Problem Set 4
Solutions
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Problem 1-22

For this problem we need the formula given in class (McQuarie 1-33) for the energy states of a particle in an three-dimensional infinite well, namely

$$\varepsilon_{n_x n_y n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \ , \ n_x, n_y, n_z = 1, 2 \ldots$$

Now we can make a table

n_x	n_y	n_z	$n_x^2 + n_y^2 + n_z^2$	*Degeneracy*
1	1	1	3	1
1	1	2	6	
1	2	1	6	3
2	1	1	6	
1	2	2	9	
2	1	2	9	3
2	2	1	9	
1	1	3	11	
1	3	1	11	3
3	1	1	11	

Problem 1-29

Start with the differential form for E

$$dE = TdS - pdV$$
$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p$$

We can use a Maxwell relation on $\left(\frac{\partial S}{\partial V}\right)_T$ from $F(T, V)$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$

So,

$$\left(\frac{\partial E}{\partial V}\right)_T - T\left(\frac{\partial p}{\partial T}\right)_V = -p$$

Problem 1-41

Show that $\overline{(x-\overline{x})^2} = \overline{x^2} - \overline{x}^2$

$$\overline{(x-\overline{x})^2} = \overline{x^2 - 2x\overline{x} + \overline{x}^2} = \overline{x^2} - \overline{2x\overline{x}} + \overline{x}^2 = \overline{x^2} - 2\overline{x}(\overline{x}) + \overline{x}^2 = \overline{x^2} - \overline{x}^2$$

Problem 1-43

Here we have to plot the Gaussian $\left[p(x) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(x-\overline{x})^2}{2\sigma^2}\right)\right]$ for several values of σ to see what happens as $\sigma \to 0$

As $\sigma \to 0,$ the function becomes sharper and sharper (remember the area under the curve is contrained to be 1, as we will see in problem 1-44a). Thus, the Gaussian approaches a delta function.

Problem 1-44

Gaussian distribution is

$$p(x) = \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(x-\overline{x})^2}{2\sigma^2}\right)$$

(a) show $\int_{-\infty}^{\infty} p(x)dx = 1$

$$\int_{-\infty}^{\infty} \frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(x-\overline{x})^2}{2\sigma^2}\right)dx$$

Let

$$u = \frac{x - \overline{x}}{\sqrt{2}\,\sigma} \text{ , then } du = \frac{dx}{\sqrt{2}\,\sigma}$$

So we now have

$$\int_{-\infty}^{\infty} \frac{1}{\sqrt{\pi}} \exp(-u^2) du$$

And using standard integral tables or the math software, it can be show that this integral is equal to 1.

(b) n^{th} central moment for $n = 0, 1, 2,\ and\ 3$

<u>For $n = 0$</u>

$$\overline{(x-\overline{x})^0} = 1 \qquad \text{see part a}$$

<u>For $n = 1$</u>

$$\overline{(x-\overline{x})} = \int_{-\infty}^{\infty}(x-\overline{x})\bullet p(x)dx = \int_{-\infty}^{\infty}\frac{(x-\overline{x})}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(x-\overline{x})^2}{2\sigma^2}\right)dx$$

Let

$$u = \frac{x-\overline{x}}{\sqrt{2}\,\sigma}\text{, then } du = \frac{dx}{\sqrt{2}\,\sigma}$$

Then

$$\overline{(x-\overline{x})} = \frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}u\bullet\exp(-u^2)du = \underbrace{\frac{1}{\sqrt{\pi}}\int_{-\infty}^{0}u\bullet\exp(-u^2)du}_{I} + \underbrace{\frac{1}{\sqrt{\pi}}\int_{0}^{\infty}u\bullet\exp(-u^2)du}_{II}$$

For I let $v = -u$ and $dv = -du$. Then

$$I = -\frac{1}{\sqrt{\pi}}\int_{0}^{-\infty}u\bullet\exp(-u^2)du - \frac{1}{\sqrt{\pi}}\int_{0}^{\infty}v\bullet\exp(-v^2)dv = -II$$

