

Chem 576 HW3

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Problem 5.3

A Debye temperature of $\theta_D = 1890\text{ K}$ is found to give an excellent fit to the molar specific heat of diamond (Fig. 5.5). Diamond is pure carbon with an atomic weight of 12 (so that 12 gm = 1 mole), and the measured mass density of diamond is approximately 3.25 gm/cm^3 .

- (a) Express c_{av} in terms of θ_D in the Debye model, and deduce the speed of sound in diamond;
 - (b) Compare the value of c_{av} found in part (a) with the measured speed of sound in diamond.
-

(a)

Derivation using the Sympy package in Python,

```
1 from sympy import *
2 from sympy import Rational as frac
3 from IPython.display import display, HTML
4 init_printing(use_unicode=True)
5
6 theta, h, nu, kb, N, V, c = symbols('theta_D h nu_m k_B N V c_av')
7 Eq(theta, h*nu/kb)
8 Eq(nu, (3/(4*pi)*N/V)**frac(1,3)*c)
9 Eq(theta, h*nu/kb).subs(nu, (3/(4*pi)*N/V)**frac(1,3)*c)
10 c_expr = solve(Eq(theta, h*nu/kb).subs(nu, (3/(4*pi)*N/V)**frac(1,3)*c), c)[0]
11 Eq(c, c_expr)
```

The output:

$$\nu_m = \frac{\sqrt[3]{6}c_{av}\sqrt[3]{\frac{N}{V}}}{2\sqrt[3]{\pi}}$$
$$\theta_D = \frac{\sqrt[3]{6}c_{av}h\sqrt[3]{\frac{N}{V}}}{2\sqrt[3]{\pi}k_B}$$
$$c_{av} = \frac{6^{\frac{2}{3}}\sqrt[3]{\pi}k_B\theta_D}{3h\sqrt[3]{\frac{N}{V}}}$$

(b)

Plug in the values

```
1 theta = 1890 ## K
2 N_A = 6.022e23 ## mol^-1
3 n = 1 ## assume 1 mol (the number does not matter here)
4 N = n*N_A ## number of carbon atoms in 1 mol of diamond
5 mw = 12 # g/mol molecular weight
6 rho = 3.25e3 # kg/m^3
7 V = n*mw/1000/rho # m^3
8 kb = 1.3806e-23 # J/K
9 h = 6.62607e-34 # J*s
10
11 c_value = solve(Eq(theta, h*nu/kb).subs(nu, (3/(4*pi)*N/V)**frac(1,3)*c),c)[0]
12 print("c_av = {:.4e}".format(c_value))
```

Result for the printout:

$$c_{av} = 1.1619 \times 10^4$$

Problem 5.6

(a) Do the integral numerically, and make a good plot of the molar heat capacity in the Debye model in Eq. (5.33). Plot the result as a function of T/θ_D

(b) Plot the molar heat capacity in the Einstein model in Eq. (2.53) as a function of T/θ_E , where $\theta_E \equiv h\nu_0/k_B$ (here ν_0 denotes the single oscillator frequency). Compare with the result in (a).

(a)

For Debye model,

$$C_V = 9Nk_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{u^4 e^u du}{(e^u - 1)^2}$$

