sum_{i=0}^{\infty} e^{-\beta i\epsilon} \right)^2 = \frac{1}{2} \left[ \frac{1}{1 - e^{-2\beta\epsilon}} + \left( \frac{1}{1 - e^{-\beta\epsilon}} \right)^2 \right] = \frac{1}{(1 - e^{-\beta\epsilon}) (1 - e^{-2\beta\epsilon})} \]

Note that in the transformation around the second equality, the second series contains terms for \( i = j \), which is identical to the first series.

(2) The single-particle partition function is

\[ Z_1 = \sum_{i=0}^{\infty} e^{-\beta i\epsilon} = \frac{1}{1 - e^{-\beta\epsilon}} \]

\[ \frac{Z_1^2}{2} = \frac{1}{2(1 - e^{-\beta\epsilon})^2} \]

\[ \ln \frac{Z_1^2}{2} = -\ln 2 - 2 \ln \left( 1 - e^{-\beta\epsilon} \right) \]

\[ \ln Z = -\ln \left( 1 - e^{-\beta\epsilon} \right) - \ln \left( 1 - e^{-2\beta\epsilon} \right) \]

\[ \ln Z - \ln \frac{Z_1^2}{2} = \ln \left( 1 - e^{-\beta\epsilon} \right) - \ln \left( 1 - e^{-2\beta\epsilon} \right) + \ln 2 = \ln \frac{2}{1 + e^{-\beta\epsilon}} \]

For the two partition functions to be close to each other, \( \beta \epsilon \ll 1 \). The latter is equivalent to that there are many states (their energy levels are 0, \( \epsilon \), \( 2\epsilon \), ...) that have energy levels less than \( k_B T \). The number of states is a lot greater than the number of particles that is 2.

6.4 \( N \) particles, \( q \) energy levels. Consider a system of \( N \) indistinguishable particles that can be at any of \( q \) equally spaced energy levels \( (0, \epsilon, 2\epsilon, ..., (q-1)\epsilon; \epsilon > 0) \), on
the condition that none of the levels accommodate two or more particles. Assume that \( N < q \).

(1) What is the state of the system in the limit of \( T = 0 \)? What is the energy of the system, \( \langle E \rangle \)?

(2) What is the state of the system in the limit of high temperature? What is \( \langle E \rangle \)?

(1) Each of the energy levels from 0 through \((N-1)\epsilon\) is singly occupied. The other levels are empty.

\[
\langle E \rangle = \sum_{i=0}^{N-1} i\epsilon = \frac{1}{2} N(N-1)\epsilon
\]

(2) All the energy levels are equally populated, but at most singly. The probability of occupancy is \( N/q \).

\[
\langle E \rangle = \sum_{i=0}^{q-1} i\epsilon \frac{N}{q} = \frac{N}{q} \frac{1}{2} q(q-1)\epsilon = \frac{1}{2} N(q-1)\epsilon
\]

6.5 Gas in a two-part box. Section 6.4 considered a two-part box that holds \( N \) indistinguishable monatomic molecules. The partition function was obtained as

\[
Z = \sum_{n=0}^{N} \frac{1}{n!(N-n)!} \left[ V_A \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} \right]^n \left[ V_B \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} \right]^{N-n}
\]

where part A has \( n \) molecules and part B has \( N-n \). Answer the following questions:

(1) Find a formula to calculate \( \langle n \rangle \) and apply it to this system.

(2) Find a formula to calculate \( \langle \Delta n^2 \rangle \) and apply it to this system.

(3) Suppose we change \( V_A \). When does \( \langle \Delta n^2 \rangle \) maximize? What is \( \langle \Delta n^2 \rangle^{1/2}/\langle n \rangle \) at the maximum?

