PYU33P15: Statistical Thermodynamics
Continuous Assessment CA2 due 12/10/2021

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JS Theoretical Physics

1.

a)

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi_n}{\partial x^2} = \varepsilon_n\,\psi_n \qquad \text{(Schrödinger equation)}$$

$$\psi_n = A\sin\left(\frac{n\,\pi\,x}{L}\right) \qquad \text{(for some } A\text{, where } n = 0, 1, 2, \dots)$$

$$\frac{\partial\psi_n}{\partial x} = \frac{A\,n\,\pi}{L}\cos\left(\frac{n\,\pi\,x}{L}\right) \qquad \text{(first derivative of } \psi_n \text{ w.r.t } x)$$

$$\frac{\partial^2\psi_n}{\partial x^2} = -\frac{A\,n^2\,\pi^2}{L^2}\sin\left(\frac{n\,\pi\,x}{L}\right) \qquad \text{(second derivative of } \psi_n \text{ w.r.t } x)$$

$$= -\frac{n^2\,\pi^2}{L^2}\psi_n \qquad \text{(substituting } \psi_n = A\sin\left(\tfrac{n\,\pi\,x}{L}\right))$$

$$\implies \frac{\hbar^2}{2m}\frac{n^2\,\pi^2}{L^2}\psi_n = \varepsilon_n\,\psi_n \qquad \text{(substituting } \tfrac{\partial^2\psi_n}{\partial x^2})$$

$$\implies \varepsilon_n = \frac{\hbar^2\,n^2\,\pi^2}{2m\,L^2} \qquad \text{(rearranging for } \varepsilon_n)$$

b)

$$N = \sum_n f^{\text{MB}}(\varepsilon_n) \qquad \text{(from (25) in notes)}$$

$$= \sum_{n=0}^{\infty} e^{\frac{\mu-\varepsilon_n}{k_B T}} \qquad \text{(substituting Maxwell-Boltzmann distribution expression)}$$

$$= e^{\frac{\mu}{k_B T}}\sum_{n=0}^{\infty} e^{-\frac{\hbar^2\pi^2}{2mL^2k_BT}\,n^2}$$

(taking $e^{\frac{\mu}{k_B T}}$ outside the sum as it has no n dependence, substituting ε_n)

$$= e^{\frac{\mu}{k_B T}}\int_0^\infty e^{-\frac{\hbar^2\pi^2}{2mL^2k_BT}\,n^2}\,dn$$

(approximating the sum as an integral as $\Delta\varepsilon_n \ll kT$ for typical values of m and L)

$$= e^{\frac{\mu}{k_B T}}\int_0^\infty e^{-a\,n^2}\,dn \qquad \text{(labelling } a \equiv \tfrac{\hbar^2\pi^2}{2mL^2k_BT} \text{ for convenience)}$$

$$= e^{\frac{\mu}{k_B T}}\,\frac{1}{2}\sqrt{\frac{2m\,L^2k_B\,T}{\hbar^2\,\pi}} \qquad \text{(computing } \textstyle\int_0^\infty e^{-a\,x^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}\text{, substituting } a)$$

$$= e^{\frac{\mu}{k_B T}}\,L\,n_Q \qquad \text{(labelling quantum concentration } n_Q \equiv \sqrt{\tfrac{mk_BT}{2\hbar^2\pi}})$$

$$\implies \mu = k_B\,T\ln\left(\frac{N}{L\,n_Q}\right) \qquad \text{(rearranging for } \mu)$$

c)

$$
\begin{aligned}
U &\equiv \langle \varepsilon \rangle && \text{(internal energy expression)} \\
&= \sum_n \varepsilon_n \, f^{\text{MB}}(\varepsilon_n) && \text{(using } \langle X \rangle = \textstyle\sum_i X_i \, f(\varepsilon_i, T, \mu)\text{)} \\
&= \sum_{n=0}^{\infty} \frac{\hbar^2 \, n^2 \, \pi^2}{2m \, L^2} \, e^{\frac{\mu}{k_B T}} \, e^{-\frac{\hbar^2 n^2 \pi^2}{2mL^2 k_B T}}
\end{aligned}
$$

(substituting ε_n and f^{MB}, splitting exponential of sum into product of exponentials for convenience)

$$
= \frac{\hbar^2 \, \pi^2}{2m \, L^2} \, e^{\frac{\mu}{k_B T}} \sum_{n=0}^{\infty} n^2 \, e^{-a \, n^2}
$$