Thus,

$$\boxed{\frac{1}{\sqrt{\pi}}\int_{-\infty}^{\infty}u\bullet\exp(-u^2)du = 0}$$

<u>For $n = 2$</u>

$$\overline{(x-\overline{x})^2} = \int_{-\infty}^{\infty}(x-\overline{x})\bullet p(x)dx = \int_{-\infty}^{\infty}\frac{(x-\overline{x})^2}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(x-\overline{x})^2}{2\sigma^2}\right)dx$$

Let

$$u = \frac{x - \overline{x}}{\sqrt{2}\,\sigma} \text{ , then } du = \frac{dx}{\sqrt{2}\,\sigma}$$

$$\overline{(x - \overline{x})^3} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} 2\sigma^2 u^2 \exp(-u^2) du = \frac{2\sigma^2}{\sqrt{\pi}} \int_{-\infty}^{\infty} u^2 \exp(-u^2) du$$

Now lets take a crack at this integral....

$$\int_{-\infty}^{\infty} u^2 \exp(-u^2) du$$

We have to do this by parts. Remembering how to do that....

$$(yx)' = y'x + yx'$$

$$\int_{-\infty}^{\infty} y'x = [yx]_{-\infty}^{\infty} - \int_{-\infty}^{\infty} yx'$$

For our case, let

$$y' = -2u \exp(-u^2) du \text{ and } x = \frac{-u}{2}$$

$$y = \exp(-u^2) \text{ and } x' = -\frac{1}{2}$$

So,

$$\int_{-\infty}^{\infty} u^2 \exp(-u^2)du = \underbrace{\left[\frac{-u}{2}\exp(-u^2)\right]_{-\infty}^{\infty}}_{=0} - \underbrace{\int_{-\infty}^{\infty}\left(-\frac{1}{2}\right)\exp(-u^2)}_{=\frac{\sqrt{\pi}}{2}}$$

Which leaves us with,

$$\boxed{\overline{(x-\overline{x})^2} = \sigma^2}$$

<u>For $n = 3$</u>

$$\overline{(x-\overline{x})^3} = \int_{-\infty}^{\infty}(x-\overline{x})^3 \bullet p(x)dx = \int_{-\infty}^{\infty}\frac{(x-\overline{x})^3}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(x-\overline{x})^2}{2\sigma^2}\right)dx$$

As before, let

$$u = \frac{x-\overline{x}}{\sqrt{2}\,\sigma}\text{, then } du = \frac{dx}{\sqrt{2}\,\sigma}$$

Then,

$$\overline{(x-\overline{x})^3} = 2\sqrt{\frac{2}{\pi}}\int_{-\infty}^{\infty} u^3 \exp(-u^2)$$

Since e^{-u^2} is a symmetric function around the origin and u^3 *is* an antisymmetric function around the origin, the integral of the product of the two functions is zero.

$$\boxed{\overline{(x-\overline{x})^3} = 0}$$

(c) $\lim\limits_{\sigma\to 0} p(x) = \lim\limits_{\sigma\to 0}\frac{1}{\sigma\sqrt{2\pi}}\exp\left(-\frac{(x-\overline{x})^2}{2\sigma^2}\right) = \delta(x-\overline{x})$, the delta function

The delta function is defined as

$$\int_{-\infty}^{\infty} \delta(x-a) \cdot \phi(x)dx = \phi(a) \text{ and } \int_{-\infty}^{\infty} \delta(x)dx = 1$$

So lets see if this works for our case

$$\lim_{\sigma \to 0} \int_{-\infty}^{\infty} \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(x-a)^2}{2\sigma^2}\right) \cdot \phi(x)dx$$

Let $u = \frac{x-a}{\sigma\sqrt{2}}$ and $du = \frac{dx}{\sigma\sqrt{2}}$

$$\lim_{\sigma \to 0} \frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-u^2) \cdot \phi\left(\sigma\sqrt{2} + a\right)$$

Since $\sigma \to 0$

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \exp(-u^2) \cdot \phi(a) = \frac{\phi(a)}{\sqrt{\pi}} \underbrace{\int_{-\infty}^{\infty} \exp(-u^2)}_{\sqrt{\pi}} = \phi(a)$$

Problem 1-49

Maximize

$$W(N_1, N_2, \ldots. N_m) = \frac{N!}{\prod_{j=1}^{m} N_j!}$$

under the contraints that $\sum N_j = N$ and $\sum E_j N_j = \varepsilon$.

