

Like our previous exercise we need to have

Solutions P.S. #4

①

Problem #1

$$\text{RHS} \rightarrow \frac{R_0^2}{\rho^2} e^{-\frac{R_0}{\rho}} = \frac{d q^2}{\rho^2 \lambda} \leftarrow \text{RHS}$$

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In[137]:= (*First I'm going to do this for singly ionized NaCl*)
rho = 0.321 × 10-8;
(*repulsive range parameter in cm*)
ANaCl = 1.747565;
(*Madelung constants for NaCl, dimensionless*)
q = 4.8 × 10-10;
(*electron charge in stat coulombs*)
zlambda = 1.05 × 10-8;
(*product of coordination number and Lambdas (in ergs) for NaCl*)
ANaCl
----- × -----
rho      zlambda

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Out[141]= 0.011946

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In[142]:= (*Now I'm going to calculate this for
the doubly ionized crystal. Only change is q2 → 4q2*)

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In[143]:= ANaCl
----- × -----
rho      zlambda

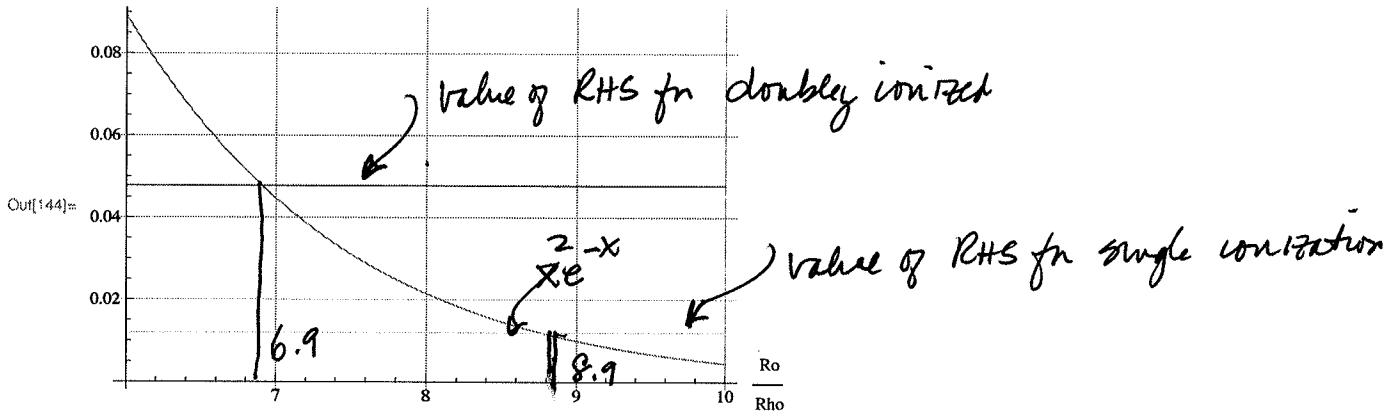
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Out[143]= 0.0477839

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In[144]:= Plot[{x2 × Exp[-x], .0119, .0478}, {x, 6, 10},
PlotStyle -> {Red, Green, Blue}, GridLines -> Automatic, AxesLabel -> {Ro / Rho}]
(* Now here I want to plot the left hand side and the value I got from above. The
intercept is going to give me the equilibrium nearest neighbor separation*)

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In[145]:= (*Looks like values are 8.9 and 6.9, for singly and doubly ionized respectively*)
ion separation single (in cm)
8.9 × rho
ion separation double (in cm)
6.9 × rho

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Out[145]= cm in ion separation single

Out[146]= 2.8569 × 10<sup>-8</sup> cm

Out[147]= cm double in ion separation

Out[148]= 2.2149 × 10<sup>-8</sup> cm

(2)

In[149]:=

(\*Now lets calculate the energy per atom for each configuration in ergs\*)

$$\text{EnergySingleion} = z\lambda \times \text{Exp}[-8.9] - \frac{A\text{NaCl} \times q^2}{8.9 \times \rho}$$

Out[149]:=  $-1.26615 \times 10^{-11}$  ergs

In[150]:=

$$\text{EnergyDoubleion} = z\lambda \times \text{Exp}[-6.9] - \frac{A\text{NaCl} \times 4 \times q^2}{6.9 \times \rho}$$

Out[151]:=  $-6.21329 \times 10^{-11}$  ergs

In[152]:=

(\*The gain in energy in eV \*)

$$(\text{EnergyDoubleion} - \text{EnergySingleion}) \times 6.24 \times 10^{11} \quad \frac{\text{eV}}{\text{erg}} \text{ conversion}$$

Out[152]:= -30.8701 eV

In[153]:=

(\*It would be about 5x lower energy to have doubly ionized if we looked at this energy alone but we also need to consider the energy to doubly ionize the Na and the electron affinity for the 2nd electron added to the Cl

The energy in eV to ionize the 1st electron in Na is 5.14eV, the 2nd costs 47.26eV. Similarly the electron affinity for the first electron in Cl is 3.61eV, couldn't even find the 2nd electron affinity for Cl (its shell is closed with just one more).

