

HW #6

7.4)

7.4 Prove Van Leeuwen's Theorem: The phenomenon of diamagnetism does not exist in classical physics.

The following hints may be helpful:

(a) If $\mathcal{H}(\mathbf{p}_1, \dots, \mathbf{p}_N; \mathbf{q}_1, \dots, \mathbf{q}_N)$ is the Hamiltonian of a system of charged particles in the absence of an external magnetic field, then $\mathcal{H}[\mathbf{p}_1 - (e/c)\mathbf{A}_1, \dots, \mathbf{p}_N - (e/c)\mathbf{A}_N; \mathbf{q}_1, \dots, \mathbf{q}_N]$ is the Hamiltonian of the same system in the presence of an external magnetic field $\mathbf{H} = \nabla \times \mathbf{A}$, where \mathbf{A} is the value of \mathbf{A} at the position \mathbf{q}_j .

(b) The induced magnetization of the system along the direction of H is given by

$$M = \left\langle -\frac{\partial \mathcal{H}}{\partial H} \right\rangle = kT \frac{\partial}{\partial H} \log Q_N$$

where \mathcal{H} is the Hamiltonian in the presence of \mathbf{H} , $H = |\mathbf{H}|$, and Q_N is the partition function of the system in the presence of \mathbf{H} .

From hint (b), we see that the induced magnetization ultimately depends on the log of the partition function & its derivative with respect to the magnetic field \vec{H} .

Therefore we need to demonstrate that, classically, Q_N is not a function of H , even when the Hamiltonian is. In general, Q_N is given by

$$Q_N = \frac{1}{N! h^{3N}} \int d^{3N} p \int d^{3N} q e^{-\beta \mathcal{H}} \quad \text{w/ } \mathcal{H} = \text{Hamiltonian}$$

In the presence of an external magnetic field $\vec{H} = \nabla \times \vec{A}$, where \vec{A} is the magnetic vector potential, we have

$$\mathcal{H}(\vec{p}, \vec{q}) \rightarrow \mathcal{H}(\vec{p} - \frac{e}{c}\vec{A}, \vec{q})$$

Therefore we see that the field merely shifts the components of the momenta. We can define a shifted momenta

$$\vec{p} \rightarrow \vec{p}' = \vec{p} - \frac{e}{c}\vec{A}$$

$$\Rightarrow \mathcal{H}(\vec{p} - \frac{e}{c}\vec{A}, \vec{q}) \rightarrow \mathcal{H}'(\vec{p}', \vec{q})$$

Since we are integrating each component of the momenta from $-\infty$ to ∞ , shifting to \vec{p}' does not change the limits of integration

As a result

$$Q_N = \frac{1}{N! h^{3N}} \int d^3p' \int d^3q e^{-\beta \mathcal{H}'(\vec{p}', \vec{q})}$$

which is indistinguishable from the partition function in the absence of an external magnetic field. Therefore, according to classical statistical mechanics, even in the presence of an external field H

$$M = \left\langle -\frac{\partial \mathcal{H}}{\partial H} \right\rangle = kT \frac{\partial}{\partial H} \ln Q_N = 0$$

There is no diamagnetism in classical SM

Why? Diamagnetism is the result of electrons experiencing a torque from the magnetic field, which changes their magnetic moments/ angular momenta. However, in classical mechanics, these changes cancel out because the angular momenta of electrons can take on any value. It's only in quantum mechanics, where we restrict the values of the angular momenta do we see diamagnetic effects.

Great resource for this:

http://www.feynmanlectures.caltech.edu/II_34.html

7.5)

7.5 Langevin's Theory of Paramagnetism. Consider a system of N atoms, each of which has an intrinsic magnetic moment of magnitude μ . The Hamiltonian in the presence of an external magnetic field \mathbf{H} is

$$\mathcal{H}(p, q) - \mu H \sum_{i=1}^N \cos \alpha_i$$

where $\mathcal{H}(p, q)$ is the Hamiltonian of the system in the absence of an external magnetic field, and α_i is the angle between \mathbf{H} and the magnetic moment of the i 'th atom. Show that

(a) The induced magnetic moment is

$$M = N\mu \left(\coth \theta - \frac{1}{\theta} \right) \quad (\theta \equiv \mu H / kT)$$

(b) The magnetic susceptibility per atom is

$$\chi = \frac{\mu^2}{kT} \left(\frac{1}{\theta^2} - \operatorname{csch}^2 \theta \right)$$

(c) At high temperatures χ satisfies Curie's law, namely $\chi \propto T^{-1}$. Find the proportional constant, which is called Curie's constant.

