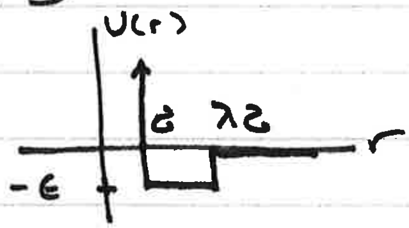
Solutions for Seminar 13

Problem 1

G & T 8.30

$B_2(T)$ for a toy pot'l

$$u(r) = \begin{cases} \infty & r < \sigma \\ -\epsilon & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$$



To Show: $f(r) = \begin{cases} -1 & r < \sigma \\ g \equiv e^{\beta\epsilon} - 1 & \sigma < r < \lambda\sigma \\ 0 & r > \lambda\sigma \end{cases}$

sol'n → Use definition $f(r) = e^{-\beta U(r)} - 1$.

Then it is trivial that the form of $f(r)$ is as given ◡̈

To Show: $B_2(T) = \frac{2\pi\sigma^3}{3}\left[1 - (\lambda^3 - 1) g\right]$

sol'n → Use $B_2(T) = -\frac{1}{2}\int^{\infty} f(r)\, d^3r$

$$\Rightarrow B_2 = -2\pi \int_0^{\sigma} (-1) r^2 dr + \ldots$$

$$+ -2\pi \int_{\sigma}^{\lambda\sigma} g r^2 dr + \phi \; ,$$

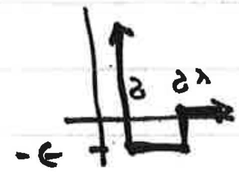
$$\therefore B_2 = \frac{2\pi\sigma^3}{3} - \frac{2\pi}{3} g\left[(\lambda\sigma)^3 - \sigma^3\right]$$

or $$B_2(T) = \frac{2\pi\sigma^3}{3}\left[1 - (\lambda^3 - 1) g(T)\right]$$

where $g(T) = e^{\epsilon/kT} - 1$

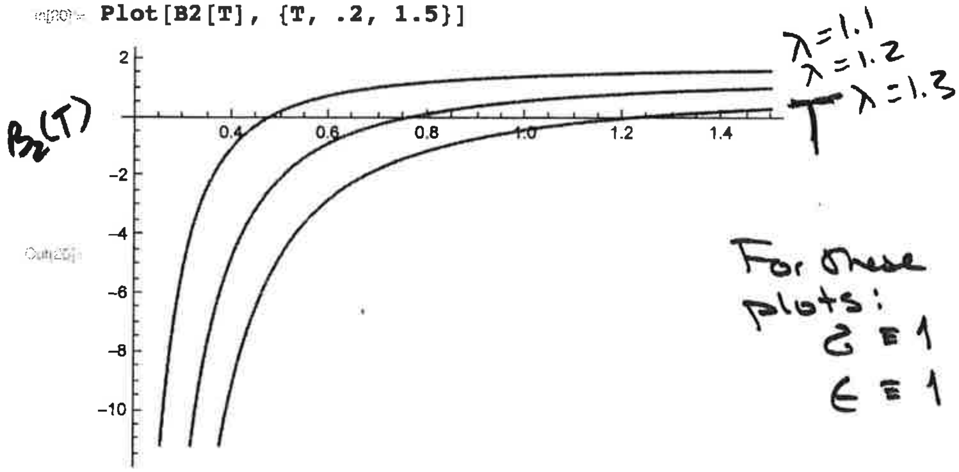
(b) Plots of $B_2(T)$

```
In[13]:= Lambda = {1.1, 1.2, 1.3}
Out[13]= {1.1, 1.2, 1.3}
In[13]:= B2[T_] := 2 * Pi / 3 * ( 1 - (Lambda^3 - 1) * Exp[1 / T - 1])
In[20]:= Plot[B2[T], {T, .2, 1.5}]
```



$$f(r) = \begin{cases} -1 & r<\sigma \\ e^{\beta\epsilon}-1 & \sigma<r<\lambda\sigma \\ 0 & r>\lambda\sigma \end{cases}$$

