

Assignment 4: Statistical Mechanics

Q1. The Dieterici equation of state for a gas is

$$p = \frac{k_B T}{v - b} \exp\left(-\frac{a}{k_B T v}\right)$$

where $v = V/N$. Find the critical point and compute the ratio $p_c v_c / k_B T_c$. Calculate the critical exponents β , δ and γ .

Q2. Consider the free energy

$$F = a(T)m^2 + b(T)m^4 + c(T)m^6$$

where $b(T) < 0$ and, for stability, $c(T) > 0$ for all T . Sketch the possible behaviours of the free energy as $a(T)$ varies and, in each case, identify the ground state and metastable states. Show that the system undergoes a phase transition at some temperature T_c . Determine the value $a(T_c)$ and the discontinuity in m at the transition.

Q3. To model a warm plasma, assume that the electron and ion distribution functions are given by

$$f_{e0}(v) = \frac{a_e}{\pi} \frac{1}{v^2 + a_e^2}, \quad f_{i0}(v) = \frac{a_i}{\pi} \frac{1}{v^2 + a_i^2}$$

Consider a plasma with $B_0=0$, and $E_0=0$.

- (a) Derive the dispersion relation (in integral form) in the Vlasov formalism assuming an electrostatic perturbation of angular frequency ω .

BONUS question

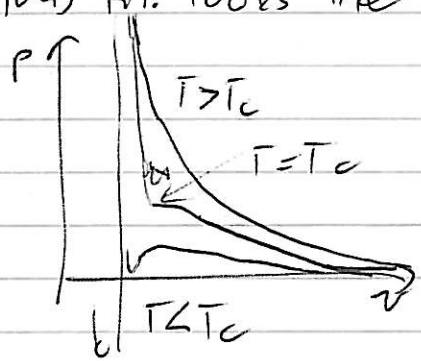
- Q3(b) Obtain an approximate expression for the dispersion relation if $\omega \leq \Omega_p$, with Ω_p the plasma frequency. Under what conditions are the waves weakly damped?

Q1/ Dieteric eqn. of state for a gas:

$$p = \frac{k_B T}{v-b} \exp\left(-\frac{a}{k_B T v}\right)$$

with $v = V/N$. Find the critical pt. & compute $p_c v_c / k_B T_c$

This fn. looks like



At critical pt. $\frac{dp}{dv} = \frac{d^2 p}{dv^2} = 0$.

$$\frac{dp}{dv} = \frac{k_B T}{v-b} \exp\left(-\frac{a}{k_B T v}\right) \left(\frac{-1}{v-b} + \frac{a}{k_B T v^2} \right) \quad (1)$$

$$\frac{d^2 p}{dv^2} = \exp\left(-\frac{a}{k_B T v}\right) \frac{k_B T}{(v-b)^3} \left(2 + \frac{a^2 (v-b)^2}{k_B^2 T^2 v^4} - \frac{2(v-b)(2v-b)2a}{v^3 k_B T} \right) \quad (2)$$

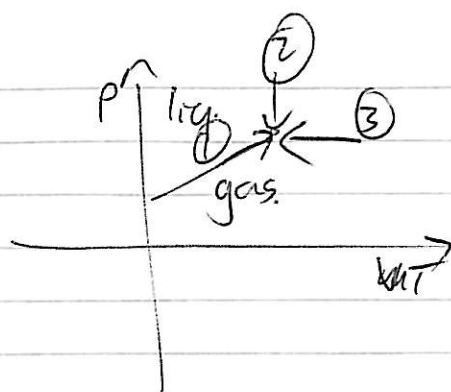
Solving (1) & (2) = 0 for T_c, v_c gives.

$$k_B T_c = \frac{a}{4b} \quad (0.5); \quad v_c = 2b \quad (0.5); \quad p_c = \frac{a^2}{4b^2 e^2} \quad (0.5)$$

$$\therefore \frac{p_c v_c}{k_B T_c} = \frac{a^2}{4b^2 e^2} \cdot \frac{2b}{(a/4b)} = \frac{2}{e^2} \quad (0.5)$$

Critical Exponents:

① Along the co-existence line.