(taking terms not depending on n outside the sum, labelling $a \equiv \frac{\hbar^2 \pi^2}{2mL^2 k_B T}$ for convenience)

$$
= \frac{\hbar^2 \, \pi^2 \, N}{2m \, L^3 \, n_Q} \int_0^{\infty} n^2 \, e^{-a \, n^2} \, dn
$$

(approximating the sum as an integral as before, substituting $e^{\frac{\mu}{k_B T}} = \frac{N}{L n_Q}$)

$$
\begin{aligned}
&= \frac{\hbar^2 \, \pi^2 \, N}{2m \, L^3} \, \frac{1}{n_Q} \, \frac{\sqrt{\pi}}{4} \, \frac{1}{a^{\frac{3}{2}}} && \text{(computing } \textstyle\int_0^{\infty} x^2 \, e^{-a \, x^2} \, dx = \frac{\sqrt{\pi}}{4a^{\frac{3}{2}}}\text{)} \\
&= \frac{\hbar^2 \, \pi^2 \, N}{2m \, L^3} \left(\frac{m \, k_B \, T}{2\hbar^2 \, \pi} \right)^{-\frac{1}{2}} \frac{\sqrt{\pi}}{4} \left(\frac{\hbar^2 \, \pi^2}{2m \, L^2 \, k_B \, T} \right)^{-\frac{3}{2}} && \text{(substituting } n_Q \text{ and } a\text{)} \\
U &= \frac{1}{2} \, N \, k_B \, T && \text{(simplifying)}
\end{aligned}
$$

The internal energy of an ideal gas of N atoms at temperature T in one dimension is $\frac{1}{2}Nk_BT$, whereas in three dimensions it is $\frac{3}{2}Nk_BT$, i.e. $U_{\text{3D}} = 3 \, U_{\text{1D}}$. In one dimension, each atom has a single degree of freedom corresponding to one translational axis, and so the translational energy of each atom is $\frac{p^2}{2m}$. In three dimensions, each atom has three degrees of freedom corresponding to three translational axes, and so the translational energy of each atom is $\frac{(p_x+p_y+p_z)^2}{2m}$. The principle of equipartition of energy dictates that each squared term in a momentum coordinate will contribute $\frac{1}{2}k_BT$ to the system's internal energy. Thus the total amount of energy contributed by all the atoms is $\frac{1}{2}Nk_BT$ for each axis, i.e. $\frac{1}{2}Nk_BT$ for one dimension, and $\frac{3}{2}Nk_BT$ for three dimensions, as calculated.

d)

$$
\begin{aligned}
\mu &= \left(\frac{\partial F}{\partial N} \right)_{T,L} && \text{(expression in terms of } \mu, F \text{ and } N\text{)} \\
\implies F &= \int_0^N \mu(N) \, dN && \text{(rearranging for } F\text{)} \\
&= \int_0^N k_B \, T \ln \left(\frac{N}{L \, n_Q} \right) dN && \text{(substituting } \mu\text{)} \\
&= k_B \, T \int_0^N (\ln(N) - \ln(L \, n_Q)) \, dN
\end{aligned}
$$

(taking $k_B \, T$ outside the integral as it has no N dependence, using $\ln \left(\frac{a}{b} \right) = \ln(a) - \ln(b)$)

$$
= k_B \, T \, (N \ln(N) - N - N \ln(L \, n_Q))
$$

(computing $\int \ln(x) \, dx = x \ln(x) - x$ and evaluating from 0 to N)

$$
\begin{aligned}
&= k_B \, T \, N \left(\ln \left(\frac{N}{L} \right) - 1 - \ln(n_Q) \right) && \text{(rearranging for convenience)} \\
&= k_B \, T \, N \left(\ln \left(\frac{N}{L} \right) - 1 - \ln \left(\frac{m \, k_B \, T}{2\hbar^2 \, \pi} \right)^{\frac{1}{2}} \right) && \text{(substituting } n_Q\text{)} \\
&= k_B \, T \, N \left(\ln \left(\frac{N}{L} \right) - 1 - \frac{1}{2} \ln \left(\frac{m \, k_B}{2\hbar^2 \, \pi} \right) - \frac{1}{2} \ln(T) \right)
\end{aligned}
$$