Where

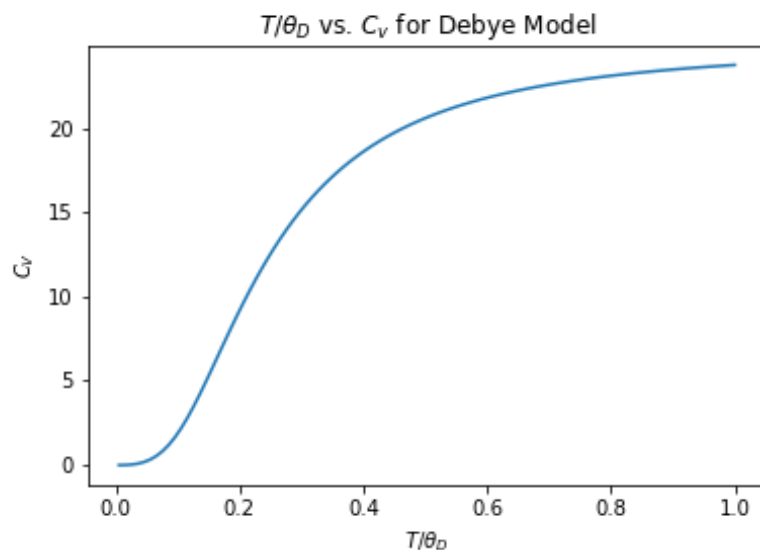
$$u = \frac{h\nu}{k_B T}$$

and

$$\theta_D = \frac{h\nu_m}{k_B}$$

Numerical integration and plotting by Python,

```
1 from scipy.integrate import quad
2 import numpy as np
3 from matplotlib import pyplot as plt
4
5 Nkb = 8.3145 # J mol^-1 K ideal gas constant
6 theta_D = 1000
7
8 def integrand(u):
9     return u**4*np.exp(u)/(np.exp(u)-1)**2
10 def Cv_Debye(T):
11     return 9*Nkb*(T/theta_D)**3*quad(integrand, 0, theta_D/T)[0]
12
13 T = np.linspace(5, 1000, 100)
14 x = T/theta_D
15 y = np.array([Cv_Debye(temp) for temp in T])
16
17 plt.plot(x,y)
```



(b)

For Einstein model,

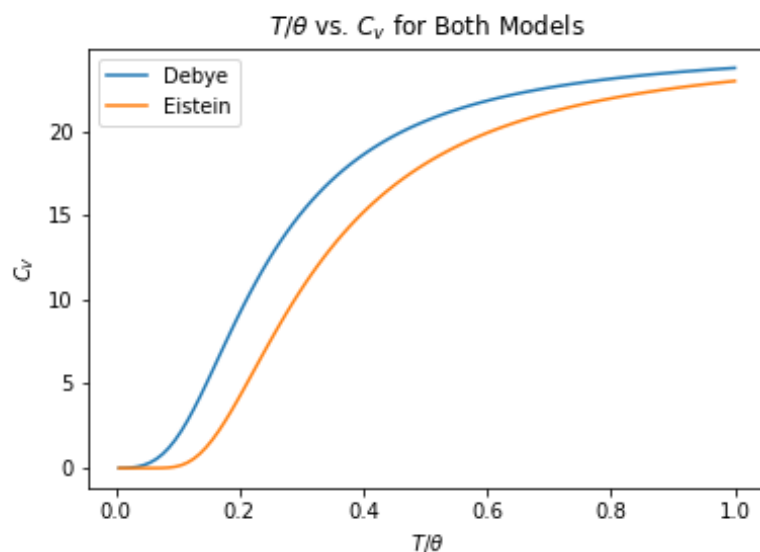
$$C_V = 3Nk_B \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}; \text{ where } \theta_E = \frac{h\nu}{k_B}$$

Plotting two the models together

```

1 def Cv_Einstein(T):
2     return 3*Nkb*(theta_E/T)**2*np.exp(theta_E/T)/(np.exp(theta_E/T)-1)**2
3
4 T = np.linspace(5, 1000, 100)
5 x = T/theta_D
6 y = np.array([Cv_Debye(temp) for temp in T])
7 plt.plot(x,y, label="Debye")
8
9 x = T/theta_E
10 y = np.array([Cv_Einstein(temp) for temp in T])
11 plt.plot(x,y, label="Einstein")

```



Problem 5.9

Consider a mass m attached to one end of a massless spring, with the other end fixed, and take $x = 0$ to mark the unextended length of the spring. Apply a constant force F to the mass which stretches the spring. The hamiltonian for this one-dimensional system is $H = p^2/2m + \kappa x^2/2 - Fx$

(a) Complete the square, and show the classical partition function is $(p.f.)_F = e^{F^2/2\kappa k_B T} (p.f.)_{osc}$ where $(p.f.)_{osc}$ is the result for a free oscillator with $F = 0$;

(b) Show the Helmholtz free energy of an assembly of N such springs is $A(N, T, V) = A(N, T, V)_{osc} - NF^2/(2\kappa)$;

(c) Show the change in the internal energy from the assembly at $F = 0$ is $\Delta E = -NF^2/2\kappa$; Derive this result by balancing forces in a system. What is the corresponding entropy change ΔS ?