Since the natural log is a monotonic function, we can maximize $\ln(W)$.

$$M = \ln W(N_1, N_2, \ldots. N_m) = \ln\left(\frac{N!}{\prod_{j=1}^{m} N_j!}\right)$$

Using Sterling approximation, this can be written as

$$N\ln N - N - \sum_j N_j \ln N_j + \sum_j N_j$$

But the maximization must be constrained therefore we intoduce Lagrange multipliers

$$M = N\ln N - N - \sum_j N_j \ln N_j + \underbrace{\sum_j N_j}_{+N} - \alpha\left(\sum N_j - N\right) - \beta\left(\sum E_j N_j - \varepsilon\right)$$

Remembering $\sum N_j = N$ and taking the derivative of M with respect to N_j

$$\left(\frac{\partial M}{\partial N_j}\right) = -\ln N_j - 1 - \alpha - \beta E_j = 0$$

$$-\ln N_j = 1 + \alpha + \beta E_j$$

$$\ln N_j = -\alpha' - \beta E_j \text{ , with } \alpha' = 1 + \alpha$$

$$\boxed{N_j = \exp(-\alpha')\exp(-\beta E_j)}$$

Problem 1-50

We want to show that the maximum of

$$W(N_1, N_2, \ldots N_m) = \frac{N!}{\prod_{j=1}^{m} N_j!}$$

occurs for $N_1 = N_2 = N_s \bullet \bullet \bullet = \frac{N}{s}$

→Maximize

$$M = \ln W = N\ln N - N - \sum N_j \ln N_j + \sum N_j$$

subject to the constraint $\sum N_j = N.$ So we must use Lagrange multipliers:

$$\widehat{M} = N\ln N - N - \sum N_j \ln N_j + \sum N_j - \alpha\left(\sum N_j - N\right)$$

$$\frac{\partial \widehat{M}}{\partial N_j} = -\ln N_j - 1 - \alpha = 0$$

$$\ln N_j = -(1 + \alpha) \Rightarrow N_j = \exp[-(1 + \alpha)]$$

But now we must determine α

$$\sum_{j=1}^{s} N_j = \sum_{j=1}^{s} \exp[-(1 + \alpha)] = S\exp[-(1 + \alpha)] = N \Rightarrow \exp[-(1 + \alpha)] = \frac{N}{s}$$

So

$$\boxed{N_j = \tfrac{N}{s}}$$

Problem 1-51

Here we use Lagrange multipliers again with the constraint $\sum_j P_j = 1$.

$$M = -\sum_{j=1}^{N} P_j \ln P_j - \alpha\left(\sum_{j=1}^{N} P_j - 1\right)$$

Maximize

$$\left(\frac{\partial M}{\partial P_j}\right) = -\ln P_j - 1 - \alpha = 0$$

$$P_j = \exp[-(1+\alpha)]$$

Determine α

$$\sum_{j=1}^{N} P_j = N\exp[-(1+\alpha)] = 1$$

$$\exp[-(1+\alpha)] = \frac{1}{N}$$

Thus

$$\boxed{P_j = \tfrac{1}{N}}$$

Problem 2-1

From stat mech we get

$$\left(\frac{\partial \overline{E}}{\partial V}\right)_{N,\beta} + \beta\left(\frac{\partial \overline{p}}{\partial \beta}\right)_{N,V} = -\overline{p}$$

And from thermo we have

$$\left(\frac{\partial E}{\partial V}\right)_{N,T} - T\left(\frac{\partial p}{\partial T}\right)_{N,V} = -p$$