We don't need to know as the gain in energy of -30.8eV is insufficient to counteract the extra 47.26 eV to remove the 2nd electron from Na. Thus the singly ionized crystal is preferred (as we observe in nature)\*

In[154]:=

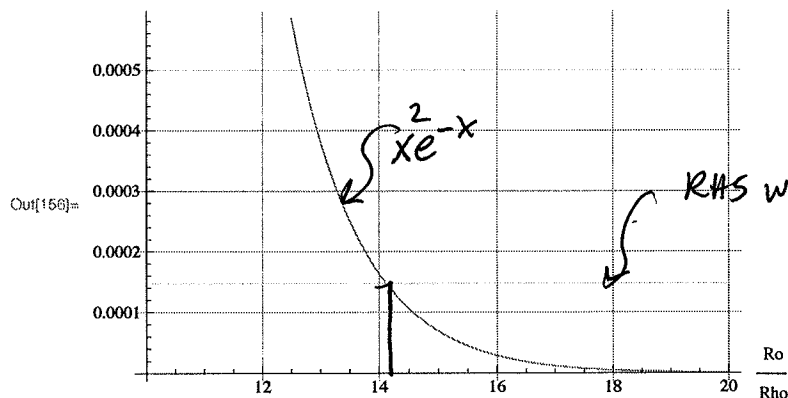
(\*Now lets do the problem with the water which effectively reduces the Coulomb interact by a factor of the dielectric (81). We can just decrease the  $q^2 \rightarrow q^2/81$ \*)

$$\text{In[155]} := \frac{A\text{NaCl}}{\rho} \times \frac{q^2}{81 \times z\lambda}$$

Out[155]:= 0.000147481

In[156]:=

Plot [ $\{x^2 \times \text{Exp}[-x], .000147\}$ , {x, 10, 20},  
PlotStyle -> {Red, Green}, GridLines -> Automatic, AxesLabel -> {Ro / Rho}]



Problem #2  
with water

3

In[157]:= (\*Looks like value for the water case is now are 14.2 \*)  
 ion separation water (in cm)  
 14.2 x rho

Out[157]:= cm in ion separation water

Out[158]:=  $4.5582 \times 10^{-8}$  cm

In[161]:= (\*Now lets calculate the energy per atom in water in eV\*)

$$\text{Energywater} = z\lambda \times \exp[-14.2] - \frac{A_{\text{NaCl}} \times q^2}{81 \times 14.2 \times \rho} \times 6.2 \times 10^{11}$$

Out[161]:= -0.0676128 eV

(\*Room temperature is a thermal energy of 0.025 eV so  
 there is only a 4x difference making dissolution much easier\*)

$$(\text{Room Temp} = 300\text{K}) k_B = \frac{1}{40} \text{ eV}$$

i.e. water dissolves salt bonds easily  
 at room temp.

$$i) \langle x \rangle_\beta = \frac{\int dx x e^{-\beta V(x)}}{\int dx e^{-\beta V(x)}}$$

$$\text{let } e^{-\beta V(x)} = e^{-\frac{\beta k}{2} (x-x_0)^2} \left[ 1 + \frac{\beta k^3}{6} (x-x_0)^3 + \dots \right]$$

You can do this because you are assuming the anharmonic ( $x^3$ ) term is a small correction to the parabolic potential

We can use a Taylor expansion

$$V(x-x_0) \approx V(x_0) + \left. \frac{dV}{dx} \right|_{x=x_0} \Delta x + \frac{1}{2!} \left. \frac{d^2 V}{dx^2} \right|_{x=x_0} \frac{\Delta x^2}{2!} + \frac{1}{3!} \left. \frac{d^3 V}{dx^3} \right|_{x=x_0} \frac{\Delta x^3}{3!} + \dots$$

let  $V(x_0)=0$  it's just the zero of energy which can be arbitrarily set

If you are at  $x=x_0$  then by definition  $\left. \frac{dV}{dx} \right|_{x=x_0} = 0$  because there is no force at equl.

