## Problem and solution

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Chapter 4

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4.6 Sketch the Gibbs potential $G(P, T)$ of the van der Waals gas as a function of $P$ at constant $T$. In particular, show the behavior in the transition region. Derive the Maxwell construction using the principle of minimization of $G$

## ((Solution))

## Maxwell construction for the $p_{r}$ vs $v_{r}$ phase diagram



Fig. $1 \quad$ The phase diagram of $v_{\mathrm{r}}$ vs $p_{\mathrm{r}}$ at $t_{\mathrm{r}}=0.96$.


Fig. Gibbs free energy at $t_{r}=0.96$.

At $t_{r}=t_{1}$,

$$
g\left(t_{r}=t_{1}, p_{r}\right)=g\left(t_{1}, p_{a}\right)+\int_{p_{a}}^{p} v_{r}\left(p_{r}, t_{1}\right) d p_{r}
$$

We assume that $p_{0}=p_{e}$ (the pressure at the point $e$ ). Then we have

$$
g\left(t_{r}=t_{1}, p_{e}\right)=g\left(t_{1}, p_{a}\right)+\int_{a b c} v_{r}\left(p_{r}, t_{1}\right) d p_{r}+\int_{c d e} v_{r}\left(p_{r}, t_{1}\right) d p_{r},
$$

Since $g\left(t_{1}, p_{a}\right)=g\left(t_{1}, p_{e}\right)$, we have

$$
\int_{a b c} v_{r}\left(p_{r}, t_{1}\right) d p_{r}+\int_{c d e} v_{r}\left(p_{r}, t_{1}\right) d p_{r}=0
$$

or

$$
\int_{e d} v_{r}\left(p_{r}, t_{1}\right) d p_{r}+\int_{d c} v_{r}\left(p_{r}, t_{1}\right) d p_{r}=\int_{a b} v_{r}\left(p_{r}, t_{1}\right) d p_{r}+\int_{b c} v_{r}\left(p_{r}, t_{1}\right) d p_{r} .
$$

We note that

$$
\int_{e d} v_{r}\left(p_{r}, t_{r}\right) d p_{1}>0, \quad \int_{d c} v_{r}\left(p_{r}, t_{1}\right) d p_{r}=-\int_{c d} v_{r}\left(p_{r}, t_{1}\right) d p_{r}
$$

and

$$
\int_{b c} v_{r}\left(p_{r}, t_{1}\right) d p_{r}>0, \quad \int_{a b} v_{r}\left(p_{r}, t_{1}\right) d p_{r}=-\int_{b a} v_{r}\left(p_{r}, t_{1}\right) d p_{r} .
$$

Then we have

$$
\int_{e d} v_{r}\left(p_{r}, t_{1}\right) d p_{r}-\int_{c d} v_{r}\left(p_{r}, t_{1}\right) d p_{r}=\int_{b c} v_{r}\left(p_{r}, t_{1}\right) d p_{r}-\int_{b a} v_{r}\left(p_{r}, t_{1}\right) d p_{r},
$$

which means that the area of the region $e-d-c$ is the same as that of the region $a-b-c$. Note that

$$
p_{a}=p_{c}=p_{e}=p_{1} .
$$

It is only after the nominal (non-monotonic) isotherm has been truncated by this equal area construction that it represents a true physical isotherm.

In summary, In the $p_{\mathrm{r}}$ vs $v_{\mathrm{r}}$ phase diagram,
(i) The a-c-e- is the coexistence line ( $p_{r}=p_{1}$ and $\left.t_{r}=t_{1}\right)$ of the liquid phase and the gas phase.
(ii) The area $(a-b-c-a)$ is the same as the area $(c-d-e-c)$ [Maxwell construction].
(iii) K is the critical point $\left(p_{\mathrm{r}}=v_{\mathrm{r}}=t_{\mathrm{r}}=1\right)$.
(iv) The line KA and the line AB are the spinodal lines.

## 4.7

(a) Calculate the free energy $A(V, T)$ for 1 mol of a van der Waals gas.

Hint: Integrate - $1 P d V$ along an isotherm. Determine the unknown additive function of $T$ by requiring $A(V, T)$ to approach that of an ideal gas as $V \rightarrow \infty$, given in Problem 3.2.
(b) Show that $C_{V}$ of a van der Waals gas is a function of $T$ only.