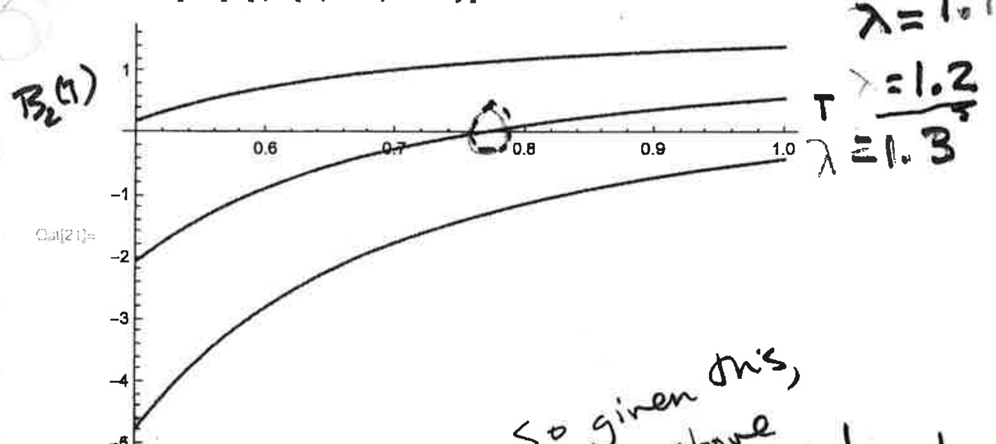
Out[20]=



For these plots:
$\sigma \equiv 1$
$\epsilon \equiv 1$

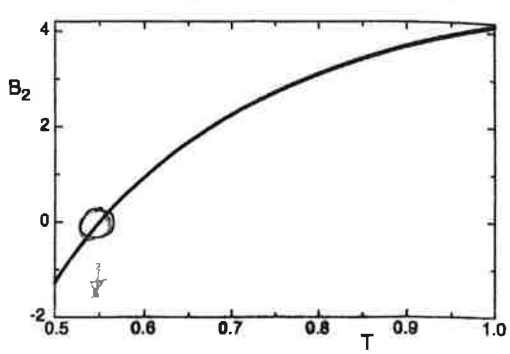
```
In[21]:= Plot[B2[T], {T, .5, 1.0}]
```

Out[21]=



So given this, curve above with $\lambda = 1.1$ is probably most similar...

$B_2(T)$ changes sign at "Boyle Temperature" of $T \simeq 0.5$



$B_2(T) = 0$ at $T \simeq 0.55$

Temperature dependence of B_2 for the Lennard-Jones potential

2-1

Problem

Finding $B_2(T)$ + Boyle temp for vdW gas: $(P + a(\frac{N}{V})^2)(V - Nb) = NkT$

from B B_2

26.3 Virial expansion

Another method of modelling real gases is to take the ideal gas equation and modify it using a power series in $1/V_m$ (where V_m is the molar volume). This leads to the following **virial expansion**:

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots \qquad (26.40)$$

In this equation, the parameters B, C, etc., are called **virial coefficients** and can be made to be temperature dependent (so that we will denote them by $B(T)$ and $C(T)$). The temperature at which the virial coefficient $B(T)$ goes to zero is called the **Boyle temperature** T_B since it is the temperature at which Boyle's law is approximately obeyed (neglecting the higher-order virial coefficients), as shown in Fig. 26.8.

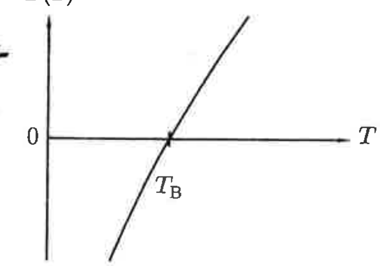


Fig. 26.8 The temperature dependence of the virial coefficient B.