(1)

\[
\langle n \rangle = V_A \frac{\partial \ln Z}{\partial V_A} = N \frac{V_A}{V_A + V_B}
\]

(2) We start with
\[ \langle n(n-1) \rangle = \frac{1}{Z} V_A^2 \frac{\partial^2 Z}{\partial V_A^2} \]

The variance is expressed as

\[ \langle \Delta n^2 \rangle = \langle n(n-1) \rangle - \langle n \rangle^2 + \langle n \rangle = \frac{1}{Z} V_A^2 \frac{\partial^2 Z}{\partial V_A^2} - \left( \frac{V_A}{Z} \frac{\partial Z}{\partial V_A} \right)^2 + \frac{V_A}{Z} \frac{\partial Z}{\partial V_A} \]

\[ = V_A^2 \frac{\partial^2 \ln Z}{\partial V_A^2} + \frac{V_A}{Z} \frac{\partial \ln Z}{\partial V_A} = V_A^2 \frac{\partial}{\partial V_A} \frac{\langle n \rangle}{V_A} + \langle n \rangle \]

With the answer to (1), the variance is calculated as

\[ \langle \Delta n^2 \rangle = V_A^2 \frac{\partial}{\partial V_A} \frac{N}{V_A + V_B} + N \frac{V_A}{V_A + V_B} = N \frac{V_A V_B}{(V_A + V_B)^2} \]

(3)

\[ \langle \Delta n^2 \rangle \leq \frac{N}{4} \]

where the maximum is reached when \( V_1 = V_2 \). At the maximum,

\[ \frac{\langle \Delta n^2 \rangle^{1/2}}{\langle n \rangle} = \left( \frac{V_B}{NV_A} \right)^{1/2} \]

### 6.6 Mixing of two gases.

A container has gas A in the left chamber of volume \( V_A \) and gas B in the right chamber of volume \( V_B \). The number of molecules in the two chambers are \( N_A \) and \( N_B \), respectively (\( N_A, N_B >> 1; N_A \) is not the Avogadro’s number here). Both chambers are in contact with a heat reservoir at temperature \( T \). The non-configurational part of the single-molecule partition function of gas A is \( q_A (= (2\pi m_A/\beta h^2)^{3/2}) \); the one for gas B is \( q_B \). The molecules do not interact with each other. We remove the partition that separates the two chambers to mix the two gases.

(1) Assume that gas A and gas B consist of the same molecules (\( q_A = q_B = q \)), and the molecules are distinguishable. How much does the free energy of the combined system change by removing the partition? Find the change \( \Delta F \). What is the entropy change \( \Delta S \)?
(2) Assume that gas A and gas B consist of the same molecules, and the molecules are indistinguishable. What is $\Delta F$? In what condition is $\Delta F = 0$? What is the entropy change $\Delta S$?

(3) Which result of $\Delta S$, (1) or (2), is reasonable? Justify your conclusion.

(4) Assume that gas A and gas B are different ($q_A \neq q_B$) and the molecules are indistinguishable within A or B. What is $\Delta F$? What is $\Delta S$?

---

(1) The partition functions of parts A and B before the mixing are

$$Z_A = (V_A q)^{N_A}, \quad Z_B = (V_B q)^{N_B}$$

The partition function of the system after the mixing is

$$Z_{A+B} = [(V_A + V_B) q]^{N_A+N_B}$$

The free energy change is

$$\Delta F = -k_B T (\ln Z_{A+B} - \ln Z_A - \ln Z_B) = -k_B T \left( N_A \ln \frac{V_A + V_B}{V_A} + N_B \ln \frac{V_A + V_B}{V_B} \right)$$

$\Delta F = \Delta U - T \Delta S$, and $\Delta U = 0$. Therefore,

$$\Delta S = k_B \left( N_A \ln \frac{V_A + V_B}{V_A} + N_B \ln \frac{V_A + V_B}{V_B} \right)$$

(2) The partition functions of parts A and B before the mixing are

$$Z_A = \frac{1}{N_A!} (V_A q)^{N_A}, \quad Z_B = \frac{1}{N_B!} (V_B q)^{N_B}$$

The partition function of the system after the mixing is

$$Z_{A+B} = \left( \frac{(V_A + V_B) q}{(N_A + N_B)!} \right)^{N_A+N_B}$$

The free energy change is

$$\Delta F = -k_B T \left[ N_A \ln \frac{N_A (V_A + V_B)}{(N_A + N_B)V_A} + N_B \ln \frac{N_B (V_A + V_B)}{(N_A + N_B) V_B} \right]$$
Obviously, $\Delta F = 0$ when $N_A/N_B = V_A/V_B$. The densities (or the pressures) are identical between the two chambers before removing the partition. It can be shown that it is the only case.

$$\Delta S = k_B \left[ N_A \ln \left( \frac{N_A(V_A + V_B)}{(N_A + N_B)V_A} \right) + N_B \ln \left( \frac{N_B(V_A + V_B)}{(N_A + N_B)V_B} \right) \right]$$