(5)

$$\frac{d^2V}{dx^2} = k \quad (\text{the spring constant})$$

$$\text{so } \left. \frac{d^2V}{dx^2} \right|_{x=x_0} \frac{(\Delta x)^2}{2!} = \frac{k(x-x_0)^2}{2}$$

$$\text{and } \left. \frac{d^3V}{dx^3} \right|_{x=x_0} = k_3 \rightarrow \left. \frac{d^3V}{dx^3} \right|_{x=x_0} \frac{\Delta x^3}{3!} = \frac{k(x-x_0)^3}{6}$$

assume this latter term is small so that

$$\begin{aligned} e^{\beta V(x)} &= e^{-\beta k \frac{(x-x_0)^2}{2}} e^{\beta k_3 \frac{(x-x_0)^3}{6}} \\ &\approx e^{-\beta k \frac{(x-x_0)^2}{2}} \left( 1 + \beta k_3 \frac{(x-x_0)^3}{6} \right) \end{aligned}$$

using  $e^x = 1+x$  for small  $x$

So how can we use integration limits that go from  $-\infty$  to  $\infty$ , will we also have  $e^{-\beta k \frac{(x-x_0)^2}{2}}$

which will go to zero anyway as  $x \rightarrow \pm\infty$  so the integral converges.

↙ In actually calculating the deviation from the equil. position ⑥

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} dx e^{-\frac{\beta k (x-x_0)^2}{2}} \left[ 1 + \frac{\beta k^3}{6} (x-x_0)^3 \right] (x-x_0)}{\int_{-\infty}^{\infty} dx e^{-\frac{\beta k (x-x_0)^2}{2}} \left[ 1 + \frac{\beta k^3}{6} (x-x_0)^3 \right]}$$

FOR THE NUMERATOR

for integrals of the form  $\int_{-\infty}^{\infty} x e^{-ax^2} dx$  the integral is odd  
therefore the  $\int$  is zero.

We need to integrate  $\int_{-\infty}^{\infty} dx e^{-\frac{\beta k (x-x_0)^2}{2}} \frac{\beta k^3}{6} (x-x_0)^4$

From Wolfram Alpha

$$\int_{-\infty}^{\infty} dx e^{-Ax^2} Bx^4 = \frac{3\sqrt{\pi} B}{4 A^{5/2}}$$

therefore  $= \frac{3\sqrt{\pi}}{4} \frac{\beta k^3}{6} \left[ \frac{2}{\beta k} \right]^{5/2}$

For the denominator

(4)

only  $\int_{-\infty}^{\infty} dx e^{-\beta k \frac{(x-x_0)^2}{2}}$  is nonzero

From Wolfram Alpha  $\int_{-\infty}^{\infty} e^{-Ax^2} dx = \frac{\sqrt{\pi}}{\sqrt{A}}$

$$\rightarrow = \sqrt{\pi} \left[ \frac{2}{\beta k} \right]^{\frac{1}{2}}$$

$$\text{so } \langle x \rangle = \frac{\frac{3}{4} \sqrt{\pi} \frac{\beta k_3}{6} \left[ \frac{2}{\beta k} \right]^{\frac{3}{2}}}{\sqrt{\pi} \left[ \frac{2}{\beta k} \right]^{\frac{1}{2}}} = \frac{3}{24} \frac{k_3}{\beta k^2} \frac{4}{1}$$

$$= \frac{1}{2} \frac{k_3 k_B T}{k^2} \quad \frac{\partial \langle x \rangle}{\partial T} = \frac{1}{2} \frac{k_3 k_B}{k^2}$$

$$\text{so } \alpha = \frac{1}{L} \frac{dL}{dT} = \frac{1}{(x_0 + \Delta x)} \frac{1}{2} \frac{k_3 k_B}{k^2}$$

$$= \frac{1}{x_0} \frac{1}{2} \frac{k_3 k_B}{k^2}$$

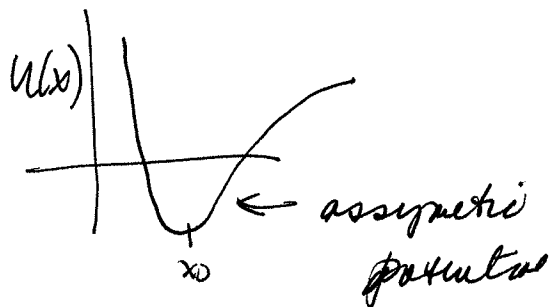
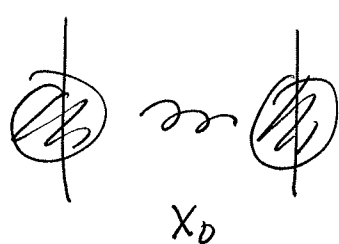
This is valid for temperatures such that

$$\beta k_3 \frac{(x-x_0)^3}{6} \ll 1 \quad \text{or} \quad \frac{k_3 (x-x_0)^3}{6} \ll kT$$