(d) Increase F slightly so that $F \rightarrow F + dF$. Show that the work done by a system is $dw = FdF/\kappa$. Explain the sign. Hence show that the work done by N systems when the force is increased from 0 to F is $\Delta W = NF^2/2\kappa$;

(e) Show that the isothermal heat flow when the force is increased reversibly from 0 to F , is given by $\Delta Q = T\Delta S$, where ΔS is the entropy change calculated in (c).

(a)

For the Hamiltonian

$$H = \frac{p^2}{2m} + \frac{\kappa x^2}{2} - Fx$$

The partition function $(p.f.)_F$

$$\begin{aligned} (p.f.)_F &= \frac{1}{h} \int_{-\infty}^{\infty} e^{-p^2/2mk_B T} dp \underbrace{\int_{-\infty}^{\infty} e^{-\kappa x^2/2k_B T} dx \int_{-\infty}^{\infty} e^{Fx/k_B T} dx}_{\textcircled{1}} \\ \textcircled{1} &= \int_{-\infty}^{\infty} e^{(-\kappa x^2 + 2Fx)/2k_B T} dx \\ &= \int_{-\infty}^{\infty} e^{-[\kappa x^2 - 2Fx + F^2/\kappa - F^2/\kappa]/2k_B T} dx \\ &= \int_{-\infty}^{\infty} e^{-\kappa[x^2 - 2Fx/\kappa + (F/\kappa)^2]/2k_B T} e^{F^2/2\kappa k_B T} dx \\ &= e^{F^2/2\kappa k_B T} \int_{-\infty}^{\infty} e^{-\kappa(x - F/\kappa)^2/2k_B T} dx \\ (p.f.)_F &= \frac{1}{h} e^{F^2/2\kappa k_B T} \int_{-\infty}^{\infty} e^{-p^2/2mk_B T} dp \int_{-\infty}^{\infty} e^{-\kappa(x - F/\kappa)^2/2k_B T} dx \end{aligned}$$

For a free oscillator with $F = 0$,

$$\begin{aligned} H &= \frac{p^2}{2m} + \frac{\kappa x^2}{2} \\ (p.f.)_{osc} &= \frac{1}{h} \int_{-\infty}^{\infty} e^{-p^2/2mk_B T} dp \int_{-\infty}^{\infty} e^{-\kappa x^2/2k_B T} dx \end{aligned}$$

If we set $x_F = x - F/\kappa$, then $dx_F = dx$, and plug in to the partition function,

$$(p.f.)_F = e^{F^2/2\kappa k_B T} \cdot \underbrace{\frac{1}{h} \int_{-\infty}^{\infty} e^{-p^2/2mk_B T} dp \int_{-\infty}^{\infty} e^{-\kappa x_F^2/2k_B T} dx_F}_{(p.f.)_{osc}}$$

Therefore,

$$(p.f.)_F = e^{F^2/2\kappa k_B T} (p.f.)_{osc}$$

(b)

$$\begin{aligned} A(N, T, V)_F &= -Nk_B T \ln (p.f.)_F \\ &= -Nk_B T \ln \left(e^{F^2/2\kappa k_B T} (p.f.)_{osc} \right) \\ &= -Nk_B T \left(\ln (p.f.)_{osc} + \frac{F^2}{2\kappa k_B T} \right) \\ &= -Nk_B T \ln (p.f.)_{osc} - \frac{NF^2}{2\kappa} \\ &= A(N, T, V)_{osc} - \frac{NF^2}{2\kappa} \end{aligned}$$

(c)

The internal energy E can be calculated from A by

$$E = -T^2 \frac{\partial}{\partial T} \left(\frac{A}{T} \right)_V$$

Denote E_F as the internal energy under constant force F and E_{osc} as the internal energy for free oscillator, in which $F = 0$.

