G25.2651: Statistical Mechanics

Notes for Lecture 8

I. DISTRIBUTION FUNCTIONS AND PERTURBATION THEORY

A. General formulation

Recall the expression for the configurational partition function:

$$Z_N = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U(\mathbf{r}_1, \ldots, \mathbf{r}_N)}$$

Suppose that the potential U can be written as a sum of two contributions

$$U(\mathbf{r}_1, \ldots, \mathbf{r}_N) = U_0(\mathbf{r}_1, \ldots, \mathbf{r}_N) + U_1(\mathbf{r}_1, \ldots, \mathbf{r}_N)$$

where U_1 is, in some sense, small compared to U_0. An extra bonus can be had if the partition function for U_0 can be evaluated analytically.

Let

$$Z_N{}^{(0)} = \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)}$$

Then, we may express Z_N as

$$Z_N = \frac{Z_N{}^{(0)}}{Z_N{}^{(0)}} \int d\mathbf{r}_1 \cdots d\mathbf{r}_N e^{-\beta U_0(\mathbf{r}_1, \ldots, \mathbf{r}_N)} e^{-\beta U_1(\mathbf{r}_1, \ldots, \mathbf{r}_N)}$$

$$= Z_N{}^{(0)} \langle e^{-\beta U_1(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \rangle_0$$

where $\langle \cdots \rangle_0$ means average with respect to U_0 only. If U_1 is small, then the average can be expanded in powers of U_1:

$$\langle e^{-\beta U_1} \rangle_0 = 1 - \beta \langle U_1 \rangle_0 + \frac{\beta^2}{2!} \langle U_1^2 \rangle_0 - \frac{\beta^3}{3!} \langle U_1^3 \rangle_0 + \cdots$$

$$= \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \langle U_1^k \rangle_0$$

The free energy is given by

$$A(N, V, T) = -\frac{1}{\beta} \ln \left(\frac{Z_N}{N! \lambda^{3N}} \right) = -\frac{1}{\beta} \ln \left(\frac{Z_N{}^{(0)}}{N! \lambda^{3N}} \right) - \frac{1}{\beta} \ln \langle e^{-\beta U_1} \rangle_0$$

Separating A into two contributions, we have

$$A(N, V, T) = A^{(0)}(N, V, T) + A^{(1)}(N, V, T)$$

where $A^{(0)}$ is independent of U_1 and is given by

$$A^{(0)}(N, V, T) = -\frac{1}{\beta} \ln \left(\frac{Z_N{}^{(0)}}{N! \lambda^{3N}} \right)$$

and

$$A^{(1)}(N, V, T) = -\frac{1}{\beta} \ln \langle e^{-\beta U_1} \rangle_0$$

$$= -\frac{1}{\beta} \ln \langle \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \langle U_1^k \rangle_0$$

We wish to develop an expansion for $A^{(1)}$ of the general form

$$A^{(1)} = \sum_{k=1}^{\infty} \frac{(-\beta)^{k-1}}{k!} \omega_k$$

where ω_k are a set of expansion coefficients that are determined by the condition that such an expansion be consistent with $\ln \langle \sum_{k=0}^{\infty} (-\beta)^k \langle U_1^k \rangle_0 / k!$.

Using the fact that

$$\ln(1+x) = \sum_{k=1}^{\infty} (-1)^{k-1} \frac{x^k}{k}$$

we have that

$$-\frac{1}{\beta} \ln \left(\sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \langle U_1^k \rangle_0 \right) = -\frac{1}{\beta} \ln \left(1 + \sum_{k=0}^{\infty} \frac{(-\beta)^k}{k!} \langle U_1^k \rangle_0 \right)$$

$$= -\frac{1}{\beta} \sum_{k=1}^{\infty} (-1)^{k-1} \frac{1}{k} \left(\sum_{l=1}^{\infty} \frac{(-\beta)^l}{l!} \langle U_1^l \rangle_0 \right)^k$$

Equating this expansion to the proposed expansion for $A^{(1)}$, we obtain

$$\sum_{k=1}^{\infty} (-1)^{k-1} \frac{1}{k} \left(\sum_{l=1}^{\infty} \frac{(-\beta)^l}{l!} \langle U_1^l \rangle_0 \right)^k = \sum_{k=1}^{\infty} (-\beta)^k \frac{\omega_k}{k!}$$