Example 26.2

Express the van der Waals equation of state in terms of a virial expansion and hence find the Boyle temperature in terms of the critical temperature.

Solution:

The van der Waals equation of state can be rewritten as

$$p = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{RT}{V}\left(1 - \frac{b}{V}\right)^{-1} - \frac{a}{V^2}, \qquad (26.41)$$

and using the binomial expansion, the term in brackets can be expanded into a series, resulting in

$$\frac{pV}{RT} = 1 + \frac{1}{V}\left(b - \frac{a}{RT}\right) + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + \cdots, \qquad (26.42)$$

which is in the same form as the virial expansion in eqn 26.40 with

$$B(T) = b - \frac{a}{RT}. \qquad (26.43)$$

The Boyle temperature T_B is defined by $B(T_B) = 0$ and hence

$$T_B = \frac{a}{bR}, \qquad (26.4$$

and hence using eqn 26.19 we have that

$$T_B = \frac{27T_c}{8}. \qquad (26.4$$

3.-1

Problem 3 → G+T 6.60 High temp FD gas

Note typo in book...

6.60. If $T \gg T_F$ at fixed density, quantum effects can be neglected and the thermal properties of an ideal Fermi gas reduce to the ideal classical gas. In the following we will find the first correction to the classical pressure equation of state.

(a) Does the pressure increase or decrease when the temperature is lowered (at constant density)? That is, what is the sign of the first quantum correction to the classical pressure equation of state? The pressure is given by [see (6.109)]

$$P = \frac{(2m)^{3/2}(kT)^{5/2}}{3\pi^2\hbar^3}\int_0^\infty \frac{x^{3/2}\,dx}{e^{x-\beta\mu}+1}. \tag{6.264}$$

In the high temperature limit, $e^{\beta\mu} \ll 1$, we can make the expansion

$$\frac{1}{e^{x-\beta\mu}+1} = e^{\beta\mu-x}\frac{1}{1+e^{-x+\beta\mu}} \tag{6.265a}$$

$$\approx e^{\beta\mu-x}[1-e^{-x+\beta\mu}]. \tag{6.265b}$$

If we use (6.265b), we obtain

$$e^{\beta\mu}\int_0^\infty x^{3/2}e^{-x}(1-e^{\beta\mu}e^{-x})\,dx = \frac{3}{4}\pi^{1/2}e^{\beta\mu}\Big[1-\frac{1}{2^{5/2}}e^{\beta\mu}\Big]. \tag{6.266}$$

Use (6.266) to show that P is given by

$$P = \frac{m^{3/2}(kT)^{5/2}}{2^{1/2}\,\pi^{3/2}\hbar^3}\,e^{\beta\mu}\Big[1-\frac{1}{2^{5/2}}e^{\beta\mu}\Big]. \tag{6.267}$$

Solution. The result (6.266) follows from an integration by parts and the substitution $u = x^{1/2}$ in the integral, which leads to Gaussian integrals.

(b) Derive an expression for N similar to (6.267). Eliminate μ and show that the leading order correction to the equation of state is given by

$$PV = NkT\Big[1+\frac{\pi^{3/2}}{4}\frac{\rho\hbar^3}{(mkT)^{3/2}}\Big], \tag{6.268a}$$

$$= NkT\Big[1+\frac{1}{2^{7/2}}\rho\lambda^3\Big]. \tag{6.268b}$$

Solution. We have $E = (3/2)PV$, $E = \int \epsilon\overline{n}(\epsilon)g(\epsilon)d\epsilon$, and $N = \int \overline{n}(\epsilon)g(\epsilon)d\epsilon$. Hence, we can write

$$N = \frac{V(2m)^{3/2}(kT)^{3/2}}{2\pi^2\hbar^3}\int_0^\infty \frac{x^{1/2}\,dx}{e^{x-\beta\mu}+1}. \tag{S6.256}$$