(using logarithm rules to separate T for next step)

$$
\begin{aligned}
S &= -\left(\frac{\partial F}{\partial T}\right)_{L,N} && \text{(expression in terms of } S,\ F \text{ and } T) \\
&= -k_B\, N \left(\ln\left(\frac{N}{L}\right) - 1 - \frac{1}{2}\ln\left(\frac{m\, k_B}{2\hbar^2\, \pi}\right) - \frac{1}{2}\ln(T)\right) - k_B\, T\, N \left(-\frac{1}{2T}\right) && \text{(computing } \tfrac{\partial F}{\partial T}) \\
&= -k_B\, N \left(\ln\left(\frac{N}{L}\right) - \frac{3}{2} - \frac{1}{2}\ln\left(\frac{m\, k_B}{2\hbar^2\, \pi}\right) - \frac{1}{2}\ln(T)\right) && \text{(simplifying)} \\
S &= -k_B\, N \left(\ln\left(\frac{N}{L\, n_Q}\right) - \frac{3}{2}\right) && \text{(expressing in terms of } n_Q)
\end{aligned}
$$

We can verify that this entropy is correct by using the expression for U in terms of F, T and S

$$
\begin{aligned}
U &= F + TS \\
&= k_B\, T\, N \left(\ln\left(\frac{N}{L}\right) - 1 - \frac{1}{2}\ln\left(\frac{m\, k_B}{2\hbar^2\, \pi}\right) - \frac{1}{2}\ln(T)\right) - k_B\, T\, N \left(\ln\left(\frac{N}{L}\right) - \frac{3}{2} - \frac{1}{2}\ln\left(\frac{m\, k_B}{2\hbar^2\, \pi}\right) - \frac{1}{2}\ln(T)\right) \\
&= \frac{1}{2} N\, k_B\, T,
\end{aligned}
$$

as before.

Mathematica calculations

```
Integrate[E^(-a x^2), {x, 0, ∞}]
```

$$\frac{\sqrt{\pi}}{2\sqrt{a}} \quad \text{if } \mathrm{Re}[a] > 0$$

```
Integrate[x^2 E^(-a x^2), {x, 0, ∞}]
```

$$\frac{\sqrt{\pi}}{4\, a^{3/2}} \quad \text{if } \mathrm{Re}[a] > 0$$

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Integrate[Log[x], x]
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-x + x Log[x]
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2.

a)

$$Z(N,T,V) \equiv \sum_r e^{-\frac{E_r}{k_B T}} \qquad \text{(partition function definition)}$$

$$\implies Z_1 = \sum_{r=0}^{\infty} e^{-\frac{\hbar\omega_E\left(r+\frac{1}{2}\right)}{k_B T}} \qquad \text{(substituting energy of a single oscillator } E_r\text{)}$$

$$= e^{-\frac{\hbar\omega_E}{2k_B T}} \sum_{r=0}^{\infty} e^{-\frac{\hbar\omega_E r}{k_B T}}$$

(expanding the exponential into a product and taking terms terms not depending on r outside the sum)

$$= e^{-\frac{\hbar\omega_E}{2k_B T}} \sum_{r=0}^{\infty} \left(e^{-\frac{\hbar\omega_E}{k_B T}}\right)^r \qquad \text{(rewriting the exponential as a geometric series)}$$

$$= e^{-\frac{\hbar\omega_E}{2k_B T}} \left(\frac{1}{1-e^{-\frac{\hbar\omega_E}{k_B T}}}\right) \qquad \left(\text{computing } \sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \text{ if } x<1.\ \frac{\hbar\omega_E}{k_B T}>0 \text{ and so } e^{-\frac{\hbar\omega_E}{k_B T}}<1\right)$$

$$= \frac{1}{e^{\frac{\hbar\omega_E}{2k_B T}} - e^{-\frac{\hbar\omega_E}{2k_B T}}} \qquad \text{(multiplying and simplifying)}$$

$$Z_1 = \frac{1}{2}\operatorname{csch}\left(\frac{\hbar\omega_E}{2k_B T}\right) \qquad \left(\text{using } \operatorname{csch}(x) = \frac{2}{e^x - e^{-x}}\right)$$

DISCUSS DISCUSS DISCUSS

b)

$$F = -k_B T \ln(Z) \qquad \text{(expression for } F \text{ in terms of } Z\text{)}$$

$$= -k_B T \ln\left(\frac{1}{2}\operatorname{csch}\left(\frac{\hbar\omega_E}{2k_B T}\right)\right) \qquad \text{(substituting } Z_1\text{)}$$

$$F = k_B T \ln\left(2\sinh\left(\frac{\hbar\omega_E}{2k_B T}\right)\right) \qquad \left(\text{using } \operatorname{csch}(x) = \frac{1}{\sinh(x)} \text{ and } \ln\left(\frac{1}{a}\right) = -\ln(a)\right)$$