Write $\bar{T} = T/T_c$; $\bar{v} = v/v_c$; $\bar{p} = p/p_c$

Hence

$$\bar{p} p_c = \frac{k_B \bar{T} T_c}{(\bar{v} v_c - b)} \cdot \exp\left(\frac{-a}{k_B \bar{T} T_c \bar{v} v_c}\right)$$

$$\Rightarrow \frac{\bar{p}}{p_c} = \frac{\bar{T}}{1 - 2\bar{v}} \cdot e^{-2/\bar{T}\bar{v}}$$

$$\text{or } \bar{p} = \frac{\bar{T}}{1 - 2\bar{v}} \exp\left(+2\left(1 - \frac{1}{\bar{T}\bar{v}}\right)\right) \quad (1)$$

This is the law of corresponding states. At $\bar{p} = \bar{v} = \bar{T} = 1$:

$$2 \quad \frac{p_c v_c}{k_B T_c} = \frac{\frac{a}{k_B T_c^2} \cdot 2k}{\frac{k_B}{k_B} \left(\frac{a}{k_B}\right)} = \frac{2}{e^2}$$

For $\bar{T} < 1$

$$\begin{aligned} \bar{p} &= \frac{\bar{T}}{1 - 2\bar{v}_{\text{liq}}} \exp\left(+2\left(1 - \frac{1}{\bar{T}\bar{v}_{\text{liq}}}\right)\right) \\ &= \frac{\bar{T}}{1 - 2\bar{v}_{\text{gas}}} \exp\left(+2\left(1 - \frac{1}{\bar{T}\bar{v}_{\text{gas}}}\right)\right) \quad (1) \end{aligned}$$

& solve for \bar{T} . Eq. is symmetric in \bar{v}_{gas} & \bar{v}_{liq} so write

$$\bar{v}_{\text{gas}} = 1 + \epsilon/2 ; \quad \bar{v}_{\text{liq}} = 1 - \epsilon/2 \quad (1)$$

& solve to leading order.

$$\begin{aligned} \frac{1 - 2\bar{v}_{\text{gas}}}{1 - 2\bar{v}_{\text{liq}}} &= \exp\left(2\left(1 - \frac{1}{\bar{T}\bar{v}_{\text{liq}}}\right) - 2\left(1 - \frac{1}{\bar{T}\bar{v}_{\text{gas}}}\right)\right) \\ &= \exp\left(\frac{2}{\bar{T}}\left(-\frac{1}{\bar{v}_{\text{liq}}} + \frac{1}{\bar{v}_{\text{gas}}}\right)\right) \end{aligned}$$

So

$$\bar{T} = \left(\ln\left(\frac{1 - 2\bar{v}_{\text{gas}}}{1 - 2\bar{v}_{\text{liq}}}\right)\right)^{-1} 2 \left(-\frac{1}{\bar{v}_{\text{liq}}} + \frac{1}{\bar{v}_{\text{gas}}}\right)$$

Performing series & substituting:

$$\begin{aligned}\bar{T} &= 1 - \frac{\epsilon^2}{12} + O(\epsilon^3) \\ &= 1 - (v_{\text{gas}} - v_{\text{liq}})^2 / 12.\end{aligned}\quad (1)$$

& so along co-existence line $v_{\text{gas}} - v_{\text{liq}} \sim (\bar{T}_c - \bar{T})^{1/2}$

$$\begin{aligned}\bar{T} &< 1. \\ &= \frac{\bar{T} - \bar{T}_c}{\bar{T}_c} \quad \left(\frac{\bar{T} - \bar{T}_c}{\bar{T}_c} \right) = \frac{(v_{\text{gas}} - v_{\text{liq}})^2}{12} \\ v_{\text{gas}} - v_{\text{liq}} &\sim (\bar{T}_c - \bar{T})^{1/2}.\end{aligned}\quad (1)$$

(2) At $\bar{T} = 1$

$$\bar{p} = \frac{\bar{T}}{1 - 2\bar{v}} \cdot \exp\left(2\left(1 - \frac{1}{\bar{T}\bar{v}}\right)\right) \quad (14)$$

Sub. $\bar{T} = 1$ & write $\bar{v} = v/v_c = 1 + \epsilon$. Then expand. (14) to $O(\epsilon^4) \Rightarrow$.

