

Q1.

(a) The isothermic quasistatic process implies that the temperature of the neon gas must be kept constant. The amount of heat which can be required to keep the temperature constant is equivalent to the work done, since we the total change in energy to be zero:

$$\Delta U = Q + W = 0 \implies Q = -W.$$

Since the gas is ideal, it suffices to find the amount of work per mole. Suppose we have n moles. The work is given by the change in volume, $W = - \int_{V_i}^{V_f} nRT \frac{dV}{V}$:

$$\frac{W}{n} = - \int_{V_i}^{V_f} \frac{nRT}{n} \frac{dV}{V} = -RT \log \left(\frac{V_f}{V_i} \right).$$

Since $Q = -W$, then $Q = RT \log \left(\frac{V_f}{V_i} \right)$. Taking $T = 293K$, $V_i = 1.0L$ and $V_f = 1.1L$, then

$$\begin{aligned} Q &= 8.3145J \text{ mol}^{-1} K^{-1} \cdot 293K \cdot \log(1.1) \\ &= 232.19J. \end{aligned}$$

Therefore you must add about $\boxed{Q = 232J}$ of heat per mole to keep the gas at a constant temperature.

(1b) It once again suffices to consider the change in entropy per mole of gas. ΔS is given by

$$\Delta S = Nk \log \left(\frac{V_f}{V_i} \right) \implies \frac{\Delta S}{n} = N_A k \log \left(\frac{V_f}{V_i} \right).$$

With $N_A = 6.02 \times 10^{23}$, $k = 1.38 \times 10^{-23} J K^{-1}$ and $\frac{V_f}{V_i} = 1.1$, ΔS is calculated to be

$$\begin{aligned} \frac{\Delta S}{n} &= (6.02 \times 10^{23})(1.38 \times 10^{-23} J K^{-1}) \log(1.1) \\ &= 0.7918 J/K. \end{aligned}$$

Therefore the change in entropy per mole of neon gas is $\boxed{\Delta S = 0.792 J/K}$.

(1c) The relation between entropy change and heat is $\Delta S = \frac{Q}{T}$. If we only consider the entropy change per mole of gas, it is equivalent to

$$\frac{\Delta S}{n} = \frac{1}{T} \frac{Q}{n}.$$

Now $\Delta S/n$ was found in part (b), while Q/n was found in part (a). With $Q/n = 232J$ and $T = 293K$, then

$$\Delta S/n = \frac{232 J}{293 K} = 0.7918 J/K,$$

which is equivalent to the change in entropy per mole found in part (b).
Therefore Q, T and S are all related as expected.

(1d) The heat capacity at constant pressure is defined as $C_P = \frac{Q}{\Delta T}$, where Q is the heat and ΔT is the change in temperature. This rearranges to $Q = C_P \Delta T$. Substituting Q into the equation for the change in entropy, $\Delta S = \frac{C_P \Delta T}{T}$. Taking $\Delta T \rightarrow dT$, the change in entropy becomes an integral across temperature changes:

$$\Delta S = C_P \int_{T_i}^{T_f} \frac{dT}{T} = C_P \log \left(\frac{T_f}{T_i} \right). \quad (1.1)$$

In Kelvin, the temperature change is $T_i = 293 K$ to $T_f = 423 K$. With $C_P = 20.79 J/(mol K)$, the change in entropy is

$$\Delta S = (20.79 J/(mol K)) \log \left(\frac{423}{293} \right) = 7.634 J/K.$$

Thus $\Delta S = 7.63 J/K$.