(3) If the density is identical, removing the partition does not change the status of the combined system, hence no change in the entropy or the free energy.

$$Z_A = \frac{(V_A q_A)^{N_A}}{N_A!}, Z_B = \frac{(V_B q_B)^{N_B}}{N_B!}, Z_{A+B} = \frac{(V_A + V_B)^{N_A+N_B} q_A^{N_A} q_B^{N_B}}{N_A! N_B!}$$

$$\Delta F = -k_B T \left( N_A \ln \left( \frac{V_A + V_B}{V_A} \right) + N_B \ln \left( \frac{V_A + V_B}{V_B} \right) \right)$$

$$\Delta S = k_B \left( N_A \ln \left( \frac{V_A + V_B}{V_A} \right) + N_B \ln \left( \frac{V_A + V_B}{V_B} \right) \right)$$

Increasing the volume accessible to $A$ molecules increases the entropy.

6.7 Open system of distinguishable particles. If molecules were distinguishable in an open system of volume $V$ in equilibrium with a reservoir of non-interacting, monatomic molecules of mass $m$ and chemical potential $\mu$ at temperature $T$, what would be $<N>$ and $<\Delta N^2>$? How does the coefficient of variation change as $<N>$ increases?

The grand partition function would be

$$Z = \sum_{N=0}^{\infty} e^{\beta \mu N} \frac{1}{1-e^{\beta \mu}} Z_1^N = \left[ 1 - e^{\beta \mu} \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} \right]^{-1}$$

$$\ln Z = -\ln \left( 1 - e^{\beta \mu} \left( \frac{2\pi m}{\beta h^2} \right)^{3/2} \right)$$
\[ \langle N \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} = -\frac{1}{\beta} \frac{-\beta e^{\beta \mu} \left( \frac{2\pi \hbar}{\beta \hbar^2} \right)^{3/2}}{1 - e^{\beta \mu} \left( \frac{2\pi m}{\beta \hbar^2} \right)^{3/2}} = \frac{1}{\beta} \frac{1}{V} \left( \frac{\beta h^2}{2\pi m} \right)^{3/2} - 1 \]

\[ \langle \Delta N^2 \rangle = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} = -\frac{1}{\beta} \left( \frac{-\beta e^{\beta \mu} \left( \frac{\beta h^2}{2\pi m} \right)^{3/2}}{1 - e^{\beta \mu} \left( \frac{2\pi m}{\beta \hbar^2} \right)^{3/2}} \right)^2 \]

which is rewritten to

\[ \langle \Delta N^2 \rangle = \langle N \rangle + \langle N \rangle^2 \]

The coefficient of variation remains mostly unchanged as \( \langle N \rangle \) increases.

### 6.8 Molecules in a small box.

Consider a system of molecules in a system of a small box of volume \( V \) in contact with a reservoir of molecules with a chemical potential \( \mu \). The temperature is uniform throughout the system and the reservoir of the molecules. In the box, the energy of the molecule is lowered by \( \varepsilon \), and therefore the single-molecule partition function is \( e^{\beta \varepsilon} V q \), where \( q \) is the non-configurational part of the single-molecule partition function. Calculate the grandpartition function of the system and find \( \langle N \rangle \) and \( \langle \Delta N^2 \rangle \).

The grand partition function is

\[ Z = \sum_{N=0}^{\infty} e^{\beta \mu N} e^{\beta \varepsilon N} (Vq)^N \frac{N!}{N!} = \exp \left( e^{\beta (\mu + \varepsilon)} Vq \right) \]

\[ \ln Z = Vq e^{\beta (\mu + \varepsilon)} \]
6.9 Division by $N!$. We learned in Section 6.4.2 that regarding molecules as distinguishable leads to an unreasonable expression of the chemical potential. Here, we will derive the division by $N!$ from thermodynamics requirement.

(1) To correct this problem, let us start with writing the partition function as

$$Z = \frac{V^N}{e^{f(N)}} \left( \frac{2\pi m}{\beta h^2} \right)^{3N/2}$$

where $f(N)$ is a function of $N$, not of $V$ or $T$. Express $\mu$ using $f(N)$.

(2) What condition results from the requirement that the expression of $\mu$ be "reasonable"? Use that condition to find $f(N)$.