a) From the previous problem we saw that M is given by

$$M = kT \frac{\partial}{\partial H} \ln Q_N \quad \textcircled{1}$$

Therefore we need to compute Q_N . The partition function is given by

$$Q_N = C \int d^{3N} q \int d^{3N} p e^{-\beta(\mathcal{H}(p, q) - \mu H \sum_{i=1}^N \cos \alpha_i)} \quad C = \text{constants that don't depend on } H$$

If we choose our coordinate system so that \vec{H} is aligned w/ the z -axis & define $\tilde{z}_i \equiv \cos \alpha_i$

$$\begin{aligned} \Rightarrow Q_N &= C \int d^{3N} p \int d^N r \int d^N \varphi \int d\tilde{z}_1 \dots d\tilde{z}_N e^{-\beta(\mathcal{H}(p, q) - \mu H \sum_{i=1}^N \tilde{z}_i)} \\ &= C \left[\int d^3 p \, dr \, d\varphi \int_{-1}^1 d\tilde{z} e^{-\beta \mathcal{H}(\tilde{p}, r, \varphi, \tilde{z}) + \beta \mu H \tilde{z}} \right]^N \end{aligned}$$

Now we can't evaluate the integral without knowing the form of $\mathcal{H}(p, q)$, but if we assume that the dependence of $\mathcal{H}(p, q)$ on \tilde{z} is much weaker than $\mu \beta H \tilde{z}$, then we can approximate that

$$\begin{aligned} Q_N &= C \left[\int d^3 p \, dr \, d\varphi e^{-\beta \mathcal{H}(\tilde{p}, r, \varphi)} \int_{-1}^1 d\tilde{z} e^{\beta \mu H \tilde{z}} \right]^N \\ &= Q_N^{(0)} \left[\int_{-1}^1 d\tilde{z} e^{\beta \mu H \tilde{z}} \right]^N = Q_N^{(0)} \left(\frac{2 \cosh(\beta \mu H)}{\beta \mu H} \right)^N \end{aligned}$$

where $Q_N^{(0)}$ is the partition function in the absence of the external field \vec{H}

up to a constant

So now we use Eqn ① to solve for the magnetization

$$\begin{aligned} M &= kT \frac{\partial}{\partial H} \ln Q_N = NkT \frac{\partial}{\partial H} \ln \left(\frac{2 \cosh \beta \mu H}{\beta \mu H} \right) \\ &= NkT \frac{\beta \mu H}{2 \cosh \beta \mu H} \left(\frac{2 \beta^2 \mu^2 H \sinh \beta \mu H - 2 \beta \mu \cosh \beta \mu H}{(\beta \mu H)^2} \right) \\ &= NkT \left(\beta \mu \coth \beta \mu H - \frac{1}{H} \right) \end{aligned}$$

$$M = \mu N \left(\coth \Theta - 1/\Theta \right) \quad \Theta = \mu H / kT = \beta \mu H$$

b) The magnetic susceptibility is given by

$$\chi = \frac{\partial m}{\partial H} \quad m \equiv \text{mean magnetization of system}$$

For this problem $m = M/N$

$$\Rightarrow \chi = \frac{1}{N} \frac{\partial M}{\partial H} = kT \left(\frac{1}{H^2} - \beta^2 \mu^2 \operatorname{csch}^2 \beta \mu H \right)$$

$$\chi = \frac{\mu^2}{kT} \left(\frac{1}{\Theta^2} - \operatorname{csch}^2 \Theta \right)$$

c) At high temperatures $\Theta \rightarrow 0$

$$\chi = \frac{\mu}{H} \left(\frac{1}{\Theta} - \Theta \operatorname{csch}^2 \Theta \right)$$

$$= \frac{\mu}{H} \left[\frac{1}{\Theta} - \Theta \left(\frac{1}{\Theta^2} - \frac{1}{3} + \frac{\Theta^2}{15} + \mathcal{O}(\Theta^4) \right) \right]$$

Taylor expansion
of $\operatorname{csch}^2 \Theta$ about
 $\Theta = 0$

$$\Rightarrow \chi \approx \frac{\mu \Theta}{3H} = \frac{\mu^2}{3kT} = \chi(T \rightarrow \infty)$$

\therefore we see Curie constant given by $C = \mu^2/3k$

7.6

7.6 Imperfect Gas. Consider a system of N molecules ($N \rightarrow \infty$) contained in a box of volume V ($V \rightarrow \infty$). The Hamiltonian of the system is

$$\mathcal{H} = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i < j} v_{ij}$$

$$v_{ij} = v(|\mathbf{r}_i - \mathbf{r}_j|)$$

where \mathbf{p}_i and \mathbf{r}_i are, respectively, the momentum and the position of the i th molecule. The intermolecular potential $v(r)$ has the qualitative form shown in the accompanying figure. Let

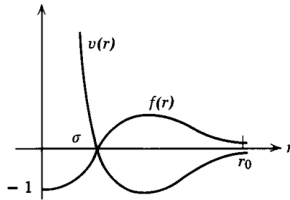
$$f_{ij} \equiv f(|\mathbf{r}_i - \mathbf{r}_j|)$$

$$f(r) \equiv e^{-\beta v(r)} - 1$$

A sketch of $f(r)$ is also shown in the same figure.