Doing the integral in (6.266) by parts gives (3/2) times the first term in the integral with $x^{1/2}$ instead of $x^{3/2}$ and (3/4) times the second term. Thus we can write down the approximation for N from (6.267):

$$N = V\frac{m^{3/2}(kT)^{3/2}}{2^{1/2}\,\pi^{3/2}\hbar^3}\,e^{\beta\mu}\Big[1-\frac{1}{2^{3/2}}e^{\beta\mu}\Big]. \tag{S6.257}$$

3-2

If we divide (6.267) by (S6.257), we obtain

$$\frac{PV}{NkT} = \frac{1 - \frac{1}{2^{5/2}} e^{\beta\mu}}{1 - \frac{1}{2^{3/2}} e^{\beta\mu}} \approx \Big[1 - \frac{1}{2^{5/2}} e^{\beta\mu}\Big]\Big[1 + \frac{1}{2^{3/2}} e^{\beta\mu}\Big] \tag{S6.258a}$$

$$\approx 1 + \Big(\frac{1}{2^{3/2}} - \frac{1}{2^{5/2}}\Big) e^{\beta\mu} = 1 + \frac{1}{2^{5/2}} e^{\beta\mu}. \tag{S6.258b}$$

If we next use (S6.257) without the second term in the bracket to obtain an expression for $e^{\beta\mu}$, we obtain the desired result. which is $PV = NkT[\,1 + \frac{1}{2^{5/2}}\rho\lambda^3\,]$ ....

(c) What is the condition for the correction term in (6.268b) to be small? Note that as the temperature is lowered at constant density, the pressure increases. What do you think would be the effect of Bose statistics in this context (see Problem 6.61)? Mullin and Blaylock have emphasized that it is misleading to interpret the sign of the correction term in (6.268b) in terms of an effective repulsive exchange "force," and stress that the positive sign is a consequence of the symmetrization requirement for same spin fermions.

Not "$\frac{1}{2^{7/2}}$" as my edition of G & T says.

Solution. We see that for fermions the correction to the pressure is an increase over the classical result. Because of the Pauli exclusion principle, fermions tend to be further apart than classical particles. Thus, to squeeze them into the same volume, a higher pressure is needed. We expect that the correction would be negative for bosons. The condition for the correction term to be small is that the thermal de Broglie wavelength be much smaller than a typical interparticle distance.

Problem 6.61. If $T \gg T_c$ at fixed density, quantum effects can be neglected and the thermal properties of an ideal Bose gas reduces to the ideal classical gas. Does the pressure increase or decrease when the temperature is lowered (at constant density)? That is, what is the first quantum correction to the classical equation of state? The pressure is given by [see (6.109)]

$$P = \frac{2^{1/2} m^{3/2} (kT)^{5/2}}{3\pi^2 \hbar^3} \int_0^\infty \frac{x^{3/2}\, dx}{e^{x-\beta\mu} - 1}. \tag{2.269}$$

Follow the same procedure as in Problem 6.60 and show that

$$PV = NkT\Big[1 - \frac{\pi^{3/2}}{2} \frac{\rho \hbar^3}{(mkT)^{3/2}}\Big]. \tag{2.270}$$

We see that as the temperature is lowered at constant density, the pressure becomes less than its classical value.

Solution. We follow the same calculation as in Problem 6.60 but replace (6.265b) by

$$\frac{1}{e^{x-\beta\mu} - 1} = e^{\beta\mu - x} \frac{1}{1 - e^{-x+\beta\mu}} \approx e^{\beta\mu - x}[1 + e^{-x+\beta\mu}]. \tag{S6.259}$$

The minus sign difference leads to the pressure being less than the classical result.