(1e) The Shomate equation for the heat capacity of a gas kept at constant pressure is

$$C_P(T) = A + BT + CT^2 + DT^3 + \frac{E}{T^2},$$

where the constants A, B, C, D and E are given by

$$\begin{aligned} A &= 20.79 J/(mol K) & B &= 4.851 \times 10^{-13} J/(mol K^2) & C &= -1.582916 \times 10^{-16} J/(mol K^3) \\ D &= 1.525102 \times 10^{-20} J/(mol K^4) & E &= 3.196347 \times 10^{-5} J K/mol \end{aligned}$$

Substituting the Shomate equation into the entropy integral (1.1), we have

$$\Delta S = \int_{T_i}^{T_f} \frac{C_P(T)}{T} dT = \int_{T_i}^{T_f} \frac{A + BT + CT^2 + DT^3 + ET^{-2}}{T} dT.$$

After some algebra, we find that the integral evaluates to

$$\Delta S = A \log \left(\frac{T_f}{T_i} \right) + B(T_f - T_i) + \frac{1}{2}C(T_f^2 - T_i^2) + \frac{1}{3}D(T_f^3 - T_i^3) - \frac{1}{2}E \left(\frac{1}{T_f^2} - \frac{1}{T_i^2} \right).$$

Calculating each of the terms seperately with $T_i = 293$, $T_f = 423$,

$$\begin{aligned} A \log \left(\frac{T_f}{T_i} \right) &= 20.79 \log(423/293) = 7.634079061 \text{ J/K} \\ B(T_f - T_i) &= 4.851 \times 10^{-13}(423 - 293) = 5.9553 \times 10^{-11} \text{ J/K} \\ \frac{1}{2}C(T_f^2 - T_i^2) &= -1.582916 \times 10^{-16}(423^2 - 293^2) = -7.366891065 \times 10^{-12} \text{ J/K} \\ \frac{1}{3}D(T_f^3 - T_i^3) &= 1.525102 \times 10^{-20}(423^3 - 293^3) = 2.568943321 \times 10^{-13} \text{ J/K} \\ -\frac{1}{2}E \left(\frac{1}{423^2} - \frac{1}{293^2} \right) &= 9.684212807 \times 10^{-11} \text{ J/K}. \end{aligned}$$

Note that the dominating term is $7.63 \dots \text{J/K}$, the value calculated in **(1d)**. All other terms are approximately zero since they are so small compared to the largest term, and thus the simplifying

result $\Delta S = A \log \left(\frac{T_f}{T_i} \right)$ is a valid approximation for the heat capacity at constant pressure.

Q2.

(a) Based on the Sakur-Tetrode equation, the change in entropy is $\Delta S = nR \log \left(\frac{V_B}{V_A} \right)$, with n being the number of moles. Under isothermal condition, temperature remains constant. Because we are working with an ideal gas, the ideal gas law applies:

$$PV = nRT, \quad (2.1)$$

with T a constant. We can rearrange (2.1) to solve for the volume in terms of pressure:

$$V = nR \frac{T}{P}. \quad (2.2)$$

Since temperature is constant, we can substitute (2.2) into the expression for the change in entropy ΔS , so we have

$$\begin{aligned} \Delta S &= nR \log \left(\frac{nRT/P_A}{nRT/P_B} \right) \\ &= nR \log (P_A/P_B). \end{aligned} \quad (2.3)$$

Applying the logarithm manipulation rule $\log(A/B) = -\log(B/A)$, (2.3) becomes

$$\boxed{\Delta S = -nR \log \left(\frac{P_B}{P_A} \right)},$$

as desired.

(2b) Under isochronic conditions, volume remains constant. Since entropy can be defined in terms of heat upon temperature, $S = Q/T$, then given the infinitesimal change in entropy $dS = \frac{dQ}{T}$. Expressing heat in terms of temperature gives us a relation including the heat capacity of the matter kept at constant volume, $Q = C_V \Delta T$, so the infinitesimal change in heat $dQ = d(C_V \Delta T) = C_V dT$. This implies that a small change in entropy can be expressed as

$$dS = C_V \frac{dT}{T}.$$

To find the net change in entropy, we can sum over every infinitesimal dT component, which gives an integral $\Delta S = \int_A^B C_V \frac{dT}{T}$. Integrating and evaluating yields the familiar result from question (1d),