To show why $\beta \neq (cont) * T$ lets see what happens if we let $\beta = \alpha T$ where α is a constant

$$\left(\frac{\partial \overline{E}}{\partial V}\right)_{N,\beta} + \alpha T\left(\frac{\partial \overline{p}}{\partial(\alpha T)}\right)_{N,V} = -\overline{p}$$

or

$$\left(\frac{\partial \overline{E}}{\partial V}\right)_{N,T} + T\left(\frac{\partial \overline{p}}{\partial T}\right)_{N,V} = -\overline{p}$$

but from a Maxwell relation we know $\left(\frac{\partial \overline{p}}{\partial T}\right)_{N,V} = \left(\frac{\partial S}{\partial V}\right)_{N,T}$ and we can write

$$\left(\frac{\partial E}{\partial V}\right)_{N,T} + T\left(\frac{\partial S}{\partial V}\right)_{N,T} = -p$$

$$\underbrace{dE = -TdS - PdV}$$

This statement violates the second law of thermodynamics because it implies that $\delta Q \leqq -TdS \rightarrow \frac{-\delta Q}{T} \geqq dS$

Problem 2-2

Given

$$\Omega(n) = \frac{n!}{n!(n-n_1)!}$$

is $n_1^* \approx \overline{n}_1$?

- n_1^* is the value of n_1 that maximizes $\Omega(n)$. From problem 1-50, we know that

$n_1^* = \frac{n}{2}$.

- $\overline{n}_1$ is given by

$$\overline{n}_1 = \frac{\sum_{n_1=0}^{n} n_1 \left(\frac{n!}{n_1!(n-n_1)!} \right)}{\sum_{n_1=0}^{n} \left(\frac{n!}{n_1!(n-n_1)!} \right)} \qquad \text{2-2-1}$$

We also know that (given in the problem):

$$y = (1+x)^n = \sum_{n_1=0}^{n} x^{n_1} \left(\frac{n!}{n_1!(n-n_1)!} \right)$$

If we take the derivative of y with respect to x we get

$$y' = n(1+x)^{n-1} = \sum_{n_1=0}^{n} n_1 x^{n_1-1} \left(\frac{n!}{n_1!(n-n_1)!} \right)$$

If we let $x = 1$:

$$n2^{n-1} = \sum_{n_1=0}^{n} n_1 \left(\frac{n!}{n_1!(n-n_1)!} \right)$$

Furthermore,

$$2^n = \sum_{n_1=0}^{n} \left(\frac{n!}{n_1!(n-n_1)!} \right)$$

So if we put this all together back in (2-2-1) we get

$$\overline{n}_1 = \frac{\sum_{n_1=0}^{n} n_1 \left(\frac{n!}{n_1!(n-n_1)!} \right)}{\sum_{n_1=0}^{n} \left(\frac{n!}{n_1!(n-n_1)!} \right)} = \frac{n2^{n-1}}{2^n} = \frac{n}{2} = n_1^*$$

$$\boxed{\overline{n}_1 = n_1^*}$$

Problem 2-5

Show that $S = -k \sum P_j \ln P_j$

We have the following three relations already

$$S = kT \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} + k \ln Q$$

$$P_j = \frac{\exp\left(\frac{-E_j}{kT} \right)}{Q}$$

and

$$Q = \sum_j \exp\left(\frac{-E_j}{kT} \right)$$

Starting with S we can write

$$S = \frac{kT}{Q} \frac{\partial Q}{\partial T} + k \ln Q = \frac{kT}{Q} \sum_j \left(\frac{E_j}{kT^2} \right) \exp\left(\frac{-E_j}{kT} \right) + k \ln Q$$

$$S = \frac{k}{Q} \sum_j \left(\frac{E_j}{kT} \right) \exp\left(\frac{-E_j}{kT} \right) + k \ln Q$$

$$S = -\frac{k}{Q} \sum_j \ln\left[\exp\left(\frac{-E_j}{kT} \right) \right] \exp\left(\frac{-E_j}{kT} \right) + k \ln Q$$

$$S = -k\sum_j \ln\left[\exp\left(\frac{-E_j}{kT}\right)\right]\underbrace{\frac{\exp\left(\frac{-E_j}{kT}\right)}{Q}}_{=P_j} + k\ln Q$$