$$\begin{aligned} E_F &= -T^2 \frac{\partial}{\partial T} \left(\frac{A_F}{T} \right)_V \\ &= -T^2 \frac{\partial}{\partial T} \left(\frac{A_{osc} - \frac{NF^2}{2\kappa}}{T} \right)_V \\ &= -T^2 \left[\frac{\partial}{\partial T} \left(\frac{A_{osc}}{T} \right)_V - \frac{\partial}{\partial T} \left(\frac{NF^2}{2\kappa T} \right) \right] \\ &= E_{osc} - T^2 \cdot \frac{NF^2}{2\kappa T^2} \\ &= E_{osc} - \frac{NF^2}{2\kappa} \end{aligned}$$

Therefore,

$$\Delta E = E_F - E_{osc} = -\frac{NF^2}{2\kappa}$$

The derivation by balancing forces is shown in section (d).

For entropy,

$$S = - \left(\frac{\partial A}{\partial T} \right)_V$$

and

$$S_F = - \frac{\partial}{\partial T} \left(A_{osc} - \frac{NF^2}{2\kappa} \right)_V = - \left(\frac{\partial A_{osc}}{\partial T} \right)_V = S_{osc}$$

Therefore,

$$\Delta S = 0$$

(d)

For a constant force F , it can be balanced by the spring where

$$F = \kappa x$$

and energy,

$$E_F = F \Delta x = \int \kappa x \, dx = \frac{1}{2} \kappa x^2 = \frac{F^2}{2\kappa}$$

When F is changed by dF ,

$$dw = dE_F = d\left(\frac{F^2}{2\kappa}\right) = \frac{1}{2\kappa} dF^2 = \frac{F dF}{\kappa}$$

Therefore, for N such systems, the work done from 0 to F is

$$\Delta W = N \int_0^F dw = N \int_0^F \frac{F dF}{\kappa} = \frac{NF^2}{2\kappa}$$

(e)

Since $\Delta E = -W$, there is no heat flow in the system.

$Q = T\Delta S = 0$, and $T \neq 0$, thus $\Delta S = 0$.

Problem 5.10

(a) Start from the partition function ($p.f.$) in Prob. 5.9(a). Show the mean displacement per system is $\langle x \rangle = k_B T (\partial/\partial F) \ln(p.f.) = F/\kappa$;

(b) Similarly, show $\langle \varepsilon \rangle = k_B T^2 (\partial/\partial T) \ln(p.f.) = \langle \varepsilon \rangle_{osc} - F^2/2\kappa$;

(c) Write the Helmholtz free energy per system as $a(T, V, N, F) = -k_B T \ln(p.f.)$ and work per system as dw . Show

$$\left(\frac{a}{F}\right)_{T,V,N} dF = -\left(\frac{F}{\kappa}\right) dF = -\langle x \rangle dF = -dw$$

(a)

$$\begin{aligned} \langle x \rangle &= k_B T \frac{\partial}{\partial F} \ln(p.f.)_F \\ &= k_B T \frac{\partial}{\partial F} \ln[e^{F^2/2\kappa k_B T} (p.f.)_{osc}] \end{aligned}$$

Since $(p.f.)_{osc}$ is free of variable F ,

$$\begin{aligned} \langle x \rangle &= k_B T \frac{\partial}{\partial F} \ln[e^{F^2/2\kappa k_B T}] \\ &= \frac{F}{\kappa} \end{aligned}$$

(b)

$$\begin{aligned}
\langle \varepsilon \rangle &= k_B T^2 \frac{\partial}{\partial T} \ln (p.f.)_F \\
&= k_B T^2 \frac{\partial}{\partial T} \ln [e^{F^2/2\kappa k_B T} (p.f.)_{osc}] \\
&= -\frac{F^2}{2\kappa} + k_B T^2 \frac{\partial}{\partial T} \ln [(p.f.)_{osc}] \\
&= \langle \varepsilon \rangle_{osc} - \frac{F^2}{2\kappa}
\end{aligned}$$

(c)