$$\boxed{\Delta S = C_V \log \left(\frac{T_B}{T_A} \right)}.$$

(2c) Under isobaric conditions, the pressure of an ideal gas going from state A to B remains constant. Applying the similar process as in **(2b)**, $dS = \frac{dQ}{T}$, and so the infinitesimal change in heat kept at constant pressure $Q = C_P \Delta T$ is then $dQ = d(C_P \Delta T) = C_P dT$. Substituting and integrating as in the prior question,

$$\Delta S = \int_A^B C_P \frac{dT}{T}$$

which implies that $\Delta S = C_P \log \left(\frac{T_B}{T_A} \right)$.

Q3.

(a) By assumption, the temperature of the resistor is equal to that of the oil bath. Taking the oil bath as a heat sink, this implies that the initial and final temperatures of the resistor are equal: $T_i = T_f$. Since $\Delta S \equiv nR \log \left(\frac{T_f}{T_i} \right)$, then the change in entropy of the resistor is 0: $\boxed{\Delta S_{res} = 0}$. Meanwhile, for the oil, although the temperature remains constant, heat release from the resistor is contributing to the entropy of the oil. With $\Delta S = \frac{Q}{T}$ and the heat release from the resistor being expressed as $Q = I^2 R \Delta t$, where Δt is the time interval, I is the current, and R the resistance, then

$$\Delta S = \frac{I^2 R \Delta t}{T}. \quad (3.1)$$

Taking $I = 75 \text{ mA}$, $R = 50 \Omega$, and $\Delta t = 30 \text{ s}$ with the temperature of the oil being kept at $T = 25^\circ \text{C} = 298 \text{ K}$, then

$$\begin{aligned} \Delta S &= \frac{(75 \times 10^{-3} \text{ A})^2 (50 \Omega) (30 \text{ s})}{298 \text{ K}} \\ &= 0.028313 \text{ J/K}. \end{aligned}$$

Rounding to the appropriate number of significant figures, the change in entropy of the oil is $\boxed{\Delta S = 0.03 \text{ J/K}}$.

(3b) The heat produced by the resistor is related by $Q = I^2 R \Delta t$ and $Q = C_V \Delta T$, since the volume change of the resistor over Δt is negligible. We wish to find an expression for the final temperature of the resistor, and thus applying the entropy equation from question (2b):

$$\Delta S = C_v \log \left(\frac{T_f}{T_i} \right) \quad (3.2)$$

The heat capacity of the resistor at constant volume is given by the product of the specific heat and the mass, that is

$$c_V \equiv \frac{C_V}{m} \implies C_V = m c_V.$$

Therefore we have that

$$I^2 R \Delta t = C_v \Delta T = m c_V \Delta T \implies \Delta T = \frac{I^2 R \Delta t}{m c_V}.$$

We proceed by finding the final temperature of the resistor, since the adiabatic wrapping around the resistor does not allow heat to escape through it, so $T_f \neq T_i$. Because $\Delta T = T_f - T_i$, then the final temperature is given by $T_f = \Delta T + T_i$. Substituting into equation (3.2),

$$\Delta S = m c_V \log \left(\frac{I^2 R \Delta t}{m c_V T_i} + 1 \right).$$

Taking $I = 75 \times 10^{-3} \text{ A}$, $R = 50 \Omega$, $\Delta t = 30 \text{ s}$, $m = 4 \times 10^3 \text{ kg}$, $c_V = 750 \text{ J/(kg K)}$, and $T_i = 25^\circ \text{C} = 298 \text{ K}$, then the change in entropy of the resistor is

$$\begin{aligned}\Delta S &= (4 \times 10^{-3} \text{ kg})(750 \text{ J/(kg K)}) \log \left(\frac{(75 \times 10^{-3} \text{ A})^2 (50 \Omega) (30 \text{ s})}{(4 \times 10^{-3} \text{ kg})(750 \text{ J/(kg K)})(298 \text{ K})} + 1 \right) \\ &= 0.02818 \text{ J/K}\end{aligned}$$

Therefore the change in entropy of the resistor is $\boxed{\Delta S = 0.03 \text{ J/K}}$, which is equivalent to of that found in question **(3a)**.

