UNIVERSITY OF STRASBOURG

Exam — Session 2

T. Charitat, J. Farago, G. Weick

Transcribed by
PIERRE GUICHARD

M1-S1 2020-2021

1 Ising dimer

Let us consider two Ising spins $s_i = \pm 1$ $(i = 1, 2)$ forming a dimer. The two spins are subject to a uniform magnetic field H, and interact through a ferromagnetic exchange interaction J. The dimer is connected to a heat reservoir which maintains its temperature T constant. In what follows, we denote $\beta = 1/k_B T$, with k_B the Boltzmann constant. The Hamiltonian of the system then reads

$$\mathcal{H} = -(s_1 + s_2)H - J s_1 s_2 .$$

(a) What is the sign of J ? Justify your answer.

The sign of J has to be positive, because, when forming a dimer, the two individual spins must reduce their energy, meaning that $-J$ has to be of negative sign.

(b) At vanishing magnetic field $(H = 0)$ and zero temperature $(T = 0)$, what are the spin configurations ?

Without any magnetic field $(H = 0)$, since it's a ferromagnetic exchange interaction, all the spins are aligned in respect to the others.

(c) Calculate the exact canonical partition function Z and the free energy F of the system.

$$\begin{aligned}
Z &= \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} e^{\beta[(s_1+s_2)H + J s_1 s_2]} \\
&= \sum_{s_1=\pm 1} \left\{ e^{\beta[(s_1+1)H + J s_1]} + e^{\beta[(s_1-1)H - J s_1]} \right\} \\
&= e^{\beta[(1+1)H+J]} + e^{\beta[(-1+1)H-J]} e^{\beta[(+1-1)H-J]} + e^{\beta[(-1-1)H+J]} \\
&= e^{\beta J} \left\{ 2\cosh(2\beta H) \right\} + 2e^{-\beta J}
\end{aligned}$$

$$\begin{aligned}
F &= -k_B T \ln Z \\
&= -k_B T \ln \left\{ e^{\beta J} \left[\{ 2\cosh(2\beta H) \} + 2e^{-2\beta J} \right] \right\} \\
&= -J - k_B T \ln \left\{ 2\cosh(2\beta H) + 2e^{-2\beta J} \right\}
\end{aligned}$$

(d) The average magnetization per spin $m = \langle s_i \rangle$ of the system is given by

$$m = -\frac{1}{2}\frac{\partial F}{\partial H} \tag{1.1}$$

(i) Justify expression (1.1).

(ii) Show that

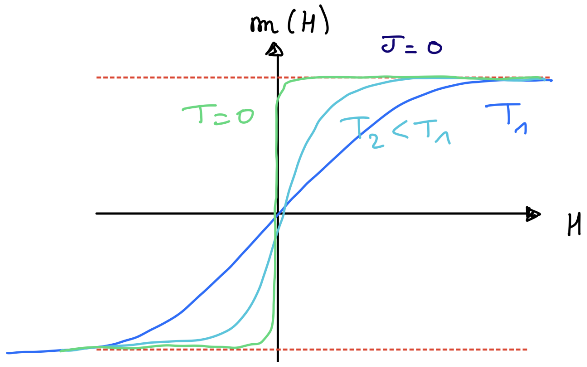
$$m = \frac{\sinh(2\beta H)}{\cosh(2\beta H) + \exp(-2\beta J)}. \tag{1.2}$$

$$\begin{aligned} m &= -\frac{1}{2}\frac{\partial F}{\partial H} \\ &= -\frac{1}{2}\frac{\partial}{\partial H}\left[-J - k_B T \ln\left\{2\cosh(2\beta H) + 2e^{-2\beta J}\right\}\right] \\ &= \frac{\sinh(2\beta H)}{\cosh(2\beta H) + e^{-2\beta J}} \end{aligned}$$

(iii) Without interaction between the two spins ($J = 0$), prove that Eq. (1.2) recovers the paramagnetic behavior $m = \tanh(\beta H)$.