$$\begin{aligned}\bar{p} = \frac{p}{p_c} &= 1 - \frac{2}{3}\epsilon^3 + O(\epsilon^4) \\ &= 1 - \frac{2}{3}\left(\frac{v - v_c}{v_c}\right)^3\end{aligned}$$

so $\frac{p}{p_c} - 1 = -\frac{2}{3}\left(\frac{v - v_c}{v_c}\right)^3 \quad (1)$

or $p - p_c \sim (v - v_c)^3 \quad (1)$

(3) Compressibility. $k = -\frac{1}{v} \frac{\partial v}{\partial p} \Big|_T \quad \text{for } T > T_c.$

At crit. pt. $\frac{\partial p}{\partial v} = 0.$

$$\frac{\partial p}{\partial v} = \exp\left(\frac{-a}{k_B T v}\right) \frac{k_B T}{v - b} \left(\frac{a}{k_B T v} - \frac{1}{v - b}\right)$$

Expand $\left. \frac{\partial p}{\partial v} \right|_{T, v=v_c}$ with $T = T_c + \epsilon T_c = T_c (1 + \epsilon)$.

$$\left. \frac{\partial p}{\partial v} \right|_{T, v=v_c} = \frac{-a}{4b^3} e^{-2/(1+\epsilon)} \epsilon \quad (1)$$

$$\approx \frac{-a}{4b^3 \epsilon^2} \epsilon + O(\epsilon^2)$$

& so $k = -\frac{1}{v} \left. \frac{\partial v}{\partial p} \right|_T \sim (T - T_c)^{-1} \quad (1)$

Critical exponents

$$v_{\text{gas}} - v_{\text{liq}} \sim (T_c - T)^{\beta} \quad \beta = \frac{1}{2}$$

$$(p - p_c) \sim (v - v_c)^{\frac{1}{\delta}} \quad \delta = \frac{1}{3}$$

$$k \sim (T - T_c)^{\gamma} \quad \gamma = -1.$$

These are the same as the Van der Waals eqn.

Q2: Consider

$$F = a(T)m^2 + b(T)m^4 + c(T)m^6$$

with $b(T) < 0$ & $c(T) > 0$.

Find solutions of $\frac{\partial F}{\partial m} = 0$ (equilibrium cond.)

$$\begin{aligned}\frac{\partial F}{\partial m} &= 2a(T)m + 4b(T)m^3 + 6c(T)m^5 \\ \frac{\partial F}{\partial m} &= m(2a + 4bm^2 + 6cm^4) \\ &= 0\end{aligned}$$

$$\text{Solns are } m=0, \quad m^2 = \frac{-4b \pm \sqrt{16b^2 - 48ac}}{12c} \quad (1)$$

If $b^2 - 48ac > 0 \Rightarrow$ real solns of m^2 exist.
 $b^2 > 3ac$

$$m^2 = \frac{-b \pm \sqrt{b^2 - 3ac}}{3c}$$

We are given $b < 0$. If $b^2 - 3ac > b^2$, solutions are

(A) $a < 0$ $m_0 = 0$, $m_1 = \pm \left(\frac{|b| + \sqrt{b^2 - 3ac}}{3c} \right)^{1/2}$ (1)

(B) If $0 < b^2 - 3ac < b^2$, solns are

$$\begin{aligned}m_0 &= 0, \quad m_1 = \pm \left(\frac{|b| + \sqrt{b^2 - 3ac}}{3c} \right)^{1/2} \\ m_2 &= \pm \left(\frac{|b| - \sqrt{b^2 - 3ac}}{3c} \right)^{1/2}\end{aligned} \quad (1)$$

~~This condition is~~

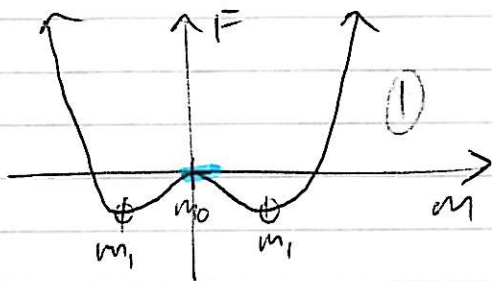
The condition $0 < b^2 - 3ac < b^2 \Rightarrow 0 < a < \frac{b^2}{3c}$

(C) Finally, if $b^2 - 3ac < 0 \Rightarrow a > \frac{b^2}{3c}$ there is only one solution