(3c) For this problem, we can model the jugs of oil as Einstein solids. For jugs A and B , when at equilibrium, the entropy is related by

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B}. \quad (3.3)$$

For $S_i = a\sqrt{n_i U_i V_i}$, where $i = A, B$. It can be verified that the partial derivative of S with respect of U gives

$$\frac{\partial S}{\partial U} = \frac{a}{2} \sqrt{\frac{nV}{U}}. \quad (3.4)$$

Suppose there are n_A moles and U_A Joules of energy in jug A . Then it is given that $n_B = 2n_A$ and $U_B = 3U_A$. Equating (3.4) into (3.3) gives that

$$\frac{a}{2} \sqrt{\frac{n_A V_A}{U_A}} = \frac{a}{2} \sqrt{\frac{n_B V_B}{U_B}} = \frac{a}{2} \sqrt{\frac{2n_A V_B}{3U_A}}.$$

After cancelling the term $\frac{a}{2} \sqrt{\frac{n_A}{U_A}}$ from both the right and lefthand side gives that relationship between the volumes:

$$\sqrt{V_A} = \sqrt{\frac{2}{3} V_B},$$

which implies that $\boxed{V_A = \frac{2}{3} V_B}$ or $\boxed{V_B = \frac{3}{2} V_A}$.

Q4.

(a) Given N steps, we find that $N_+ = N - N_-$. The multiplicity of N steps in the N_+ direction is

$$\Omega(N, N_+) = \frac{N!}{N_+!N_-!} \equiv \frac{N!}{N_+!(N - N_+)!}.$$

Taking $N_+ = \frac{N}{2} + x$ and substituting it into the multiplicity,

$$\Omega(N, N_+) = \frac{N!}{\left(\frac{N}{2} + x\right)!(N - \frac{N}{2} - x)!} = \frac{N!}{\left(\frac{N}{2} + x\right)!\left(\frac{N}{2} - x\right)!}.$$

Taking the logarithm of the multiplicity will allow us to more easily work with approximations since logarithms are easy to manipulate:

$$\begin{aligned} \log(\Omega(N, N_+)) &= \log\left(\frac{N!}{\left(\frac{N}{2} + x\right)!\left(\frac{N}{2} - x\right)!}\right) \\ &= \log(N!) - \log\left(\left(\frac{N}{2} + x\right)!\left(\frac{N}{2} - x\right)!\right) \\ &= \log(N!) - \left[\log\left(\frac{N}{2} + x\right)! + \log\left(\frac{N}{2} - x\right)!\right]. \end{aligned}$$

This allows us to easily apply Stirling's approximation: for large N , $\log(N!) \approx N \log N - N + \frac{1}{2} \log(2\pi N)$. Our equation expands to

$$\begin{aligned} \log(\Omega(N, N_+)) &\approx N \log N - N + \frac{1}{2} \log(2\pi N) - \left[(N/2 + x) \log(N/2 + x) - (N/2 + x) \right. \\ &\quad \left. + \frac{1}{2} \log(2\pi(N/2 + x)) + (N/2 - x) \log(N/2 - x) - (N/2 - x) + \frac{1}{2} \log(2\pi(N/2 - x)) \right] \\ &= N \log N - N + \frac{1}{2} \log(2\pi) + \frac{1}{2} \log N - \left[(N/2 + x) \log(N/2(1 + 2x/N)) - (N/2 + x) \right. \\ &\quad \left. + \frac{1}{2} \log(\pi N(1 + 2x/N)) + (N/2 - x) \log(N/2(1 + 2x/N)) \right. \\ &\quad \left. - (N/2 - x) + \frac{1}{2} \log(\pi N(1 - 2x/N)) \right]. \end{aligned}$$