$$\begin{aligned} m &= \frac{\sinh(2\beta H)}{\cosh(2\beta H) + 1} \\ &= \frac{e^{2\beta H} - e^{-2\beta H}}{2\left[\dfrac{e^{2\beta H} + e^{-2\beta H}}{2} + 1\right]} \\ &= \frac{e^{2\beta H} - e^{-2\beta H}}{e^{2\beta H} + e^{-2\beta H} + 2} \\ &= \frac{e^{2\beta H} - e^{-2\beta H}}{(e^{\beta H} + e^{-\beta H})^2} \\ &= \frac{(e^{\beta H} - e^{-\beta H})(e^{\beta H} + e^{-\beta H})}{(e^{\beta H} + e^{-\beta H})^2} \\ &= \tanh(\beta H) \end{aligned}$$

(iv) For a given value of J, plot m as a function of H for various temperatures. What happens in the $T = 0$ limit? Does the system present a phase transition?



When T reach 0, m tend to be the sign function. This sytem has a phase transition for $T = 0$.

(e) The zero-field magnetic susceptibility is defined as

$$\chi = \left.\frac{\partial m}{\partial H}\right|_{H=0}$$

Calculate χ and comment on the $T = 0$ limit.

$$\begin{aligned}
\chi &= \left.\frac{\partial m}{\partial H}\right|_{H=0} \\
&= \frac{\partial}{\partial H}\left.\left\{\frac{\sinh(2\beta H)}{\cosh(2\beta H) + e^{-2\beta J}}\right\}\right|_{H=0} \\
&= \left.\frac{2\beta e^{-2\beta J}}{(\cosh(2\beta H) + e^{-2\beta J})^2}\right|_{H=0} \\
&= \frac{2\beta e^{-2\beta J}}{(1 + e^{-2\beta J})^2}
\end{aligned}$$

Let's check the limit for $T \to 0$,

$$\lim_{T\to 0} \chi \approx \frac{2\beta(1 - 2\beta J)}{(2 - 2\beta J)} \approx \beta \qquad\qquad \lim_{x\to 0} e^x \approx 1 + x$$

$$\to \infty$$

We know that when the magnetic suseptibility diverges, there is a phase transition. Meaning here, the phase transition occurs at $T = 0$, which is coherent with what we drew for $m(H)$ earlier.

2 Van der Waals equation of state

Let us consider a system of $N \gg 1$ classical particles with mass m occupying a three-dimensional volume V at the temperature T. The particles have no internal degrees of freedom. The Hamiltonian of the system reads

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + U(\vec{r}_1, \cdots, \vec{r}_N)$$

where $\vec{r}_i$ and $\vec{p}_i$ are the position and momentum of the i^{th} particle, and U is the interaction energy of the system.

2.1 Semiclassical partition function

We recall that the canonical partition function of the system is given, in the dilute limit, by

$$Z = \frac{1}{(2\pi\hbar)^{3N} N!} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N \mathrm{d}^3\vec{p}_1 \cdots \mathrm{d}^3\vec{p}_N e^{-\beta\mathcal{H}},$$

Using the result

$$\int_{-\infty}^{+\infty} \mathrm{d}u e^{-u^2} = \sqrt{\pi},$$

show that

$$Z = \frac{1}{N! \Lambda_T^{3N}} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)}, \tag{2.1}$$

where $\Lambda_T = (2\pi\hbar^2/mk_BT)^{1/2}$ is the thermal de Broglie wavelength.