Problem → High T, but not quite high enough for quantum effects to be Neglected ... G+T 6.61 Bose gas

- We will begin with Ⓐ + show Ⓑ. But see end of these notes for derivn of Ⓐ starting with Ω as in equ. 6.108.

$$P = \frac{2^{1/2} m^{3/2} (kT)^{5/2}}{3\pi^2 \hbar^3} \int_0^\infty \frac{x^{3/2}\, dx}{e^{x-\beta\mu} - 1} \qquad Ⓐ \quad \text{G+T (6.269)}$$

Let's take high T limit ⟺ $e^{\beta\mu} \ll 1$ (Recall, $\mu < 0$)

- Goal is to find $PV \cong NkT\left[1 + \rho \times \text{something}\right]$ where Ⓑ ≡ G+T (6.270) says $\text{something} = -\frac{\pi^{3/2}}{2} \frac{\hbar^3}{(mkT)^{3/2}}$, a

Correction to ideal gas law which vanishes as $\rho = N/V \to 0$

- OK, so $e^{\beta\mu} \ll 1 \Rightarrow \frac{1}{e^{x-\beta\mu} - 1} = \frac{e^{\beta\mu} e^{-x}}{1 - e^{\beta\mu} e^{-x}}$

$$\simeq e^{\beta\mu} e^{-x}\left[1 + e^{\beta\mu} e^{-x}\right]$$

$$\text{Thus } P \cong \frac{2^{1/2} m^{3/2} (kT)^{5/2}}{3\pi^2 \hbar^3}\, e^{\beta\mu} \int_0^\infty x^{3/2} e^{-x}\left[1 + e^{\beta\mu} e^{-x}\right] dx \quad *$$

call this C

Using Mathematica to perform integrals above:

$$P \simeq C e^{\beta\mu}\left[\frac{3\sqrt{\pi}}{4} + e^{\beta\mu} \frac{3\sqrt{\pi}}{2^{9/2}}\right];$$

$$P \simeq C e^{\beta\mu} \frac{3\sqrt{\pi}}{4}\left[1 + \frac{e^{\beta\mu}}{2^{5/2}}\right]$$

s- note: like $e^{\beta\mu}$ is param. This is fugacity: $z = e^{\beta\mu}$.

Furthermore, $\frac{N}{V} = \frac{z}{\lambda^3}$, $z = \frac{\lambda^3}{(V/N)} = \lambda^3 \frac{N}{V}$

So small z ⟺ dilute + or classical via high T or both!

This is good, have $P(e^{\beta\mu}, T)$.

Now do similar calculn for N/V

$$N = \frac{n_s V (2m)^{3/2}}{4\pi^2 \hbar^3} \int_0^\infty \frac{\epsilon^{1/2}\, d\epsilon}{e^{\beta\epsilon - \beta\mu} - 1} \qquad \text{G + T } (6.106\text{b})$$

Thus, with $n_s = 1$

$$\frac{N}{V} \approx \frac{m^{3/2}(kT)^{3/2}}{2^{1/2}\pi^2 \hbar^3} \int_0^\infty \frac{x^{1/2}\, dx}{e^{x - \beta\mu} - 1}$$

call this D

similarly to above, $e^{\beta\mu} \ll 1$

$$\Rightarrow \frac{N}{V} \approx D \int_0^\infty \frac{x^{1/2} e^{\beta\mu} e^{-x}}{1 - e^{\beta\mu} e^{-x}}\, dx$$

$$\frac{N}{V} \approx D e^{\beta\mu} \int_0^\infty x^{1/2} e^{-x} \left[1 + e^{\beta\mu} e^{-x}\right] dx$$

Mathematica

$$= D e^{\beta\mu} \left[\frac{\sqrt{\pi}}{2} + e^{\beta\mu} \frac{\sqrt{\pi}}{2^{5/2}}\right]$$

$$\frac{N}{V} = D e^{\beta\mu} \frac{\sqrt{\pi}}{2} \left[1 + \frac{e^{\beta\mu}}{2^{3/2}}\right]$$