Many of these steps follow from the logarithm manipulation rules: $\log(AB) = \log A + \log B$ and $\log(A/B) = \log A - \log B$. Since we are assuming $x \ll N$, then $\frac{x}{N} \ll 1$, which means we can apply a Taylor expansion to the log function, since for $\varepsilon \ll 1$, $\log(1 + \varepsilon) \approx \varepsilon$. We have

$$\log(\Omega(N, N_+)) = N \log N - N + \frac{1}{2} \log(2\pi) + \frac{1}{2} \log N - \left[(N/2 + x) \log(N/2) + (N/2 + x) \log(1 + 2x/N) \right.$$

$$\begin{aligned}
& - (N/2 + x) + \frac{1}{2} \log(\pi N) + \frac{1}{2} \log(1 + 2x/N) \\
& + (N/2 - x) \log(N/2) + (N/2 - x) \log(1 + 2x/N) \\
& - (N/2 - x) + \frac{1}{2} \log(\pi N) + \frac{1}{2} \log(1 + 2x/N) \Big] \\
& \approx N \log N - N + \frac{1}{2} \log(2\pi) + \frac{1}{2} \log N - \left[(N/2 + x) \log(N/2) + (N/2 + x) \cdot 2x/N \right. \\
& \quad \left. - (N/2 + x) + \frac{1}{2} \log(\pi N) + x/N \right. \\
& \quad \left. + (N/2 - x) \log(N/2) + (N/2 - x) \cdot 2x/N - (N/2 - x) + \frac{1}{2} \log(\pi N) + x/N \right].
\end{aligned}$$

The next steps follow from expanding and simplifying the equation, since it is just algebra. It can be verified that

$$\log(\Omega(N, N_+)) = (N + 1/2) \log(2) - \frac{1}{2} \log(\pi N) - \frac{4x^2}{N}.$$

This completes the approximation step. We can revert back to our initial function by raising each side to the exponent of base e :

$$\Omega(N, N_+) = 2^{N+1/2} \cdot (\pi N)^{1/2} \cdot e^{-4x^2/N}$$

Rewriting yields

$$\boxed{\Omega(N, N_+) = \sqrt{\frac{2}{\pi N}} 2^N e^{-4x^2/N}}$$

(4b) We begin by calculating the value of x for when $\Omega(N, N_+)$ falls off to e^{-1} , the half width. Setting $e^{4x^2/N} = e^{-1}$, this occurs when $1 = 4x^2/N$, so $x = \pm \frac{\sqrt{N}}{2}$. Note that applying dimensional analysis on x yields nothing but a number, so x has no dimensions. We require that the final displacement of forward steps is within the half width:

$$0 \leq x \leq \frac{\sqrt{N}}{2}.$$

If each step is quantized to length ℓ , the final displacement is given by $\Delta d = x\ell$. Here, $[\Delta d] = L$ (the final displacement has dimensions of length). Then, you would expect to end up a distance

$$\boxed{\Delta d = \frac{\sqrt{N}}{2} \ell}$$

from your starting point.

(4c) Since we are looking to find the net displacement of a particle in 1 dimension, we can apply our solution from (4b). ℓ is simply given by $\ell = 150 \times 10^{-9}m$, and the average time between collisions is $3 \times 10^{-10}s/C$. If $t = 1s$, then the number of collisions, or steps N , is

$$N = \frac{1s}{3 \times 10^{-10}s/C} = \frac{1}{3} \times 10^{10} \text{ collisions.}$$

Substituting these values in,

$$\begin{aligned} \Delta d &= \frac{\sqrt{N}}{2} \ell \\ &= \frac{\sqrt{1/3 \times 10^{10}}}{2} \cdot (150 \times 10^{-9}m) \\ &= 0.00433m. \end{aligned}$$

Rounding off, $\boxed{\Delta d = 4.3 \times 10^{-3}m.}$

Q5.