$$\begin{aligned}
Z &= \frac{1}{(2\pi\hbar)^{3N} N!} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N \mathrm{d}^3\vec{p}_1 \cdots \mathrm{d}^3\vec{p}_N e^{-\beta\mathcal{H}} \\
&= \frac{1}{(2\pi\hbar)^{3N} N!} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N \mathrm{d}^3\vec{p}_1 \cdots \mathrm{d}^3\vec{p}_N e^{-\beta[\sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m} + U(\vec{r}_1, \cdots, \vec{r}_N)]} \\
&= \frac{1}{(2\pi\hbar)^{3N} N!} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)} \int \mathrm{d}^3\vec{p}_1 \cdots \mathrm{d}^3\vec{p}_N e^{-\beta[\sum_{i=1}^{N} \frac{\vec{p}_i^2}{2m}]} \qquad P_i = \sqrt{\frac{\beta}{2m}} p_i \\
&= \frac{(2mk_BT)^{3N/2}}{(2\pi\hbar)^{3N} N!} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)} \int \mathrm{d}^3\vec{P}_1 \cdots \mathrm{d}^3\vec{P}_N e^{-\sum_{i=1}^{N} \vec{P}_i^2} \\
&= \frac{(2mk_BT\pi)^{3N/2}}{(2\pi\hbar)^{3N} N!} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)} \\
&= \frac{1}{N! \Lambda_T^{3N}} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)}
\end{aligned}$$

2.2 The ideal gas case

Let us first consider the case of an ideal gas, for which it is assumed that $U(\vec{r}_1, \cdots, \vec{r}_N) = 0$.

(a) In the noninteracting case, calculate the partition function (2.1) and the free energy F in the thermodynamic limit. [1]

$$\begin{aligned} Z &= \frac{1}{(2\pi\hbar)^{3N} N!} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N \mathrm{d}^3\vec{p}_1 \cdots \mathrm{d}^3\vec{p}_N e^{-\beta\mathcal{H}} \\ &= \frac{1}{N!\Lambda_T^{3N}} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N e^{-\beta U(\vec{r}_1, \cdots, \vec{r}_N)} \\ &= \frac{1}{N!\Lambda_T^{3N}} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N \\ &= \frac{V^N}{N!\Lambda_T^{3N}} \end{aligned}$$

$$\begin{aligned} F &= -k_B T \ln Z \\ &= -Nk_B T \ln(V) + k_B T \ln(N!) + Nk_B T \ln\left(\Lambda_T^3\right) \\ &= -Nk_B T \ln(V) + Nk_B T(\ln(N) - 1) + Nk_B T \ln\left(\Lambda_T^3\right) \\ &= -Nk_B T \left\{ \ln\left(\frac{V}{N\Lambda_T^3}\right) + 1 \right\} \end{aligned}$$

(b) Deduce from the previous question the equation of state of the system.

We know the expression of the pressure,

$$p = -\frac{\partial F}{\partial V} = \frac{Nk_B T}{V}$$

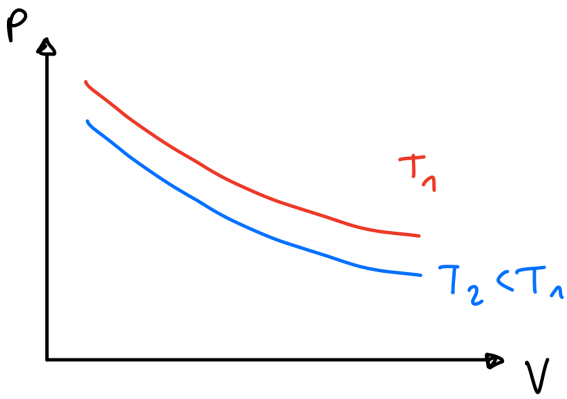
Meaning the well known equation of state for a perfect gas,

$$pV = Nk_B T$$

(c) In a P-V diagram, sketch the isothermal curves. Does the ideal gas model enable one to describe the liquid-gas phase transition ?

---

[1] We recall Stirling's formula $\ln n! \simeq n \ln n - n$ for $n \gg 1$



There is no phase transition, indeed, we need to have interactions in order to exhibit a phase transition.