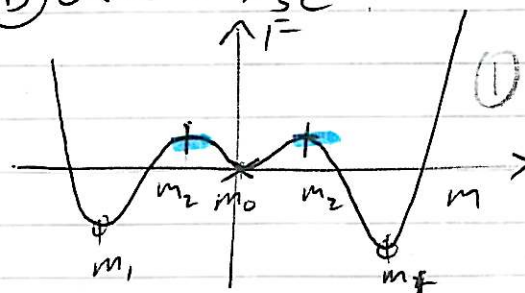
$$m_0 = 0. \quad (1)$$

There are hence 3 regimes. The system behaviour is as follows:

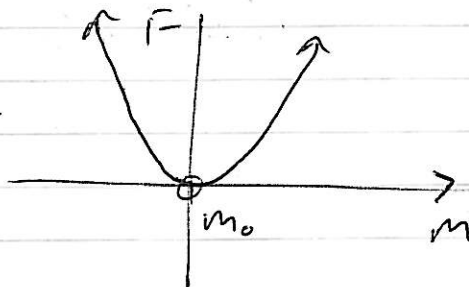
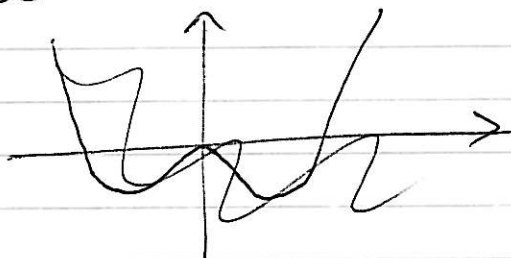
(A) $a < 0$



(B) $0 < a < \frac{b^2}{3c}$



(C) $a > \frac{b^2}{3c}$



o = ground state

x = metastable state

+ = unstable state

The system undergoes a transition at $a^* = \frac{b^2}{3c}$

For $a(T) > \frac{b^2}{3c}$ $m_0 = 0$ is the ground state.

For $a(T) < \frac{b^2}{3c}$ $m_1 (\neq 0)$ is the ground state.

Q3 To model a warm plasma assume that

$$\hat{f}_{e0}(v) = \frac{a_e}{\pi} \frac{1}{v^2 + a_e^2} \quad ; \quad \hat{f}_{i0}(v) = \frac{a_i}{\pi} \frac{1}{v^2 + a_i^2}$$

Consider a plasma with $E_0 = B_0 = 0$.

(a) Vlasov eqn. for species f

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \nabla f + \frac{q}{m} (\underline{E} + \underline{v} \times \underline{B}) \cdot \frac{\partial f}{\partial \underline{v}} = 0 \quad (1)$$

There are two species: ions and electrons. For both species can write

$$f = f_0(v) + f_1(x, v, t) \quad (1)$$

as problem is 1D. To first order, perturbed Vlasov eqn. is

$$\frac{\partial f_1}{\partial t} + \underline{v}_0 \cdot \nabla f_1 + \frac{q}{m} (\underline{E}_1 \cdot \frac{\partial f_0}{\partial \underline{v}}) = 0 \quad (1)$$

Assume $f_{e1} \propto e^{i(kx - \omega t)}$, $f_{i1} \propto e^{i(kx - \omega t)}$, so.

$$-i\omega f_1 + ikv f_1 + \frac{q}{m} E_1 \frac{\partial f_0}{\partial v} = 0$$

For ions:

$$f_{i1} = \frac{-ie E_1 \frac{\partial f_{i0}}{\partial v}}{\omega - kv} \quad (1)$$

For electrons:

$$f_{e1} = \frac{ie E_1 \frac{\partial f_{e0}}{\partial v}}{\omega - kv} \quad (2)$$

Poisson's eqn:

$$\epsilon_0 \nabla \cdot \underline{E} = -en_e + en_i \quad (1)$$

As $E_0 = 0 \quad \therefore -en_{e0} + en_{i0} = 0 \rightarrow n_{e0} = n_{i0}$

$$\int_{-\infty}^{\infty} \hat{f}_{e0}(v) dv = \frac{q_e}{|q_i|} \int_{-\infty}^{\infty} \frac{a_e}{\pi} \frac{1}{v^2 + a_e^2} dv = 1$$

$$\int_{-\infty}^{\infty} \hat{f}_{i0}(v) dv = \int_{-\infty}^{\infty} \frac{a_i}{\pi} \frac{1}{v^2 + a_i^2} dv = 1$$

[Note that the question gave $f_{e0}(v)$ & $f_{i0}(v)$ - but by integrating] it is obvious that this was the probability, not the distn. fn.