This must be solved for each of the undetermined parameters ω_k, which can be done by equating like powers of β on both sides of the equation. Thus, from the β^1 term, we find, from the right side:

$$\text{Right Side}: \quad -\frac{\beta \omega_1}{1!}$$

and from the left side, the $l = 1$ and $k = 1$ term contributes:

$$\text{Left Side}: \quad -\frac{\beta \langle U_1 \rangle_0}{1!}$$

from which it can be easily seen that

$$\omega_1 = \langle U_1 \rangle_0$$

Likewise, from the β^2 term,

$$\text{Right Side}: \quad \frac{\beta^2}{2!} \omega_2$$

and from the left side, we see that the $l = 1, k = 2$ and $l = 2, k = 1$ terms contribute:

$$\text{Left Side}: \quad \frac{\beta^2}{2} \left(\langle U_1^2 \rangle_0 - \langle U_1 \rangle_0^2 \right)$$

Thus,

$$\omega_2 = \langle U_1^2 \rangle_0 - \langle U_1 \rangle_0^2$$

For β^3, the right sides gives:

$$\text{Right Side}: \quad -\frac{\beta^3}{3!} \omega_3$$

the left side contributes the $l = 1, k = 3$, $k = 2, l = 2$ and $l = 3, k = 1$ terms:

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$$\text{Left Side}: -\frac{\beta^3}{6}\langle U_1^3\rangle + (-1)^2 \frac{1}{3}\left(-\beta\langle U_1\rangle_0\right)^3 - \frac{1}{2}\left(-\beta\langle U_1\rangle_0 + \frac{1}{2}\beta^2\langle U_1^2\rangle\right)^2$$

Thus,

$$\omega_3 = \langle U_1^3\rangle_0 + 2\langle U_1\rangle_0^3 - 3\langle U_1\rangle_0\langle U_1^2\rangle_0$$

Now, the free energy, up to the third order term is given by

$$A = A^{(0)} + \omega_1 - \frac{\beta}{2}\omega_2 + \frac{\beta^2}{6}\omega_3\cdots$$

$$= -\frac{1}{\beta}\ln\left(\frac{Z_N^{(0)}}{N!\lambda^{3N}}\right) + \langle U_1\rangle_0 - \frac{\beta}{2}\left(\langle U_1^2\rangle_0 - \langle U_1\rangle_0^2\right) + \frac{\beta^2}{6}\left(\langle U_1^3\rangle_0 - 3\langle U_1\rangle_0\langle U_1^2\rangle_0 + 2\langle U_1\rangle_0^3\right) + \cdots$$

In order to evaluate $\langle U_1\rangle_0$, suppose that U_1 is given by a pair potential

$$U_1(\mathbf{r}_1, ..., \mathbf{r}_N) = \frac{1}{2}\sum_{i\neq j} u_1(|\mathbf{r}_i - \mathbf{r}_j|)$$

Then,

$$\langle U_1\rangle_0 = \frac{1}{Z_N^{(0)}}\int d\mathbf{r}_1\cdots d\mathbf{r}_N \frac{1}{2}\sum_{i\neq j} u_1(|\mathbf{r}_i - \mathbf{r}_j|)e^{-\beta U_0(\mathbf{r}_1,...,\mathbf{r}_N)}$$

$$= \frac{N(N-1)}{2Z_N^{(0)}}\int d\mathbf{r}_1 d\mathbf{r}_2 u_1(|\mathbf{r}_1 - \mathbf{r}_2|)\int d\mathbf{r}_3\cdots d\mathbf{r}_N e^{-\beta U_0(\mathbf{r}_1,...,\mathbf{r}_N)}$$

$$= \frac{N^2}{2V^2}\int d\mathbf{r}_1 d\mathbf{r}_2 u_1(|\mathbf{r}_1 - \mathbf{r}_2|)g_0^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$$

$$= \frac{\rho^2 V}{2}\int_0^\infty 4\pi r^2 u_1(r)g_0(r)dr$$

The free energy is therefore given by

$$A(N, V, T) = -\frac{1}{\beta}\ln\left(\frac{Z_N^{(0)}}{N!\lambda^{3N}}\right) + \frac{1}{2}\rho^2 V\int_0^\infty 4\pi r^2 u_1(r)g_0(r)dr - \frac{\beta}{2}\left(\langle U_1^2\rangle_0 - \langle U_1\rangle_0^2\right)\cdots$$