2.3 Role of the molecular interactions

Let us now consider the interactions between pairs of molecules only, so that the interaction energy in Eq. (2.1) reads

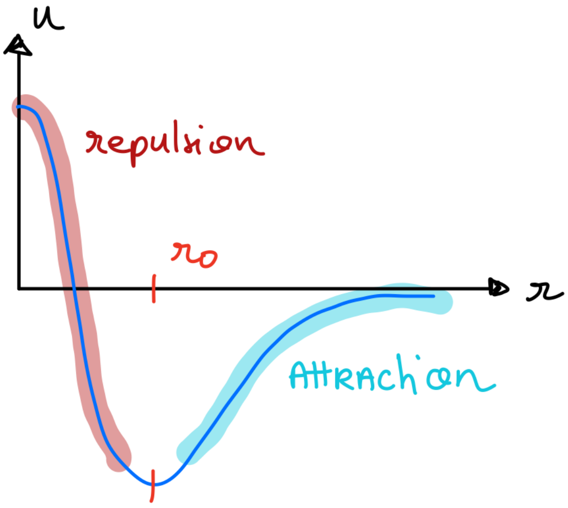
$$U(\vec{r}_1, \cdots, \vec{r}_N) = \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^{N} u(r_{ij})$$

where $u(r_{ij})$ is the potential energy between two pairs of molecules separated by the distance $r_{ij} = |\vec{r}_i - \vec{r}_j|$. In what follows, we assume that $u(r)$ is a Lennard–Jones potential that takes the form

$$u(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]. \tag{2.2}$$

The Lennard–Jones potential has a minimum at $r = r_0 = 2^{1/6}\sigma$, for which it takes the value $u(r_0) = -\varepsilon$.

(a) Sketch the Lennard–Jones potential (2.2) as a function of r, and indicate on your graph where are the repulsive and attractive part of the interaction.



(b) Let us first consider the attractive part $\propto -r^{-6}$ of $u(r)$ and neglect the correlations between the particles. Within a mean-field approximation, assuming that the density of particles is uniform, show that

$$U(\vec{r}_1, \cdots, \vec{r}_N) \simeq -\frac{aN^2}{V},$$

with

$$a = -\frac{1}{2}\int \mathrm{d}^3\vec{r}u(r).$$

$$U(\vec{r}_1, \cdots, \vec{r}_N) = \frac{1}{2}\sum_{\substack{i,j=1 \\ (i\neq j)}}^{N} u(r_{ij})$$

We can fix $\vec{r}_i$, so we can take $\vec{r}_i = \vec{0}$,

$$\sum_{j=1}^{N} u(r_{ij}) = \sum_{j=1}^{N} u(\vec{r}_j)$$

But, there is a lot's of particles, so we can replace the summation by an integral,

$$= \sum_{j=1}^{N} u(\vec{r}_j) \approx \int \mathrm{d}^3\vec{r}n(\vec{r})u(r)$$

where $n(\vec{r})$ is the density of particles, we can say that this density is homogeneous, $n(\vec{r}) = N/V$ and so,

$$\sum_{j=1}^{N} u(r_{ij}) \approx \frac{N}{V}\int \mathrm{d}^3\vec{r}u(r)$$

This integral doesn't depend on i, we can call it $-2a$, so,

$$U(\vec{r}_1, \cdots, \vec{r}_N) \simeq \frac{1}{2}\left(-\frac{2aN}{V}\right) N$$

where the right N comes from the summation over i. Meaning, that, in the end,

$$U(\vec{r}_1, \cdots, \vec{r}_N) \simeq -\frac{aN^2}{V},$$

(c) Close to a given particle, the approximation above is not valid any longer and one has to take into account the repulsive part $\propto r^{-12}$ of the pair potential (2.2). To this end, we assume that the particles are hard spheres of radius R and that each particle has an excluded volume b. Give an expression of b as a function of R. Justify that when integrating over the particle positions in Eq. (2.1), one has to integrate over $V - Nb$ instead of V, as was done in the ideal gas case.

$$V_{\text{true volume}} = V_{\text{total}} - (N-1)b \approx V_{\text{total}} - Nb \qquad\qquad b = \frac{4}{3}\pi(2R)^3$$