---

(1)

$$\langle N \rangle = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} = \frac{1}{\beta} \beta V q e^{\beta (\mu + c)} = \ln Z$$

$$\langle \Delta N^2 \rangle = \frac{1}{\beta} \frac{\partial \langle N \rangle}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu} = \ln Z = \langle N \rangle$$

---

(2) For the right hand side to be a function of intensive quantity, $Ve^{f}$ must be intensive. Then, $e^{f} = a N$, where $a$ is a constant, which leads to

$$f' = \ln a + \ln N$$

This differential equation is solved as

$$f = N \ln a + N (\ln N - 1) + b \cong N \ln a + \ln N! + b$$
where \( b \) is another constant. The partition function is now

\[
Z = \frac{V^N}{e^b a^N N! \left( \frac{2\pi m}{\beta} \right)^{3N/2}}
\]

We know that \( e^b \) does not matter, since we take the derivative of \( \ln Z \) to obtain all thermodynamic functions. The \( a^N \) in the denominator is like \((2\pi m/\beta)^{3N/2}\). In fact, the classical expression for the partition function of a rigid-dumbbell model has the rotation part of a single-molecule partition function as \(1/a\). We can safely set \( a = 1 \) and \( b = 0 \) for the monatomic molecule.

6.10 Van der Waals gas. Van der Waals equation of state,

\[
\left( p + a \frac{N^2}{V^2} \right)(V - Nb) = \frac{N}{\beta}
\]

where \( a \) and \( b \) are constants of \( N, V, \) and \( \beta \), is known to give a good approximation to the state of a non-ideal gas. The equation expresses \( p \) as a function of \( N, V, \) and \( \beta \). Assume monatomic gas for simplicity. Interactions between molecules causes \( a \) and \( b \) to be non-zero.

(1) Use \( p = \beta^{-1} \partial \ln Z / \partial V \) to find the expression for \( \ln Z \). The constant of the integration should be determined by comparing the expression you have obtained (in the vanishing limit of \( a \) and \( b \)) with the \( \ln Z \) of the ideal monatomic gas.

(2) What is \( U \) of the van der Waals gas?

(3) What is the chemical potential \( \mu \)?

(4) Does a positive \( b \) increase \( \mu \) relative to the value for \( b = 0 \)?

(1)

\[
p = \frac{1}{\beta} \frac{\partial \ln Z}{\partial V} = \frac{N}{\beta(V - Nb)} - a \frac{N^2}{V^2}
\]

Integration leads to

\[
\ln Z = N \ln(V - Nb) + a \beta \frac{N^2}{V} + f(N, \beta)
\]
where \( f(N, \beta) \) is a function of \( N \) and \( \beta \). This equation, with \( a = 0 \) and \( b = 0 \), must reproduce \( \ln Z \) of the ideal monatomic gas. Therefore,

\[
N \ln V + f(N, \beta) = N(\ln V - \ln N + 1) + \frac{3N}{2} \ln \frac{2\pi m}{\beta h^2}
\]

Thus, we find

\[
f(N, \beta) = -N(\ln N - 1) + \frac{3N}{2} \ln \frac{2\pi m}{\beta h^2}
\]

and

\[
\ln Z = N \ln(V - Nb) - N(\ln N - 1) + a\beta \frac{N^2}{V} + \frac{3N}{2} \ln \frac{2\pi m}{\beta h^2}
\]

(2)

\[
U = -\frac{\partial \ln Z}{\partial \beta} = -a \frac{N^2}{V} + \frac{3N}{2\beta}
\]

(3)

\[
F = -\frac{1}{\beta} \ln Z = -\frac{1}{\beta} N \ln(V - Nb) + \frac{1}{\beta} N(\ln N - 1) - a \frac{N^2}{V} - \frac{3N}{2\beta} \ln \frac{2\pi m}{\beta h^2}
\]

\[
\mu = \frac{\partial F}{\partial N} = -\frac{1}{\beta} \ln(V - Nb) + \frac{1}{\beta} \ln N + \frac{N}{\beta} \frac{b}{V - Nb} - 2a \frac{N}{V} - \frac{3}{2\beta} \ln \frac{2\pi m}{\beta h^2}
\]

\[
\beta \mu = -\ln(V - Nb) + \ln N + \frac{Nb}{V - Nb} - 2a \beta \frac{N}{V} - \frac{3}{2} \ln \frac{2\pi m}{\beta h^2}
\]