Finally put P + N/V together:

$$\frac{PV}{NkT} = \frac{C\, e^{\beta\mu}\, 3\sqrt{\pi}/4 \left[1 + e^{\beta\mu}/2^{5/2}\right]}{kT D\, e^{\beta\mu} \sqrt{\pi}/2 \left[1 + e^{\beta\mu}/2^{3/2}\right]}$$

-or-

$$\frac{PV}{NkT} \approx \frac{C}{kTD} \frac{3}{2} \left[1 + \frac{e^{\beta\mu}}{2^{5/2}}\right]\left[1 - \frac{e^{\beta\mu}}{2^{3/2}}\right]$$

$$\approx \frac{C}{kTD} \frac{3}{2} \left[1 - \frac{e^{\beta\mu}}{2^{5/2}}\right]$$

$$\frac{P}{\left(\frac{N}{V}\right)kT} \quad \text{so } P = \frac{N}{V} kT \left(\frac{C}{kTD}\right)\frac{3}{2}\left[1 - \frac{e^{\beta\mu}}{2^{5/2}} + \cdots\right]$$

- Mopping up: $e^{\beta\mu} \approx \frac{N}{V}\lambda^3 + \cdots$

There are higher-order terms but we must stop here b/c we already have term at this order as correction!

GCE

$$\boxed{\frac{V}{\lambda^3}e^{\beta\mu} = N \quad \text{semi when } Z_1 \gg N/V}$$

$\mu \ll 0$

$Z_G = e^{\beta\mu} \underbrace{Z_1}_{V/\lambda_h^3}$

$$\frac{C}{D} = \frac{2kT}{3}$$

Thx Mathematica!

$$\therefore \frac{PV}{NkT} = \left[1 - \frac{N}{V}\frac{\lambda^3}{2^{5/2}}\right]$$

or,

$$\frac{PV}{NkT} = \left[1 - \frac{N}{V}\frac{\pi^{3/2}\hbar^3}{2m^{3/2}(kT)^{3/2}}\right]$$

B

G+T 2.70

Huzzah!

End of notes ... let's just show Eq. A follows from def of Ω.

st Eq (6.108)...

$$\Omega = \frac{\mp kT n_s V}{4\pi^2 \hbar^3} (2m)^{3/2} \int_0^\infty \epsilon^{1/2} \ln\left[1 \pm e^{-\beta(\epsilon-\mu)}\right] d\epsilon$$

polz'n etc... Bosons ... Bosons

We know $\Omega = -PV$. Thus, subbing in $x = \beta\epsilon$ we have

$$P = -\frac{n_s (2m)^{3/2} kT \beta^{-3/2}}{4\pi^2 \hbar^3} \int_0^\infty x^{1/2} \left[\ln(1 - e^{\beta\mu} e^{-x})\right] dx$$

Now integrate by parts: let

$$u = \ln\left[1 - e^{\beta\mu} e^{-x}\right] \qquad du = \frac{e^{\beta\mu} e^{-x}}{[1 - e^{\beta\mu} e^{-x}]}$$

$$dv = x^{1/2} dx \Rightarrow v = \tfrac{2}{3} x^{3/2}$$

Thus

$$P = \underbrace{uv \Big|_0^\infty}_{0} + \frac{n_s (2m)^{3/2} (kT)^{5/2}}{4\pi^2 \hbar^3} \frac{2}{3} \int_0^\infty \frac{x^{3/2} e^{\beta\mu} e^{-x}}{1 - e^{\beta\mu} e^{-x}} dx$$

so ... now setting $n_s = 1$ (why now? why not!)

$$P = 2^{1/2} m^{3/2} (kT)^{5/2} \frac{2}{3} \int_0^\infty \frac{x^{3/2} e^{-x+\beta\mu}}{1 - e^{-x+\beta\mu}} dx$$

so

$$P = \frac{2^{1/2} m^{3/2} (kT)^{5/2}}{3\pi^2 \hbar^3} \int_0^\infty \frac{x^{3/2}}{e^{x-\beta\mu} - 1} dx$$