(d) Considering the appriximations of questions (b) and (c) above, show that Eq. (2.1) takes the form

$$Z \simeq \frac{(V-Nb)^N}{N!\Lambda_T^{3N}} e^{\beta a N^2/V},$$

and calculate F in the thermodynamic limit.

$$\begin{aligned} Z &= \frac{1}{N!\Lambda_T^{3N}} \int \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N e^{-\beta U(\vec{r}_1,\cdots,\vec{r}_N)} \\ &\approx \frac{1}{N!\Lambda_T^{3N}} \int_{V-Nb} \mathrm{d}^3\vec{r}_1 \cdots \mathrm{d}^3\vec{r}_N e^{-\beta U(\vec{r}_1,\cdots,\vec{r}_N)} \\ &= \frac{(V-Nb)^N}{N!\Lambda_T^{3N}} e^{\beta a N^2/V} \end{aligned}$$

$$\begin{aligned} F &= -k_B T \ln Z \\ &= -k_B T \ln\left\{\frac{(V-Nb)^N}{N!\Lambda_T^{3N}} e^{\beta a N^2/V}\right\} \\ &= -N k_B T \ln\left(\frac{V-Nb}{\Lambda_T^3}\right) - \frac{aN^2}{V} + (-N\ln N + N)(-k_B T) \end{aligned}$$

(e) Deduce from the above results the van der Waals equation of state

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_BT \tag{2.3}$$

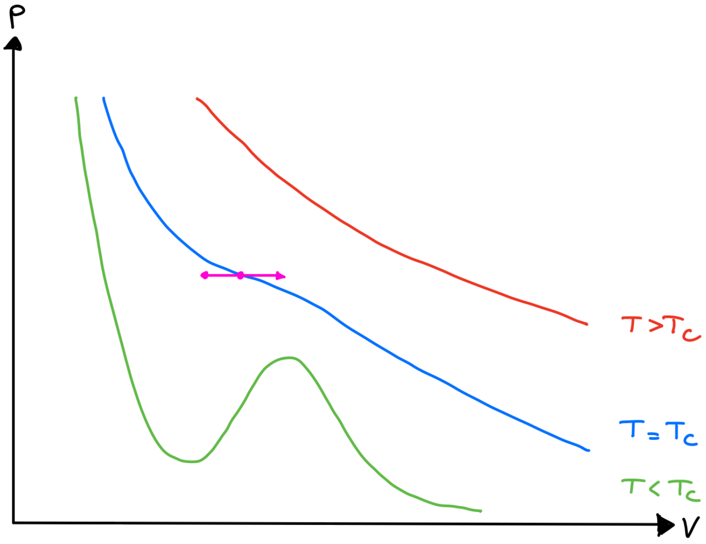
$$\begin{aligned} p &= -\frac{\partial F}{\partial V} \\ &= \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2} \end{aligned}$$

We indeed recover van der Waals equation of state,

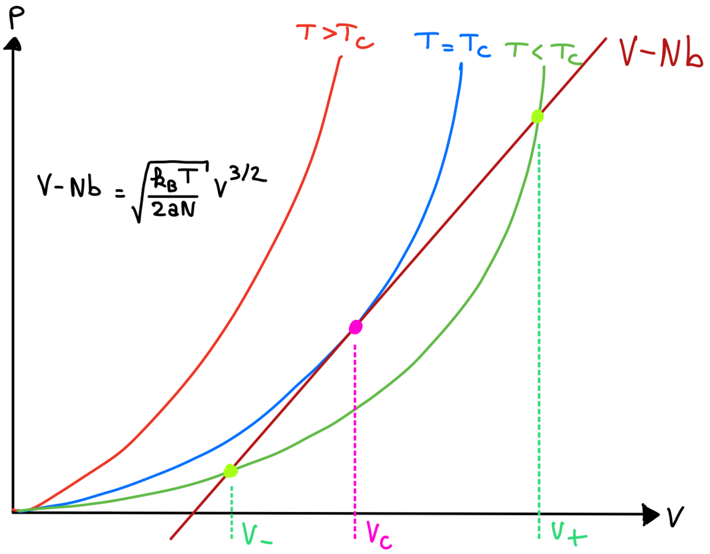
$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = Nk_BT$$