(a) We begin with the formula for the multiplicity of an Einstein solid: $\Omega(N, q) = \frac{(q + N - 1)!}{q!(N - 1)!}$. Given that $N! = N(N - 1)!$, then $(N - 1)! = \frac{N!}{N}$. Inspecting the term in the numerator, $(q + N - 1)! = \frac{(q + N)!}{q + N}$ and $[(N - 1)!]^{-1} = \frac{N}{N!}$ in the denominator. This gives

$$\Omega(N, q) = \frac{(q + N)!}{q!N!} \cdot \frac{N}{q + N}.$$

Since N and q are both large, we can apply Stirling's approximation to the leading term with the factorials. The approximation is $N! \approx N^N e^{-N} \sqrt{2\pi N}$. Then

$$\Omega(N, q) \approx \frac{(q + N)^{q+N} e^{-(q+N)} \sqrt{2\pi(q + N)}}{(q^q e^{-q} \sqrt{2\pi q}) (N^N e^{-N} \sqrt{2\pi N})} \cdot \frac{N}{q + N}$$

Note that $\frac{e^{-(q+N)}}{e^{-q}e^{-N}} = \frac{e^{-(q+N)}}{e^{-(q+N)}} = 1$, so the approximation simplifies to

$$\Omega(N, q) \approx \frac{(q + N)^{q+N}}{q^q N^N} \cdot \sqrt{\frac{2\pi(q + N)}{(2\pi)^2 q N}} \cdot \frac{N}{q + N}.$$

Squaring and taking the square root of the last term allows us to manipulate the expression under the square root sign:

$$\begin{aligned} \Omega(N, q) &= \frac{(q + N)^{q+N}}{q^q N^N} \cdot \sqrt{\frac{2\pi(q + N)}{(2\pi)^2 q N}} \cdot \sqrt{\frac{N^2}{(q + N)^2}} \\ &= \frac{(q + N)^{q+N}}{q^q N^N} \cdot \sqrt{\frac{(q + N)}{2\pi q N} \frac{N^2}{(q + N)^2}} \\ &= \frac{(q + N)^{q+N}}{q^q N^N} \cdot \sqrt{\frac{N}{2\pi q (q + N)}}. \end{aligned}$$

Therefor, the multiplicity can be expressed as $\Omega(N, q) = \frac{(q + N)^{q+N}}{q^q N^N} \cdot \sqrt{\frac{N}{2\pi q (q + N)}}.$

(5b) By definition, the entropy is defined as $S = k \log \Omega$, where k is Boltzmann's constant and Ω is the multiplicity expression. The total entropy of an Einstein solid can then be expressed as

$$S = k \log \Omega = k \log \left(\frac{(q + N)^{q+N}}{q^q N^N} \right),$$

which is a result of setting the square root expression to 1 from question (5a). Applying the logarithm expansion rules,

$$S_{\Omega} = k [(q + N) \log(q + N) - q \log q - N \log N].$$

(5c) I will begin by finding the total energy of the Einstein solid. In doing this, we can find a more simple expression for $\frac{1}{T} = \frac{\partial S}{\partial U} = \frac{\partial S}{\partial q} \frac{\partial q}{\partial U}$, because U will be dependent on q , which is the amount of energy units in each oscillator. Suppose there are N oscillators and q energy units (and hence $N/3$ atoms). In simple quantum oscillators, energy is quantized to $\varepsilon = \hbar\omega$ with ω the oscillator frequency. The total energy is then the amount of energy from each of the q energy units ($q\varepsilon$) superposed with the energy from each ground state oscillator.

In an oscillator, the energy levels are quantized to $E_n = \varepsilon \left(n + \frac{1}{2}\right)$, and with $n = 0$, $E = \frac{1}{2}\varepsilon$. This is the ground state energy of each oscillator. Therefore

$$U = \frac{1}{2}N\varepsilon + q\varepsilon. \quad (5.1)$$

The partial derivative with respect to q is $\frac{\partial U}{\partial q} = \varepsilon$.