Since $\sum P_j = 1$

$$S = -k\sum_j P_j \cdot \ln\left[\exp\left(\frac{-E_j}{kT}\right)\right] + k\ln Q\left(\sum_j P_j\right)$$

$$S = -k\sum_j P_j \cdot \ln\left[\exp\left(\frac{-E_j}{kT}\right)\right] - k\sum_j P_j \cdot \ln\left(\frac{1}{Q}\right)$$

$$S = -k\sum_j P_j \ln\left[\frac{\exp\left(\frac{-E_j}{kT}\right)}{Q}\right]$$

$$\boxed{S = -k\sum\nolimits_j P_j \ln P_j}$$

Problem 2-8

$$\frac{\partial Q}{\partial \beta} = \sum_j -E_j \exp(-\beta E_j)$$

$$\overline{E} = \frac{\sum_j E_j \exp(-\beta E_j)}{Q} = \frac{-\frac{\partial Q}{\partial \beta}}{Q} = -\frac{\partial \ln Q}{\partial \beta}$$

$$\boxed{\overline{E} = -\frac{\partial \ln Q}{\partial \beta}}$$

Problem 2-10

•First derive $\overline{E} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$ starting from the result of problem 2-8, namely

$$\overline{E} = -\frac{\partial \ln Q}{\partial \beta}$$

From the chain rule

$$\overline{E} = -\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} \frac{\partial T}{\partial \beta}$$

We know $\beta = \frac{1}{kT}$ so $\frac{\partial T}{\partial \beta} = -kT^2$, thus

$$\overline{E} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

We can check this by taking $kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$.

$$kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = kT^2\frac{\left(\frac{\partial Q}{\partial T}\right)_{N,V}}{Q} = kT^2\frac{\frac{\partial}{\partial T}\left[\sum \exp\left(-\frac{E_j}{kT}\right)\right]_{N,V}}{Q}$$

$$kT^2\frac{\frac{\partial}{\partial T}\left[\sum \exp\left(-\frac{E_j}{kT}\right)\right]}{Q} = \frac{\sum \exp\left(-\frac{E_j}{kT}\right)\cdot\frac{E_j}{kT^2}}{Q}$$

The kT^2 cancels and we are left with

$$kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = \underbrace{\frac{\sum E_j \exp\left(-\frac{E_j}{kT}\right)}{Q}}_{\text{definition of } \overline{E}}$$

So we have shown again that indeed $\overline{E} = kT^2\frac{\partial \ln Q}{\partial T}$.

•Now for the relation involving $\overline{p}$

$$\overline{p} = \frac{\sum p_j \exp\left(-\frac{E_j}{kT}\right)}{Q} = \frac{\sum\left(-\frac{\partial E_j}{\partial V}\right)\exp\left(-\frac{E_j}{kT}\right)}{Q} = \frac{kT\frac{\partial}{\partial V}\left(\sum_j \exp\left(-\frac{E_j}{kT}\right)\right)_{N,T}}{Q}$$

$$\boxed{\overline{p} = \frac{kT\left(\frac{\partial Q}{\partial V}\right)}{Q} = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}}$$

Problem 2-11

Starting with $F = -kT\ln Q$ (Remember $F = A$)

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}$$

$$\boxed{S = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} + k\ln Q} \qquad \text{Eqn. 2-33}$$

$$p = -\left(\frac{\partial F}{\partial V}\right)_{T,N}$$

$$\boxed{\overline{p} = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N}} \qquad \text{Eqn. 2-32}$$

$$F = E - TS \rightarrow E = F + TS$$

$$E = -kT\ln Q + T \bullet \left[kT\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} + k\ln Q\right]$$

$$\boxed{\overline{E} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N}} \qquad \text{Eqn. 2-31}$$