(a) Show that the equation of state of the system is

$$\frac{Pv}{kT} = 1 + v \frac{\partial Z(v, T)}{\partial v}$$



where $v \equiv V/N$ and

$$Z(v, T) \equiv \frac{1}{N} \log \left[\frac{1}{V^N} \int d^3 r_1 \cdots d^3 r_N \prod_{i < j} (1 + f_{ij}) \right]$$

(b) By expanding the product $\prod (1 + f_{ij})$, show that

$$Z(v, T) = \frac{1}{N} \log \left[\frac{1}{V^N} \int d^3 r_1 \cdots d^3 r_N \left(1 + \sum_{i < j} f_{ij} + \cdots \right) \right]$$

$$= \log \left[1 + \frac{N}{2V} \int d^3 r f(r) + \cdots \right]^{1/N}$$

(c) Show that at low densities, i.e.,

$$r_0^3/v \ll 1$$

it is a good approximation to retain only the first two terms in the series appearing in the expression $Z(v, T)$. Hence the equation of state is approximately given by

$$\frac{Pv}{kT} \approx 1 - \frac{1}{2v} \int_0^\infty dr 4\pi r^2 f(r)$$

The coefficient of $1/v$ is called the *second virial coefficient*.

Note. (i) Retaining the first two terms in the series appearing in $Z(v, T)$ is a good approximation because $Z(v, T)$ is the logarithm of the N th root of the series. The approximation is certainly invalid for the series itself

(ii) If all terms in the expansion of $\prod (1 + f_{ij})$ were kept, we would have obtained a systematic expansion of Pv/kT in powers of $1/v$. Such an expansion is known as the *virial expansion*.

(iii) The complete virial expansion is difficult to obtain by the method described in this problem. It is obtained in Chapter 10 via the grand canonical ensemble. See (10.27) and (10.30).

We can start by constructing the partition function based on this Hamiltonian

$$Q_N = \frac{1}{N! h^{3N}} \int d^{3N} p \int d^{3N} r e^{-\beta \sum_{i=1}^N p_i^2 / 2m - \beta \sum_{i < j} v(|\vec{r}_i - \vec{r}_j|)} \quad (1)$$

For this problem we want to solve for the equation of state, which we can find by solving for the pressure.

$$P = - \left(\frac{\partial A}{\partial V} \right)_{N, T} = kT \frac{\partial}{\partial V} \ln Q_N \quad (2)$$

Therefore, the only information that we need from Eqn. (1) are the parts of Q_N that depend on V . So we can rewrite Q_N as

$$Q_N = \left(\frac{V^N}{N! h^{3N}} \int d^{3N} p e^{-\beta \sum_{i=1}^N p_i^2 / 2m} \right) \left(\frac{1}{V^N} \int d^{3N} r e^{-\beta \sum_{i < j} v(|\vec{r}_i - \vec{r}_j|)} \right)$$

$\equiv Q_N^{\text{ideal}}$ ← partition function for an ideal gas

$$Q_N = \frac{Q_N^{\text{ideal}}}{V^N} \int d^{3N} r \prod_{i < j} e^{-\beta v(|\vec{r}_i - \vec{r}_j|)}$$

Now defining the correction function $1 + f_{ij} \equiv e^{-\beta v_{ij}}$ w/ $v_{ij} \equiv v(|\vec{r}_i - \vec{r}_j|)$, we define

$$\tilde{Z} \equiv \frac{1}{V^N} \int d^{3N} r \prod_{i < j} (1 + f_{ij})$$

$$\Rightarrow Q_N = Q_N^{\text{ideal}} \tilde{Z}$$

Plugging this into Eqn (2)

$$\frac{P}{kT} = \frac{\partial}{\partial V} (\ln Q_N^{\text{ideal}} + \ln \tilde{Z})$$

$$= \frac{N}{V} + \frac{\partial \ln \tilde{Z}}{\partial V}$$

where we used the knowledge that $PV = NkT$ is the ideal gas law that we would derive from $\frac{\partial}{\partial V} \ln Q_N^{\text{ideal}}$