c)

$$\bar{\varepsilon} = \sum_r \varepsilon_r \, P(\varepsilon_r) \qquad \text{(mean definition)}$$

$$= \sum_{r=0}^{\infty} \hbar\omega_E \left(r + \frac{1}{2}\right) e^{\frac{-\hbar\omega_E\left(r+\frac{1}{2}\right)}{k_B T}} \frac{1}{Z} \qquad \text{(substituting } \varepsilon_r \text{ and } P(\varepsilon_r)\text{)}$$

$$= \hbar\omega_E \left(\frac{1}{Z}\sum_{r=0}^{\infty} r\, e^{-\frac{\hbar\omega_E\left(r+\frac{1}{2}\right)}{k_B T}} + \frac{1}{2Z}\sum_{r=0}^{\infty} e^{-\frac{\hbar\omega_E\left(r+\frac{1}{2}\right)}{k_B T}}\right)$$

(substituting and splitting the sums for convenience)

$$= \hbar\omega_E \left(\frac{1}{Z} e^{-\frac{\hbar\omega_E}{2k_B T}} \sum_{r=0}^{\infty} r\, e^{-\frac{\hbar\omega_E r}{k_B T}} + \frac{1}{2}\right)$$

(noticing the second sum is simply Z, taking terms not depending on r outside the first sum)

$$= \hbar\omega_E \left(\left(e^{\frac{\hbar\omega_E}{2k_B T}} - e^{-\frac{\hbar\omega_E}{2k_B T}}\right) e^{-\frac{\hbar\omega_E}{2k_B T}} \sum_{r=0}^{\infty} r \left(e^{-\frac{\hbar\omega_E}{k_B T}}\right)^r + \frac{1}{2}\right)$$

(substituting Z in exponential form, rewriting sum as geometric series)

$$= \hbar\omega_E \left(\left(e^{\frac{\hbar\omega_E}{2k_B T}} - e^{-\frac{\hbar\omega_E}{2k_B T}}\right) e^{-\frac{\hbar\omega_E}{2k_B T}} e^{-\frac{\hbar\omega_E}{k_B T}} \sum_{r=0}^{\infty} r \left(e^{-\frac{\hbar\omega_E}{k_B T}}\right)^{r-1} + \frac{1}{2}\right)$$

(taking a term outside the sum to rewrite the power inside the sum as $r-1$ for the next step)

$$= \hbar\omega_E \left(\left(e^{\frac{\hbar\omega_E}{2k_B T}} - e^{-\frac{\hbar\omega_E}{2k_B T}}\right) e^{-\frac{3\hbar\omega_E}{2k_B T}} \sum_{r=0}^{\infty} \frac{d}{dx}\left(x^r\right) + \frac{1}{2}\right)$$

(labelling $x \equiv e^{-\frac{\hbar\omega_E}{k_B T}}$ and noticing the term inside the sum is a derivative w.r.t. x, multiplying exponentials)

$$= \hbar\omega_E \left(\left(e^{-\frac{\hbar\omega_E}{k_B T}} - e^{-\frac{2\hbar\omega_E}{k_B T}}\right) \frac{d}{dx}\left(\frac{1}{1-x}\right) + \frac{1}{2}\right)$$

(sum of derivatives = derivative of sum, computing $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$, multiplying exponentials)

$$= \hbar\omega_E \left(\left(x - x^2\right) \frac{1}{(1-x)^2} + \frac{1}{2}\right)$$

(computing $\frac{d}{dx}\frac{1}{1-x} = \frac{1}{(1-x)^2}$, writing all exponentials in terms of x for convenience)

$$= \hbar\omega_E \left(\frac{x}{1-x} + \frac{1}{2}\right) \qquad \text{(dividing first term by } 1-x\text{)}$$

$$= \frac{\hbar\omega_E}{2}\left(\frac{2x+1-x}{1-x}\right) \qquad \text{(simplifying to get a single fraction)}$$

$$= \frac{\hbar\omega_E}{2}\left(\frac{x^{\frac{1}{2}} + x^{-\frac{1}{2}}}{x^{-\frac{1}{2}} - x^{\frac{1}{2}}}\right) \qquad \text{(multiplying top and bottom by } x^{-\frac{1}{2}}\text{)}$$

$$= \frac{\hbar\omega_E}{2}\left(\frac{e^{-\frac{\hbar\omega_E}{2k_B T}} + e^{\frac{\hbar\omega_E}{2k_B T}}}{e^{\frac{\hbar\omega_E}{2k_B T}} - e^{-\frac{\hbar\omega_E}{2k_B T}}}\right) \qquad \text{(substituting } x\text{)}$$