(4) Let \( \mu_0 \) be the \( \mu \) when \( b = 0 \):

\[
\beta \mu_0 = -\ln V + \ln N - 2a \beta \frac{N}{V} - \frac{3}{2} \ln \frac{2\pi m}{\beta h^2}
\]

\[
\beta(\mu - \mu_0) = -\ln \frac{V - Nb}{V} + \frac{Nb}{V - Nb} = -\ln \left( 1 - \frac{Nb}{V} \right) + \frac{1}{1 - \frac{Nb}{V}} - 1
\]

Let \( x \equiv Nb/V \). Then,
\[
\beta(\mu - \mu_0) = g\left(\frac{Nb}{V}\right)
\]

where
\[
g(x) \equiv -\ln(1 - x) + \frac{1}{1 - x} - 1
\]

This function has \(g(0) = 0\) and
\[
g'(x) = \frac{1}{1 - x} + \frac{1}{(1 - x)^2} > 0
\]

for \(0 < x < 1\). Therefore, \(g(x) > 0\) in the range. A positive \(b\) increase \(\mu\).

**6.11 Sign of chemical potential.** We have learned that a gas of \(N\) monatomic molecules in volume \(V\) has a chemical potential \(\mu\) given as
\[
\mu = k_B T \left( \ln \frac{N}{V} - \frac{3}{2} \ln \frac{2\pi m}{\beta h^2} \right)
\]

Is this \(\mu\) positive or negative?

With the definition of \(\lambda_T\) (Eq. (5.59)),
\[
\frac{\mu}{k_B T} = \ln \frac{\lambda_T^3}{V/N}
\]

Since \(\lambda_T << (V/N)^{1/3}\) unless the pressure is excessively high, \(\mu < 0\).

**6.12 Two-part box with different temperatures.** Consider a two-part box connected by a porous, insulating plug. Box \(i\) of volume \(V_i\) is held at temperature \(T_i\) \((i = 1, 2)\). The boxes hold monatomic molecules.

(1) Let \(N_i\) be the number of molecules in box \(i\). Then, \(N_1 + N_2 = \text{constant}\). Write the Helmholtz free energy \(F\) of the two-part box using \(N_1\) and \(N_2\).

(2) Minimize \(F\) by changing \(N_i\). What relationship holds between \(\mu_1\) and \(\mu_2\), where \(\mu_i\) is the chemical potential of a molecule in box \(i\)?

(1) The partition function \(Z_i\) of box 1 is
\[
Z_1 = \frac{V_1^{N_1}}{N_1!} \left( \frac{2\pi m}{\beta_1 h^2} \right)^{3N_1/2}
\]

Then,
\[ F_1 = - k_B T_1 \ln Z_1 = - N_1 k_B T_1 \left( \ln V_1 - \ln N_1 + 1 + \frac{3}{2} \ln \frac{2\pi m}{\beta_1 h^2} \right) \]

Likewise,
\[ F_2 = - N_2 k_B T_2 \left( \ln V_2 - \ln N_2 + 1 + \frac{3}{2} \ln \frac{2\pi m}{\beta_2 h^2} \right) \]
\[ F = F_1 + F_2. \]
\[ F = - N_1 k_B T_1 \left( \ln V_1 - \ln N_1 + 1 + \frac{3}{2} \ln \frac{2\pi m}{\beta_1 h^2} \right) - N_2 k_B T_2 \left( \ln V_2 - \ln N_2 + 1 + \frac{3}{2} \ln \frac{2\pi m}{\beta_2 h^2} \right) \]
\[ (2) \]
\[ F = - k_B T_1 \left( \ln V_1 - \ln N_1 + \frac{3}{2} \ln \frac{2\pi m}{\beta_1 h^2} \right) + k_B T_2 \left( \ln V_2 - \ln N_2 + \frac{3}{2} \ln \frac{2\pi m}{\beta_2 h^2} \right) = 0 \]
\[ \mu_1 = k_B T_1 \left( \ln \frac{N_1}{V_1} - \frac{3}{2} \ln \frac{2\pi m}{\beta_1 h^2} \right) \]

Therefore,
\[ \mu_1 = \mu_2 \]