Problem 2-13

For a particle confined to a cube of length a we are asked to show $p_j = \frac{2}{3}\frac{E_j}{V}$. We can start with the equation for the energy states of a particle in an three-dimensional infinite well, namely

$$E_j = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)\ ,\ n_x, n_y, n_z = 1, 2\ldots$$

Remembering that $a^3 = V$ or $a = V^{\frac{1}{3}}$ we can write E_j in terms of V

$$E_j = \frac{h^2 V^{-\frac{2}{3}}}{8m}(n_x^2 + n_y^2 + n_z^2)$$

$$p_j = -\left(\frac{\partial E_j}{\partial V}\right) = \frac{2}{3}\frac{h^2 V^{-\frac{5}{3}}}{8m}(n_x^2 + n_y^2 + n_z^2) = \frac{2}{3} \bullet \frac{1}{V} \bullet \underbrace{\frac{h^2 V^{-\frac{2}{3}}}{8m}(n_x^2 + n_y^2 + n_z^2)}_{E_j}$$

So we have

$$\boxed{p_j = \frac{2}{3}\frac{E_j}{V}}$$

and taking the ensemble average gives us

$$\overline{p} = \frac{2}{3}\frac{\overline{E}}{V}$$

Problem 2-14

$$Q(N,V,T) = \frac{1}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} V^N$$

For $\overline{p}$,

$$\overline{p} = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T.N}$$

$$\ln Q = \ln\left(\frac{1}{N!}\right) + \frac{3N}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + N\ln V$$

$$\overline{p} = \frac{kTN}{V}$$

Now for $\overline{E}$

$$\overline{E} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = kT^2\left(\frac{3N}{2}\frac{\frac{2\pi mk}{h^2}}{\frac{2\pi mkT}{h^2}}\right)$$

$$\overline{E} = \frac{3N}{2}kT$$

Ideal gas equation of state is obtained when $Q = f(T)V^N \rightarrow \ln Q = \ln f(T) + N\ln V$

$$\overline{p} = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T.N} = kT\left(\frac{\partial(\ln f(T))}{\partial V}\right)_{T,N} + kT\frac{\partial(N\ln V)}{\partial V}$$

$$\boxed{\overline{p} = \frac{NkT}{V}}$$

Problem 2-15

We are given Q as

$$Q = \left(\frac{\exp\left(\frac{-h\upsilon}{2kT}\right)}{1 - \exp\left(\frac{-h\upsilon}{kT}\right)} \right)^{3N} \exp \frac{U_o}{kT}$$

substituting in $\Theta = \frac{h\nu}{k}$

$$Q = \left(\frac{\exp(\frac{-\Theta}{2T})}{1 - \exp(\frac{-\Theta}{T})} \right)^{3N} \exp \frac{U_o}{kT}$$

To find c_v we need to use the following two relations

$$E = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V}$$

$$c_v = \left(\frac{\partial E}{\partial T} \right)$$

Using your favorite math package (Maple), we can get E as

$$E = \frac{\frac{1}{2} e^{-\frac{U_o}{kT}} \left[3Nk\Theta\, e^{\frac{U_o}{kT}} - 12Nk\Theta\, e^{\frac{U_o+\Theta k}{kT}} + 9Nk\Theta\, e^{\frac{2\Theta k+U_o}{kT}} - 2U_o\, e^{\frac{U_o}{kT}} + 4U_o e^{\frac{U_o+\Theta k}{kT}} - 2U_o e^{\frac{2\Theta k+U_o}{kT}} \right]}{\left(-1 + e^{\frac{\Theta}{T}}\right)^2}$$

and c_v as

$$c_v = \left(\frac{\partial E}{\partial T} \right) = 3 \frac{kN\Theta^2 e^{\frac{\Theta}{T}}}{T^2 \left(-1 + e^{\frac{\Theta}{T}}\right)^2}$$

Now we can take the $\lim\limits_{T \to \infty} c_v$ and we find that

$$\lim_{T\to\infty} 3\frac{k\Theta^2 e^{\frac{\Theta}{T}} N}{T^2\left(-1+e^{\frac{\Theta}{T}}\right)^2} = \boxed{3Nk}$$