$$\bar{\varepsilon} = \frac{\hbar\omega_E}{2}\coth\left(\frac{\hbar\omega_E}{2k_B T}\right) \qquad \text{(using } \coth(x) = \tfrac{e^x+e^{-x}}{e^x-e^{-x}}\text{)}$$

$$U = 3N\,\bar{\varepsilon} \qquad \text{(}N\text{ oscillators with 3 degrees of freedom in a solid)}$$

$$U = \frac{3N\,\hbar\omega_E}{2}\coth\left(\frac{\hbar\omega_E}{2k_B T}\right)$$

d)

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \qquad \text{(expression for constant volume heat capacity)}$$

$$= \frac{3N\,\hbar\omega_E}{2}\left(-\operatorname{csch}^2\left(\frac{\hbar\omega_E}{2k_B\,T}\right)\left(-\frac{\hbar\omega_E}{2k_B\,T^2}\right)\right) \qquad \text{(computing the derivative)}$$

$$C_V = \frac{3N\,\hbar^2\,\omega_E^2}{4k_B\,T^2}\operatorname{csch}^2\left(\frac{\hbar\omega_E}{2k_B\,T}\right) \qquad \text{(simplifying)}$$

$$= \frac{3N\,\hbar^2\,\omega_E^2}{4k_B\,T^2}\left(\frac{2}{e^{\frac{\hbar\omega_E}{2k_BT}} - e^{-\frac{\hbar\omega_E}{2k_BT}}}\right)^2 \qquad \left(\text{using } \operatorname{csch}(x) = \tfrac{2}{e^x - e^{-x}}\right)$$

$$= \frac{3N\,\hbar^2\,\omega_E^2}{k_B\,T^2}\left(\frac{e^{\frac{\hbar\omega_E}{2k_BT}}}{e^{\frac{\hbar\omega_E}{k_BT}} - 1}\right)^2$$

(factoring out $2^2 = 4$, multiplying top and bottom of squared term by $e^{\frac{\hbar\omega_E}{2k_BT}}$)

$$= \frac{3N\,\hbar^2\,\omega_E^2}{k_B\,T^2}\frac{e^{\frac{\hbar\omega_E}{k_BT}}}{\left(e^{\frac{\hbar\omega_E}{k_BT}} - 1\right)^2} \qquad \text{(squaring the numerator)}$$

$$= 3N\,k_B\left(\frac{\theta_E}{T}\right)^2\frac{e^{\frac{\theta_E}{T}}}{\left(e^{\frac{\theta_E}{T}} - 1\right)^2} \qquad \left(\text{labelling } \theta_E \equiv \tfrac{\hbar\omega_E}{k_B}\right)$$

$$= C_V^{\text{phonon}},$$

i.e. the constant volume heat capacity for the Einstein solid is the same as that of phonon gas.

e)

$$S \equiv k_B \ln\Omega \qquad \text{(entropy in terms of the multiplicity function)}$$

$$= k_B \ln\left(\frac{(3N+n-1)!}{n!\,(3N-1)!}\right)$$

(multiplicity function for $3N$ oscillators with n total quanta of energy, from CA1 Q1)

$$\approx 3k_B\,N\left[\left(1+\frac{n}{3N}\right)\ln\left(1+\frac{n}{3N}\right) - \frac{n}{3N}\ln\left(\frac{n}{3N}\right)\right] \qquad \text{(CA1 Q1c)}$$

$$U = 3N\,\hbar\omega_E\left(\frac{1}{2}+\bar{r}\right)$$

(internal energy in terms of number of oscillators $3N$ each with average quanta of energy $\bar{r}$)

$$= 3N\,\hbar\omega_E\left(\frac{1}{2}+\frac{n}{3N}\right) \qquad \text{(noticing that total quanta of energy } n = 3N\,\bar{r})$$