For Helmholtz energy per system, a ,

$$\begin{aligned}
a(T, V, N, F) &= \frac{A(T, V, N, F)}{N} \\
&= -k_B T \ln (p.f.)_F \\
&= -k_B T \ln (p.f.)_{osc} - \frac{F^2}{2\kappa} \\
&= a(N, T, V)_{osc} - \frac{F^2}{2\kappa}
\end{aligned}$$

From problem 5.9,

$$dw = \frac{F dF}{\kappa}$$

Therefore,

$$\begin{aligned}
\left(\frac{\partial a(T, V, N, F)}{\partial F} \right)_{A, T, V} dF &= \left[\left(\frac{\partial a(T, V, N)_{osc}}{\partial F} \right)_{A, T, V} - \frac{d}{dF} \frac{F^2}{2\kappa} \right] dF \\
&= 0 - \frac{F}{\kappa} dF \\
&= -\langle x \rangle dF \\
&= -dw
\end{aligned}$$

and for N such systems,

$$\left(\frac{\partial A(T, V, N, F)}{\partial F} \right)_{A, T, V} dF = -N \langle x \rangle dF$$

Define induced dipole moment \mathcal{D} as

$$\mathcal{D} = N \langle x \rangle$$

The analog of the thermodynamic relation is

$$dA = -SdT - PdV + \mu dN - \mathcal{D}dF$$

Problem 5.11

The Lennard-Jones (or “6-12”) interatomic two-body potential is a useful empirical potential of the form $U(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$ where (ϵ, σ) are positive constants (see Fig. 5.19). Calculate the second virial coefficient $B(T)$ at high temperature with this potential.

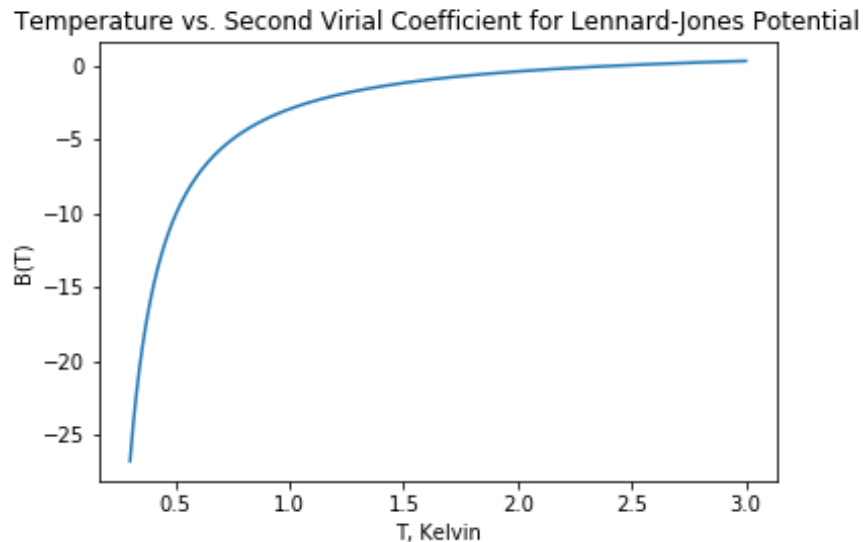
The second virial coefficient $B(T)$ is

$$B(T) = 2\pi \int_0^\infty \left[1 - e^{-U(r)/k_B T}\right] r^2 dr$$

Using numerical integration with Python.