We can proceed by calculating $\frac{1}{T}$, which is given by

$$\begin{aligned} \frac{1}{T} &= \frac{\partial S}{\partial q} \frac{\partial q}{\partial U} \\ &= k \frac{\partial}{\partial q} [(q + N) \log(q + N) - q \log q - N \log N] \cdot \frac{1}{\varepsilon} \\ &= \frac{k}{\varepsilon} \left[\log(q + N) + \frac{q}{q + N} + \frac{N}{q + N} - \frac{q}{q} - \log(q) - 0 \right] \\ &= \frac{k}{\varepsilon} [\log(q + N) - \log(q)] \\ &= \frac{k}{\varepsilon} \log \left(1 + \frac{N}{q} \right). \end{aligned} \quad (5.2)$$

This gives an implicit expression for the Einstein solid's temperature as a function of its energy. Since q is the number of energy units in the solid, we can express q as a function of N and U . From (5.1), $q = \frac{1}{\varepsilon}U - \frac{1}{2}N$. Assuming $q \neq 0$ and applying this substitution into (5.2) gives the temperature in terms of the energy and the number of oscillators, however one could make the substitution $N = \frac{2}{\varepsilon}U - 2q$ and have T in terms of the number of energy units and the energy. I will stick with the prior. Then

$$\frac{1}{T} = \frac{k}{\varepsilon} \log \left(1 + \frac{N}{U/\varepsilon - N/2} \right) \quad (5.3)$$

Taking the reciprocal yields the temperature in terms of U and N :

$$T = \frac{\varepsilon}{k \log \left(1 + \frac{N}{U/\varepsilon - N/2} \right)}.$$

If we ignore the ground state energy of each oscillator and just consider the energy from the q energy units, then $T = \frac{\varepsilon}{k \log \left(1 + \frac{N\varepsilon}{U} \right)}$.

(5d) If we consider equation (5.3), we can raise each side of the expression to an exponent of base e , which is

$$e^{\varepsilon/kT} = 1 + \frac{N}{U/\varepsilon - N/2}.$$

We can proceed by solving for U . After some algebra, we find $U = \frac{N\varepsilon}{e^{\varepsilon/kT} - 1} + \frac{N\varepsilon}{2}$. Note that this equation is consistent with equation (5.1), with $q = \frac{N}{e^{\varepsilon/kT} - 1}$. This q is always defined because $\varepsilon/kT = \hbar\omega/kT \neq 0$, and thus U is defined. The volume of the solid does not change (because it is a solid), so the heat capacity kept at constant volume is given by $C_V = \frac{\partial U}{\partial T}$. Some algebra follows:

$$\begin{aligned} C_V &= \frac{\partial}{\partial T} \left[\frac{N\varepsilon}{e^{\varepsilon/kT} - 1} \right] + \frac{\partial}{\partial T} \left[\frac{N\varepsilon}{2} \right] \\ &= \frac{1}{(e^{\varepsilon/kT} - 1)^2} \cdot \left[0 - \varepsilon N \frac{\partial}{\partial T} [e^{\varepsilon/kT} - 1] \right] && \text{by quotient rule} \\ &= -\frac{\varepsilon N [e^{\varepsilon/kT} \cdot (-\varepsilon/kT^2)]}{(e^{\varepsilon/kT} - 1)^2} \\ &= \frac{\varepsilon^2}{T^2} \frac{N}{k} \cdot \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT} - 1)^2}. \end{aligned}$$

Therefore with N oscillators and $\varepsilon = \hbar\omega$, the heat capacity of the solid is given by

$$C_V = \frac{\varepsilon^2}{T^2} \frac{N}{k} \cdot \frac{e^{\varepsilon/kT}}{(e^{\varepsilon/kT} - 1)^2}.$$