Also, $U = 3N\,\bar{\varepsilon}$ (from c)

$$= 3N\,\hbar\omega_E\left(\frac{1}{2}+\frac{x}{1-x}\right) \qquad \left(\text{from c, where } x \equiv e^{-\frac{\hbar\omega_E}{k_BT}}\right)$$

$$= 3N\,\hbar\omega_E\left(\frac{1}{2}+\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}} - 1}\right) \qquad \text{(substituting } x \text{ and simplifying)}$$

$$\implies \frac{n}{3N} = \frac{1}{e^{\frac{\hbar\omega_E}{k_BT}} - 1} \qquad \text{(equating the two expressions for } U)$$

$$\implies S = 3k_B\,N\left[\left(1+\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\right)\ln\left(1+\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\right)-\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\ln\left(\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\right)\right] \quad \left(\text{substituting } \tfrac{n}{3N}\right)$$

$$= 3k_B\,N\left[\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\left(\ln\left(1+\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\right)-\ln\left(\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\right)\right)+\ln\left(1+\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\right)\right]$$
$$\text{(expanding and rearranging)}$$

$$= 3k_B\,N\left[\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\left(\ln\left(e^{\frac{\hbar\omega_E}{k_BT}}-1+1\right)\right)+\ln\left(1+\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\right)\right] \quad \left(\text{using } \ln(a)-\ln(b)=\ln\left(\tfrac{a}{b}\right)\right)$$

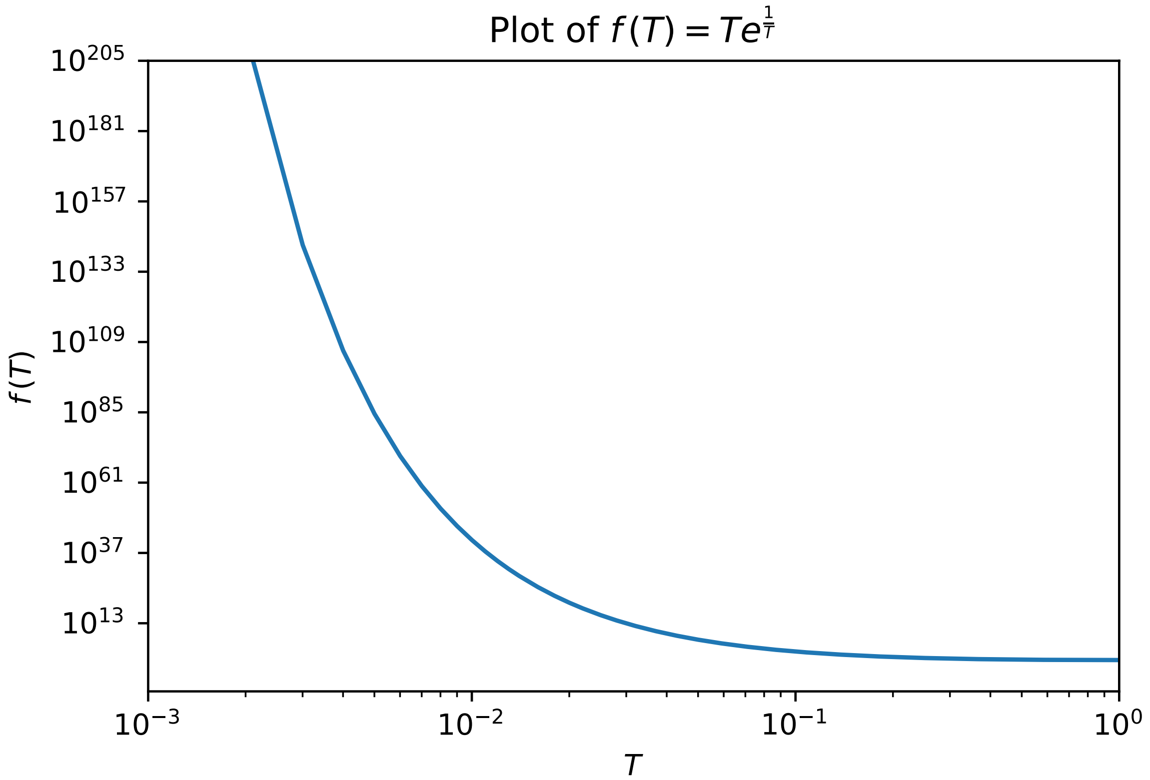
$$S(T,N) = 3k_B\,N\left[\frac{\hbar\,\omega_E}{k_B\,T\left(e^{\frac{\hbar\omega_E}{k_BT}}-1\right)}+\ln\left(1+\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\right)\right] \quad \left(\text{using } \ln\left(e^a\right)=a\right)$$

f)

$$\ln\left(1+\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}-1}\right) \approx \ln\left(1+\frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}}\right) \quad \left(\text{using } e^{\frac{\hbar\omega_E}{k_BT}} \gg 1 \text{ for large } T\right)$$
$$\approx \ln(1) \quad \left(\text{using } \frac{1}{e^{\frac{\hbar\omega_E}{k_BT}}} \ll 1 \text{ for large } T\right)$$
$$= 0$$

$$\implies S \approx \frac{3\,N\,\hbar\,\omega_E}{T\,e^{\frac{\hbar\omega_E}{k_BT}}} \quad \left(\text{using } e^{\frac{\hbar\omega_E}{k_BT}} \gg 1 \text{ for large } T\right)$$