Last part

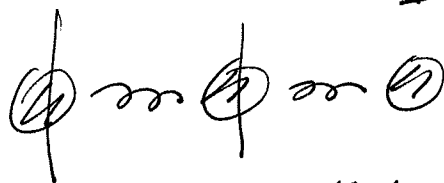
(8)

Why is this invalid for a multiatom chain?



For just 2 atoms as they move apart because of the anharmonic term  $\sim x^3$  there is not a problem but in a chain.

The center atom experiences the potential due to another neighbor.



Which makes the potential symmetric again.

To be perfectly frank, I'm not too happy with my explanation and wonder if Simon is wrong about it not working.

Wouldn't the whole chain expand?



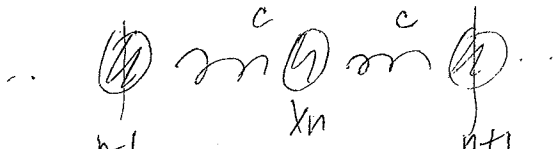
9.2

(9)

(A) Normal mode is a collective oscillation where all particles move at the same frequency

A phonon is a discrete quantum of vibration

Phonons obey Bose statistics because you can occupy one vibrational mode with multiple phonons.

(B)   $F(x_n) = C(x_{n+1} - x_n) + C(x_{n-1} - x_n)$   
 $m \ddot{x}_n = C(x_{n+1} + x_{n-1} - 2x_n)$

Try Solution =  $Ae^{i\omega t - ika}$

$$-m\omega^2 Ae^{i(\omega t - kna)} = CAe^{i(\omega t - kna)} \left[ e^{-ika} + e^{ika} - 2 \right]$$

$$m\omega^2 = 2C[1 - 2\cos ka] = 4C \sin^2 \frac{ka}{2}$$

$$\boxed{\omega = 2\sqrt{\frac{C}{m}} \sin \frac{ka}{2}}$$

(C)  $Ae^{i\omega t - ika} \quad (k \Rightarrow k + \frac{2\pi}{a}) \Rightarrow Ae^{i\omega t - i(k + \frac{2\pi}{a})a} = Ae^{i\omega t - ika} e^{-i2\pi} = Ae^{i\omega t - ika}$

$$\left( \omega \Rightarrow 2\sqrt{\frac{C}{m}} \sin \left[ \frac{k + \frac{2\pi}{a}}{a} \right] a = 2\sqrt{\frac{C}{m}} \sin ka = \omega(k) \right)$$

$$Ae^{i\omega t - ika}$$

Periodic boundary condition  $\rightarrow k_{\max} = \frac{2\pi}{L}$

where  $L = Na$

$$k_{\max} = \frac{\pi/a}{2\pi/L} = \frac{L}{2a} = \frac{N}{2} + \text{the } -k \text{ modes}$$

So total  $N$  modes

⑦ Phase Velocity =  $\frac{\omega}{k} = \frac{2\sqrt{\frac{c}{m}} \sin \frac{ka}{2}}{k}$  (see plot) page 12

Group Velocity =  $\frac{\partial \omega}{\partial k} = 2\sqrt{\frac{c}{m}} \cos \frac{ka}{2} \frac{a}{2}$   
 $= \sqrt{\frac{c}{m}} a \cos \frac{ka}{2}$  (see plot) page 12

Sound velocity is the  $k \rightarrow 0$  limit for phase velocity

So it around  $\sqrt{\frac{c}{m}} a$

The compressibility is  $\beta$  with  $\frac{1}{\beta} = B$  (bulk modulus) see page 72