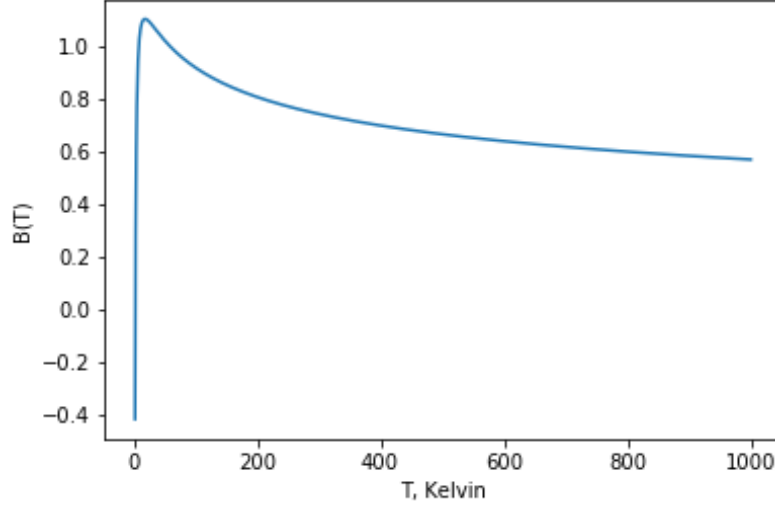
```
1 from scipy.integrate import quad
2 import numpy as np
3 from matplotlib import pyplot as plt
4
5 kb = 1.3806e-23 # J/K
6 sigma = 1
7 epsilon = 1e-23 # J (the value needs to be comparable to kb)
8
9 def integrand(r, T):
10     U = 4*epsilon*((sigma/r)**12-(sigma/r)**6)
11     return (1-np.exp(-U/(kb*T)))*r**2
12
13 def B(T):
14     return 2*pi*quad(integrand, 0, np.inf, args = T)[0]
15
16 T = np.linspace(0.3,3,1000)
17 BT = np.array([B(x) for x in T])
18
19 plt.plot(T, BT)
```

For temperature range $0.3 < T < 3K$,



For temperature range $2 < T < 1000K$,

Temperature vs. Second Virial Coefficient for Lennard-Jones Potential



The coefficient stabilizes at around 0.57 for high temperatures.

Problem 5.12

The model interatomic two-body potential in Eq. (5.89) has a hard core at a distance σ in the relative coordinate r , surrounded by $a - c/r^6$ Van der Waal's attraction.

- (a) Identify Van de Waal's parameters (a, b) in terms of the parameters (σ, c) by matching the second virial coefficients in Eqs. (5.92) and (5.93);
- (b) Discuss the role of the parameters (a, b) in Van de Waal's equation of state in Eq. (5.73) in terms of the properties of the potential.
-

(a)

Since

$$\begin{aligned} B(T) &= \frac{2\pi\sigma^3}{3} \left[1 - \frac{c}{\sigma^6 k_B T} \right] \\ &= \frac{2\pi\sigma^3}{3} - \frac{2\pi c}{3\sigma^3 k_B T} \end{aligned}$$

and

$$B(T)_{\text{VW}} = b - \frac{a}{k_B T}$$

We can find

$$\begin{aligned} a &= \frac{2\pi\sigma^3}{3} \\ b &= \frac{2\pi c}{3\sigma^3} \end{aligned}$$

(b)

The Van der Waals equation is

$$P(V) = \frac{k_B T}{V - b} - \frac{a}{V^2}$$

The Van der Waals equation of state shows that

$$a \uparrow \implies P(V) \downarrow$$

and

$$b \uparrow \implies P(V) \uparrow$$

Therefore, a reduces the pressure and contributes to the attractive force, whereas b increases pressure and contributes to the the repulsive force.

Problem 5.16

Show the third virial coefficient with the Van der Waal's equation of state is

$$C(T) = b^2$$

According to the equation for virial expansion,

$$\frac{P}{k_B T} = \frac{1}{V} + \frac{B(T)}{V^2} + \frac{C(T)}{V^3} + \dots$$

For Van der Waals equation,

$$\begin{aligned} P(V) &= \frac{k_B T}{V - b} - \frac{a}{V^2} \\ \frac{P(V)}{k_B T} &= \frac{1}{V - b} - \frac{a}{k_B T V^2} \end{aligned}$$

Using Taylor series expansion,

$$\begin{aligned} \frac{1}{V - b} &= \frac{1}{V} + \frac{b}{V^2} + \frac{b^2}{V^3} + \dots \\ \frac{P(V)}{k_B T} &= \frac{1}{V} + \left(b - \frac{a}{k_B T} \right) \frac{1}{V^2} + \frac{b^2}{V^3} + \dots \end{aligned}$$

Therefore,

$$C(T) = b^2$$