If we switch to the notation $v = V/N$

$$\Rightarrow \frac{P}{kT} = \frac{1}{v} + \frac{1}{N} \frac{\partial \ln \tilde{Z}}{\partial v}$$

Or defining the function required for the problem

$$Z \equiv \frac{1}{N} \ln \tilde{Z}$$

$$\Rightarrow \frac{Pv}{kT} = 1 + v \frac{\partial Z}{\partial v}$$

b) In this part we just need to expand the product

$$\prod_{i < j} (1 + f_{ij}) = 1 + \sum_{i < j} f_{ij} + \sum_{i < j} \sum_{k < l} f_{ij} f_{kl} + \dots$$

If this expansion is not obvious, consider just 3 particles so that

$$\begin{aligned} \prod_{i < j} (1 + f_{ij}) &= (1 + f_{12})(1 + f_{13})(1 + f_{23}) \\ &= (1 + f_{12} + f_{13} + f_{12}f_{13})(1 + f_{23}) \\ &= 1 + f_{12} + f_{13} + f_{23} + f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23} + f_{12}f_{13}f_{23} \\ &= 1 + \sum_{i < j} f_{ij} + \sum_{i < j} \sum_{k < l} f_{ij} f_{kl} + \dots \end{aligned}$$

For this problem we will focus on the first two terms

$$\begin{aligned} \Rightarrow Z(v, T) &= \frac{1}{N} \ln \left[\frac{1}{V^N} \left(\int d^{3N}r (1) + \int d^{3N}r \sum_{i < j} f_{ij} + \dots \right) \right] \\ &= \ln \left[1 + \frac{1}{V^N} \sum_{i < j} \int d^{3N}r f_{ij} \right]^{1/N} \end{aligned}$$

The remaining integral only depends on 2 of N particles (particles i & j) therefore we can initially integrate over $d^{3N-2}r$

$$Z(v, T) = \ln \left[1 + \frac{1}{V^N} \sum_{i < j} V^{N-2} \int d^3r_i d^3r_j f_{ij} \right]^{1/N}$$

We can rewrite the integral over the positions of particle i & j by defining the separation vector

$$\vec{r} = \vec{r}_i - \vec{r}_j \quad \text{w/} \quad \frac{\partial \vec{r}}{\partial \vec{r}_i} = 1$$

$$\Rightarrow \int d^3 r_i d^3 r_j f(|\vec{r}_i - \vec{r}_j|) = \int d^3 r_j d^3 r f(|\vec{r}|)$$

We see that the integrand no longer depends on $\int d^3 r_j$ so we can evaluate this immediately

$$\Rightarrow Z(N, V, T) = \ln \left[1 + \frac{1}{V} \sum_{i < j} \int d^3 r f(r) + \dots \right]^{1/N}$$

The sum $\sum_{i < j}$ will essentially give us $N(N-1)/2$ identical copies of the integral. Approximating that $N-1 \approx N$ for $N \gg 1$, we have

$$Z(N, V, T) = \ln \left[1 + \frac{N^2}{2V} \int d^3 r f(r) + \dots \right]^{1/N}$$

Despite what the book has written, I think this is the right answer.

(c) When working with low densities, we can perform the virial expansion of the equation of state

$$\frac{P}{\rho kT} = 1 + B_2(T)\rho + B_3(T)\rho^2 + \dots$$

where $\rho = 1/v \ll 1$ & the coefficients $B_i(T)$ are known as virial coefficients. For ideal gases, where intermolecular interactions are dismissed $B_i(T) = 0$. For low-densities we only need to retain the first correction, $B_2(T)$.

We see that our solution to part (b) is this same expansion (times N), but we have taken the log of this expansion. Therefore, since we are dealing with low-densities, we only need to keep the first two terms, leading to

$$Z(N, V, T) \approx \frac{1}{N} \left(\frac{N^2}{2V} \int d^3 r f(r) \right)$$

Or recognizing that f is only a function of $|\vec{r}|$, we further simplify to

$$Z(v, T) = \frac{1}{2v} \int_0^{\infty} 4\pi r^2 f(r) dr$$

$$\Rightarrow \frac{Pv}{kT} = 1 + v \frac{\partial}{\partial v} \left(\frac{1}{2v} \int_0^{\infty} dr 4\pi r^2 f(r) \right)$$

$$\Rightarrow \frac{Pv}{kT} = 1 - \frac{1}{2v} \int_0^{\infty} dr 4\pi r^2 f(r)$$

or in the language of the virial expansion

$$\frac{P}{\rho kT} = 1 + B_2(T)\rho \quad \text{w/ } B_2(T) = -2\pi \int_0^{\infty} dr r^2 f(r)$$