Hint. Use $C_{V}=-T\left(\partial^{2} A / \partial T^{2}\right)_{V}\left(\right.$ Problem 3.1). Show $\left(\partial C_{V} / \partial V_{T}=0\right.$.

## ((Solution))

For ideal gas, the partition function is given by

$$
Z_{1}=n_{Q} V
$$

so the free energy $F$ is calculated as

$$
\begin{aligned}
F & =-k_{B} T \ln \left(\frac{Z_{1}^{N}}{N!}\right) \\
& =-k_{B} T\left(N \ln Z_{1}-\ln N!\right) \\
& \approx-k_{B} T\left(N \ln Z_{1}-N \ln N+N\right) \\
& =-k_{B} T N\left[\ln \left(\frac{Z_{1}}{N}\right)+1\right] \\
& =-k_{B} T N\left[\ln \left(\frac{n_{Q}}{n}\right)+1\right]
\end{aligned}
$$

where $n=\frac{N}{V}$, and $n_{Q}$ is the quantum concentration;

$$
n_{Q}=\left(\frac{m k_{B} T}{2 \pi \hbar^{2}}\right)^{3 / 2}=\left[\frac{m k_{B} T}{2 \pi \frac{h^{2}}{4 \pi^{2}}}\right]^{3 / 2}=\left[\frac{2 \pi m k_{B} T}{h^{2}}\right]^{3 / 2}=\frac{\left(2 \pi m k_{B} T\right)^{3 / 2}}{h^{3}},
$$

where $m$ is a mass of atom.

$$
\begin{aligned}
f & =\frac{F}{N}=-k_{B} T\left\{\ln \left[n_{Q}(v-b)\right]+1\right\}-\frac{a}{v} \\
& =-k_{B} T \ln (v-b)-\frac{a}{v}-k_{B} T\left[\ln \left(n_{Q}\right)+1\right] \\
& =-k_{B} T \ln (v-b)-\frac{a}{v}+\Phi(T)
\end{aligned}
$$

where

$$
\begin{aligned}
\Phi(T) & =-k_{B} T\left[\ln \left(n_{Q}\right)+1\right] \\
& =-k_{B} T\left\{\ln \left[\frac{\left(2 \pi m k_{B} T\right)^{3 / 2}}{h^{3}}\right]+1\right\} \\
& =-k_{B} T\left\{\ln T^{3 / 2}+\ln \frac{\left(2 \pi m k_{B}\right)^{3 / 2}}{h^{3}}+1\right\} \\
& =-k_{B} T\left(\ln T^{3 / 2}+\ln \alpha+1\right) \\
& =-k_{B} T\left(\frac{3}{2} \ln T+\ln \alpha+1\right)
\end{aligned}
$$

with the constant $\alpha$
$\alpha=\frac{\left(2 \pi m k_{B}\right)^{3 / 2}}{h^{3}}$.

In summary the Helmholtz free energy is obtained as

$$
f=-\frac{a}{v}-k_{B} T\left[\ln (v-b)+\frac{3}{2} \ln T+\ln \alpha+1\right] .
$$

The pressure $P$ is obtained as

$$
P=-\left(\frac{\partial F}{\partial V}\right)_{T, N}=-\left(\frac{\partial f}{\partial v}\right)_{T, N}=\frac{k_{B} T}{v-b}-\frac{a}{v^{2}},
$$

or more simply,

$$
\left(P+\frac{a}{v^{2}}\right)(v-b)=k_{B} T
$$

## ((van der Waals equation))

or

$$
P=-\frac{a}{v^{2}}+\frac{k_{B} T}{v-b} .
$$

Since $v=\frac{V}{N}$, the above van der Waals equation can be rewritten as

$$
\left(P+\frac{N^{2} a}{V^{2}}\right)(V-b N)=N k_{B} T .
$$

(b) The heat capacity

$$
\frac{C_{V}}{N}=-T\left(\frac{\partial^{2} f}{\partial T^{2}}\right)_{V}=\frac{3 k_{B}}{2}, \quad \text { which is constant. }
$$

or

$$
C_{V}=\frac{3 N k_{B}}{2}
$$

## 4.8