To 1st order: $\epsilon_0 i k E_1 = -e n_{e1} + e n_{i1}$
 $= n_0 e \left(\int_{-\infty}^{\infty} \hat{f}_{i1} dv - \int_{-\infty}^{\infty} \hat{f}_{e1} dv \right) \quad (3)$

with $n_0 = n_{e0} = n_{i0}$

Substitute (1), (2) into (3) gives:

$$\epsilon_0 i k E_1 = n_0 e \left[-\frac{ie}{m_i} E_1 \int \frac{\frac{\partial \hat{f}_{i0}}{\partial v}}{\omega - kv} dv - \frac{ie}{m_e} E_1 \int \frac{\frac{\partial \hat{f}_{e0}}{\partial v}}{\omega - kv} dv \right]$$

$$1 = -\frac{n_0 e^2}{\epsilon_0 k m_e} \cdot \frac{1}{k} \left[\frac{m_e}{m_i} \int \frac{\frac{\partial \hat{f}_{i0}}{\partial v}}{\omega - kv} dv + \int \frac{\frac{\partial \hat{f}_{e0}}{\partial v}}{\omega - kv} dv \right]$$

$$= -\frac{\Omega_p^2}{k} \left[\frac{m_e}{m_i} \int \frac{-\frac{Z v a_i}{\pi (v^2 + a_i^2)^2} \frac{1}{\omega - kv} dv + \int \frac{-\frac{Z v a_e}{\pi (v^2 + a_e^2)^2} \frac{1}{\omega - kv} dv \right] \quad (1)$$

where $\Omega_p = \left(\frac{n_0 e^2}{\epsilon_0 m_e} \right)^{\frac{1}{2}}$ is the plasma frequency.

If $a_i \sim a_e$ (comparable) then

$$1 \approx \frac{\Omega_p^2}{k} \cdot \frac{Z a_e}{\pi} \int_{-\infty}^{\infty} \frac{v}{(v^2 + a_e^2)^2} \cdot \frac{1}{\omega - kv} dv \quad (4)$$

(b) Compute dispersion relation if $\omega \lesssim \Omega_p$.

Eq. (4) has a pole at $\omega = kv$. $v = \omega/k$. If $\frac{\omega}{k} > 0$ then the contour integral can be performed

$$+ \int \frac{v}{(v^2 + a_e^2)^2} \frac{1}{v - \omega/k} dv = \frac{k^2 \pi}{Z a_e (a_e k - i\omega)^2}$$

Hence,
$$1 = \frac{\Omega_p^2}{k} \cdot \frac{2ae}{\pi} \left(-\frac{1}{k} \right) \frac{k^2 \pi}{2ae(aek - iw)^2}$$

$$= \frac{-\Omega_p^2}{(aek - iw)^2}$$

2 so $-w^2 - 2aekwi + ae^2 k^2 = -\Omega_p^2$

with solns
$$w = \frac{-2aeki \pm \sqrt{-4ae^2 k^2 + 4(ae^2 k^2 + \Omega_p^2)}}{2}$$

$$= -aek i \pm \Omega_p$$

ie $w/k = -ae i \pm \frac{\Omega_p}{k}$

But $ae > 0$ 2 so $\frac{ae i}{k} \text{Im}(w/k) < 0$.

This violates our assumption.

Search for solns. with $w/k < 0$

$$\int \frac{g(u)}{u - w/k} du = \int_{-\infty}^{\infty} \frac{g(u)}{u - w/k} du + 2\pi i g(w/k)$$

$$= \frac{k^2 \pi}{2ae(aek - iw)^2} + \frac{2\pi i w/k}{(w/k)^2 + ae^2}$$

Hence
$$1 = \frac{\Omega_p^2}{k^2} \frac{2ae}{\pi} \left[\frac{k^2 \pi}{2ae(aek - iw)^2} + \frac{2\pi i w/k}{(w/k)^2 + ae^2} \right]$$

Solving for w
$$w/k = iae(3 \pm 2\sqrt{2})$$

These solns have $\text{Im}(w/k) > 0$ b/c $ae > 0$.

\Rightarrow ~~There are~~ no solutions that have $\text{Im}(w/k) = 0$.

ie they are all real.