$\beta = \frac{1}{Ca}$  see equation 8.1

and  $\rho$  in 1D is  $\frac{m}{a}$

So  $V_s = \sqrt{\frac{c}{m}} a = \sqrt{\frac{Ca^2}{m}} = \sqrt{\frac{1}{\beta \rho}} !$

$$g(\omega) = \frac{\# \text{ modes}}{d\omega} = \frac{\# \text{ modes}}{dk} \frac{dk}{d\omega}$$

$$\frac{\# \text{ modes}}{dk} = \frac{\overset{k_{\max} - k}{2\pi}}{k_{\min}} = \frac{2\pi}{2\pi/L} = \frac{2\pi L}{2\pi} = \frac{L}{\pi}$$

from Part ①

$$\frac{\partial \omega}{\partial k} = \sqrt{\frac{c}{m}} a \cos \frac{ka}{2}$$

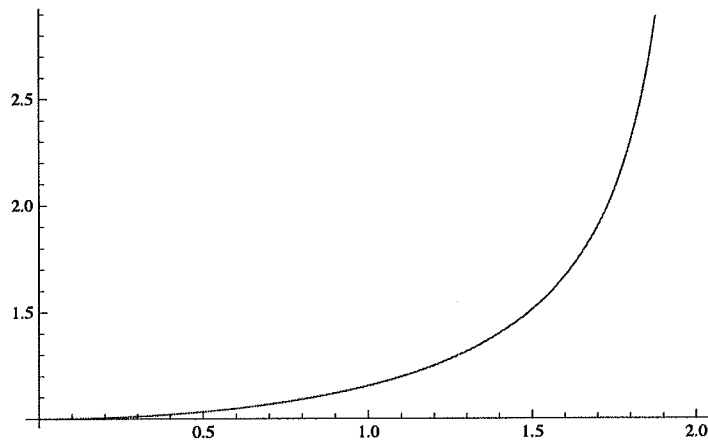
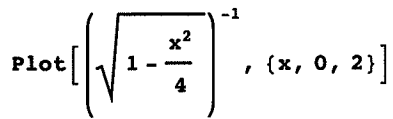
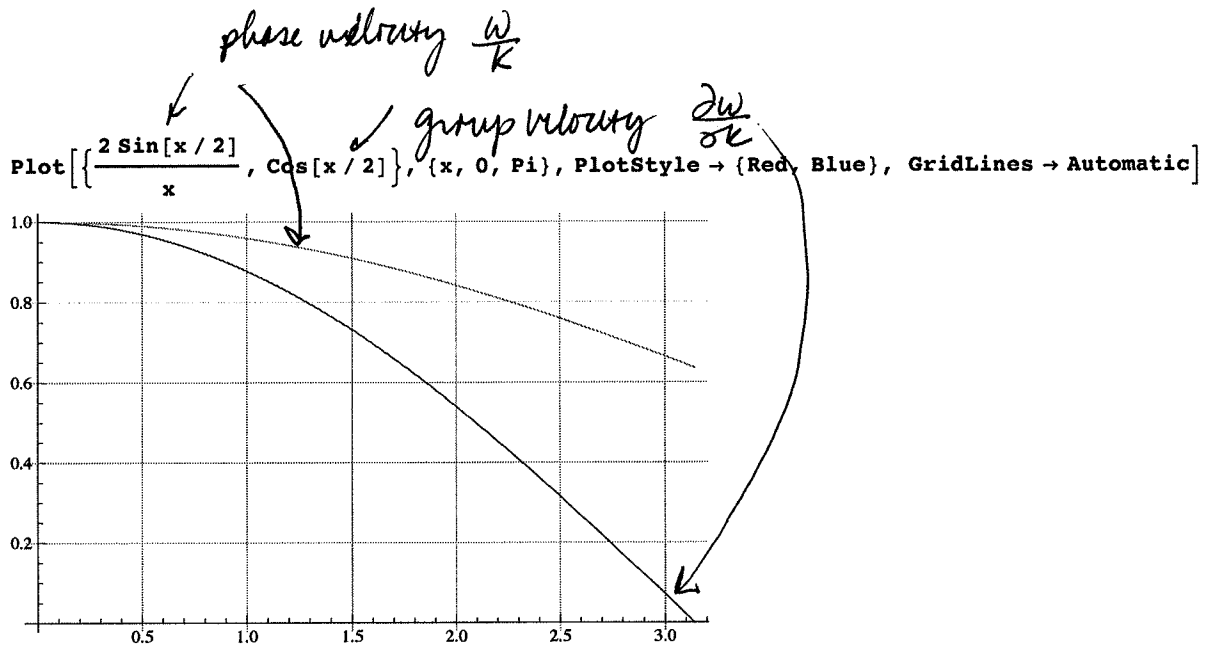
$$\therefore g(\omega) = \frac{L}{\pi} \sqrt{\frac{m}{ca^2}} \frac{1}{\cos ka/2}$$