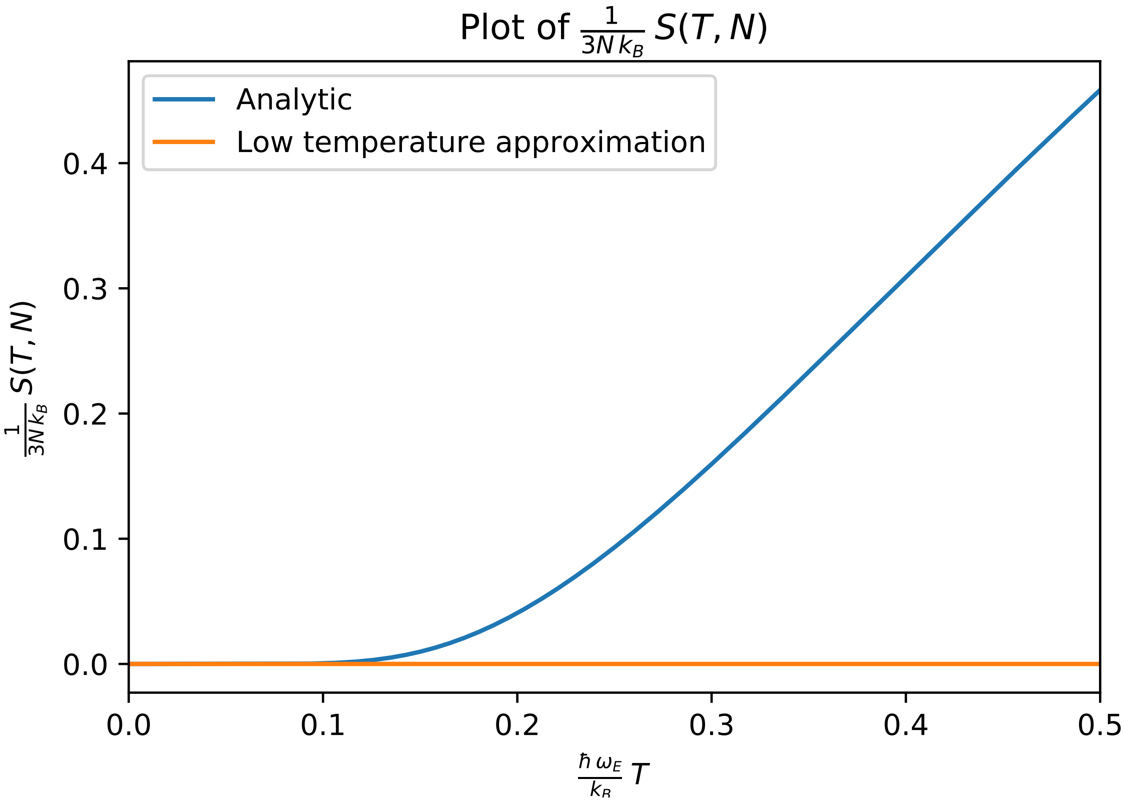
From plotting the function $f(T) = T\,e^{\frac{1}{T}}$, we can see that $\lim_{T\to 0} f(T) = \infty$, and so $\frac{1}{f(T)}$ is approximately 0 for small T.



Since $S = \frac{3N\hbar\omega_E}{Te^{\frac{\hbar\omega_E}{k_B T}}} = \frac{3Nk_B}{f\left(\frac{k_B T}{\hbar\omega_E}\right)}$ is simply a scaling of $\frac{1}{f(T)}$ and T, we can deduce that S must also be 0 for small T, i.e.

$$S(T,N) \approx 0$$

Below is the plot of $\frac{1}{3Nk_B} S\left(\frac{\hbar\omega_E}{k_B} T, N\right)$ and the corresponding low temperature approximation (we scale T and S by constants in order to plot without assigning values to N, k_b, $\hbar$ and ω_E).



g)

$$e^{\frac{\hbar\omega_E}{k_B T}} = 1 + \frac{\hbar\,\omega_E}{k_B\,T} + \frac{\hbar^2\,\omega_E^2}{k_B^2\,T^2} + \ldots \qquad \text{(expressed as a series)}$$