B. Derivation of the Van der Waals equation

As a specific example of the application of perturbation theory, we consider the Van der Waals equation of state. Let U_0 be given by a pair potential:

$$U_0(\mathbf{r}_1, ..., \mathbf{r}_N) = \frac{1}{2}\sum_{i\neq j} u_0(|\mathbf{r}_i - \mathbf{r}_j|)$$

with

$$u_0(r) = \begin{cases} 0 & r > \sigma \\ \infty & r \leq \sigma \end{cases}$$

This potential is known as the *hard sphere* potential. In the low-density limit, the radial distribution function can be shown to be given correctly by $g_0(r) \sim \exp(-\beta u_0(r))$ or

$$g_0(r) = \begin{cases} 1 & r > \sigma \\ 0 & r \leq \sigma \end{cases}$$

$$= \theta(r - \sigma)$$

$u_1(r)$ is taken to be some arbitrary attractive potential, whose specific form is not particularly important. Then, the full potential $u(r) = u_0(r) + u_1(r)$ might look like:
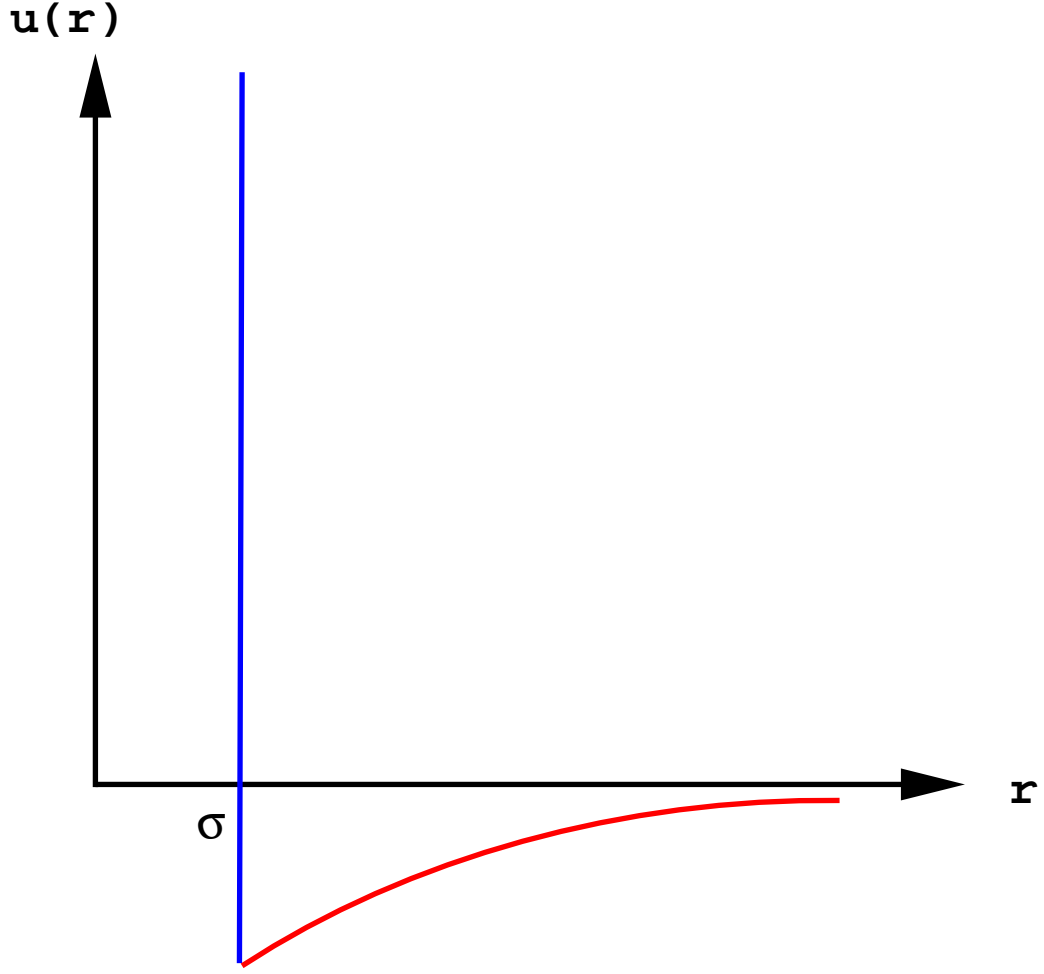
FIG. 1.