Recall  $\omega = 2\sqrt{\frac{c}{m}} \sin \frac{ka}{2} \rightarrow \omega^2 = \frac{4c}{m} \sin^2 \frac{ka}{2}$

$$\omega^2 = \frac{4c}{m} [1 - \cos^2 \frac{ka}{2}] \Rightarrow 1 - \frac{m\omega^2}{4c} = \cos^2 \frac{ka}{2}$$

$$g(\omega) = \frac{L}{\pi} \sqrt{\frac{m}{ca^2}} \frac{1}{\sqrt{1 - \frac{m\omega^2}{4c}}}$$

See plot.



$$\frac{g(\omega)}{\frac{L}{\pi} \sqrt{\frac{m}{Ca^2}}}$$

$\omega$  in units of  $2\sqrt{\frac{C}{m}}$

① Heat capacity

$$C = \frac{\partial E}{\partial T}$$

(13)

$$E = \int_0^{w_{\max}} g(w) \hbar w (n + \frac{1}{2}) dw$$

$$w_{\max} = 2\sqrt{\frac{c}{m}}$$

$$\text{where } n = \frac{1}{e^{\beta \hbar w} - 1}$$

$$\frac{\partial E}{\partial T} = \frac{\partial E}{\partial \beta} \frac{\partial \beta}{\partial T}$$

$$\frac{\partial E}{\partial \beta} = \int_0^{\infty} g(w) \hbar w dw \frac{(-1) e^{\beta \hbar w} \hbar w}{(e^{\beta \hbar w} - 1)^2}$$

$$\frac{\partial \beta}{\partial T} = -\frac{1}{k_B T^2}$$

$$\therefore C = \int_0^{\infty} \frac{g(w) (\hbar w)^2 dw}{k_B T^2 (e^{\beta \hbar w} - 1)^2} e^{\beta \hbar w}$$

B'

② for  $T \rightarrow \infty \beta \rightarrow 0$   
 $x = \beta \hbar w \quad \frac{e^x}{(e^x - 1)^2} \xrightarrow{x \rightarrow 0} \frac{1}{x^2} - \frac{1}{12} + \frac{x^2}{240} + \dots$

$$T \rightarrow \infty$$

$$C \approx \int_0^{w_{\max}} \frac{g(w) (\hbar w)^2 dw}{k_B T^2} \left[ \frac{1}{(\beta \hbar w)^2} - \frac{1}{12} \right]$$

(14)

$$C = \int_0^{w_{\max}} g(w) dw k_B - \int_0^{w_{\max}} \frac{g(w) (\hbar w)^2}{12 k_B T^2}$$

$$= \int_0^{w_{\max}} \frac{L}{\pi} \sqrt{\frac{m}{c a^2}} \frac{dw}{\sqrt{1 - \frac{m w^2}{4c}}} k_B$$

$$- \int_0^{w_{\max}} \frac{L}{\pi} \sqrt{\frac{m}{c a^2}} \frac{(\hbar w)^2}{12 k_B T^2} \frac{dw}{\sqrt{1 - \frac{m w^2}{4c}}}$$

$$w_{\max} = 2 \sqrt{\frac{c}{m}}$$

From Wolfram Alpha

$$\int_0^{\frac{1}{\sqrt{B}}} \frac{dx}{\sqrt{1 - Bx^2}} = \frac{\pi}{2\sqrt{B}}$$

$$\text{and } \int_0^{\frac{1}{\sqrt{B}}} \frac{A x^2}{\sqrt{1 - Bx^2}} = \frac{\pi A}{4B^{3/2}}$$

$$\text{So } C = \frac{L}{\pi} \sqrt{\frac{m}{c a^2}} k_B \frac{\pi}{2} 2 \sqrt{\frac{c}{m}}$$

$$- \frac{L}{\pi} \sqrt{\frac{m}{c a^2}} \frac{\hbar^2}{12 k_B T^2} \frac{\pi}{4} \frac{4c}{m} 2 \sqrt{\frac{c}{m}}$$

$$= \frac{L}{a} k_B - \frac{L}{a} \frac{\hbar^2}{12 k_B T^2} \frac{2c}{m}$$

$$= N k_B - N k_B \left[ \frac{\hbar^2}{6 (k_B T)^2} \frac{c}{m} \right] \checkmark$$