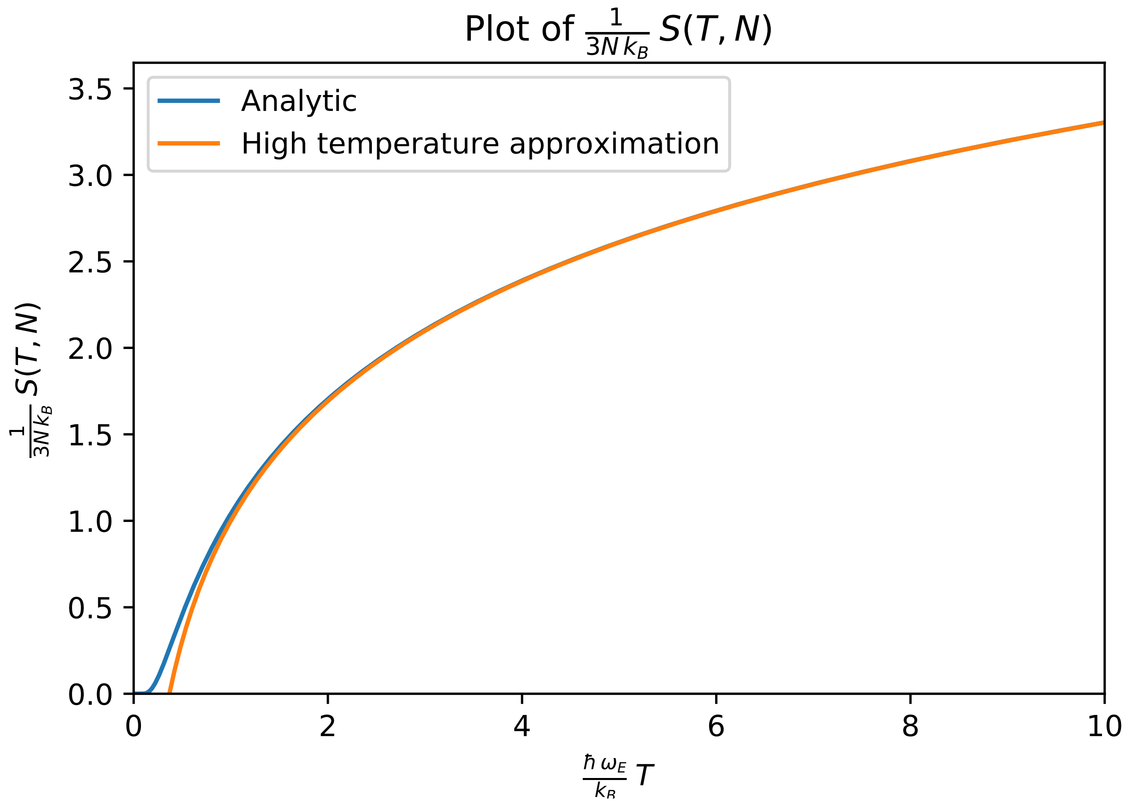
$$\implies e^{\frac{\hbar\omega_E}{k_B T}} - 1 = \frac{\hbar\,\omega_E}{k_B\,T} + \frac{\hbar^2\,\omega_E^2}{k_B^2\,T^2} + \ldots$$

$$\approx \frac{\hbar\,\omega_E}{k_B\,T} \qquad \text{(for large } T\text{, i.e. small } \tfrac{1}{T}\text{, terms of quadratic order and higher don't contribute)}$$

$$\implies S \approx 3k_B\,N\left[\frac{\hbar\,\omega_E}{k_B\,T}\,\frac{k_B\,T}{\hbar\,\omega_E} + \ln\left(1 + \frac{k_B\,T}{\hbar\,\omega_E}\right)\right] \qquad \text{(substituting } e^{\frac{\hbar\omega_E}{k_B T}} - 1\text{)}$$

$$S(T,N) \approx 3k_B\,N\left(1 + \ln\left(\frac{k_B\,T}{\hbar\,\omega_E}\right)\right) \qquad \text{(using } \tfrac{k_B\,T}{\hbar\,\omega_E} \gg 1 \text{ for large } T\text{)}$$

Below is the plot of $\frac{1}{3Nk_B} S\left(\frac{\hbar\omega_E}{k_B} T, N\right)$ and the corresponding high temperature approximation (scaling T and S as before).



Mathematica calculations

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Sum[x^n, {n, 0, ∞}]
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$$\frac{1}{1 - x}$$