2.4 Isothermal curves

(a) Sketch the isothermal curves (2.3) in a $P - V$ diagram. In particular, show that there exists a critical temperature T_c below which the isothermal curves are no longer monotonic functions.



(b) For the critical isothermal curve, there exists an inflection point (P_c, V_c) called the critical point. Give the expressions of P_c, V_c, and T_c as a function of a and b.



At V_c, the slopes are equal, meaning,

$$\begin{cases} \dfrac{\partial}{\partial V}(V-Nb) = \dfrac{\partial}{\partial V}\left(\sqrt{\dfrac{k_B T}{2aN}}V^{3/2}\right) \\ V - Nb = \sqrt{\dfrac{k_B T}{2aN}}V^{3/2} \end{cases}$$

From the first equation we get,

$$1 = \sqrt{\frac{k_B T_c}{2aN}}V_c^{1/2}$$

Meaning,

$$k_B T_c = \frac{8}{9}\frac{aN}{V_c}$$

From the second equation,

$$\begin{aligned} V - Nb &= \sqrt{\frac{k_B T}{2aN}}V^{3/2} \\ &= \frac{2}{3}V_c \end{aligned}$$

Meaning,

$$V_c = 3Nb$$

So now,

$$k_B T_c = \frac{8}{9}\frac{aN}{V_c} = \frac{8}{9}\frac{aN}{3Nb} = \frac{8}{27}\frac{a}{b}$$

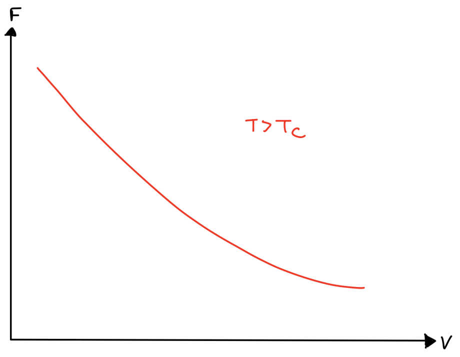
Then, the pressure,

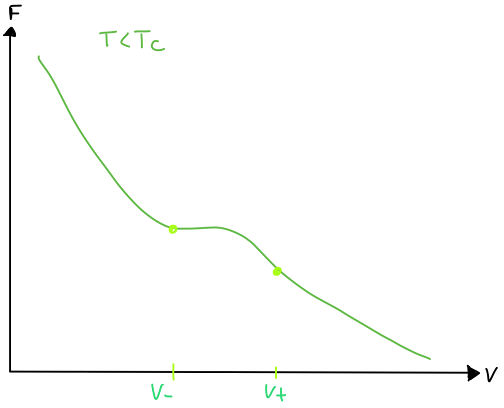
$$\begin{aligned} P_c &= \frac{Nk_BT_c}{V_c - Nb} - a\frac{N^2}{V_c^2} \\ &= \frac{N\frac{8}{27}\frac{a}{b}}{2Nb} - \frac{aN^2}{9N^2b^2} \end{aligned}$$

Meaning,

$$P_c = \frac{1}{27}\frac{a}{b^2}$$

(c) Plot the free energy F as a function of V for $T > T_c$ and $T < T_c$.





(d) One can show that a thermodynamical system for which $(\partial P/\partial V)_T > 0$ is unstable. What are the regions in the $P - V$ and $F - V$ diagrams which correspond to thermodynamically unstable states ?

The region in between V_- and V_+ is thermodynamically unstable.

(e) Qualitatively explain how to remedy to this incoherence of the van der Waals model, and how to describe the liquid-gas transition.