Now, the first term in $A^{(1)}$ is

$$A^{(1)} \approx = \frac{1}{2}\rho^2 V \int_0^\infty 4\pi r^2 u_1(r) g_0(r)$$

$$= \frac{1}{2}\rho^2 V \int_0^\infty 4\pi r^2 u_1(r) \theta(r - \sigma)$$

$$= 2\pi\rho^2 V \int_\sigma^\infty r^2 u_1(r) dr \equiv -aN\rho$$

where

$$a = -2\pi \int_\sigma^\infty dr r^2 u_1(r) > 0$$

is a number that depends on σ and the specific form of $u_1(r)$.

Since the potential $u_0(r)$ is a hard sphere potential, $Z_N{}^{(0)}$ can be determined analytically. If σ were 0, then u_0 would describe an ideal gas and

$$Z_N{}^{(0)} = V^N$$

However, because two particles may not approach each other closer than a distance σ between their centers, there is some excluded volume:
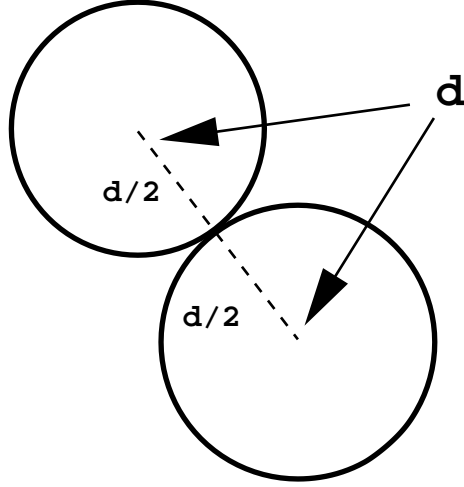
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FIG. 2.

If we consider two hard spheres at closest contact and draw the smallest imaginary sphere that contains both particles, then we find this latter sphere has a radius σ:
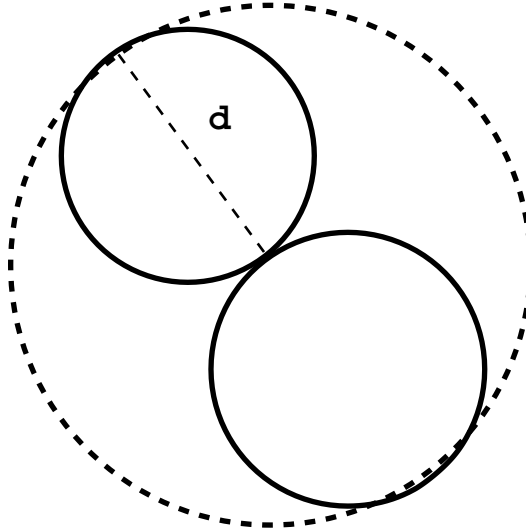

FIG. 3.

Hence the excluded volume for these two particles is

$$\frac{4}{3}\pi\sigma^3$$

and hence the excluded volume per particle is just half of this:

$$\frac{2}{3}\pi\sigma^3 \equiv b$$

Therefore Nb is the total excluded volume, and we find that, in the low density limit, the partition function is given approximately by

$$Z_N{}^{(0)} = (V - Nb)^N$$

Thus, the free energy is

$$A(N, V, T) \approx -\frac{1}{\beta} \ln \left[\frac{(V - Nb)^N}{N! \lambda^{3N}} \right] - \frac{aN^2}{V}$$

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If we now use this free energy to compute the pressure from

$$P = -\left(\frac{\partial A}{\partial V}\right)_{N,T}$$

we find that

$$\frac{P}{kT} = \frac{N}{V - Nb} - \frac{aN^2}{kTV^2}$$
$$= \frac{\rho}{1 - \rho b} - \frac{a\rho^2}{kT}$$

This is the well know Van der Waals equation of state. In the very low density limit, we may assume that $\rho b << 1$, hence

$$\frac{1}{1 - \rho b} \approx 1 + \rho b$$

Thus,

$$\frac{P}{kT} \approx \rho + \rho^2 \left(b - \frac{a}{kT}\right)$$

from which we can approximate the second virial coefficient:

$$B_2(T) \approx b - \frac{a}{kT} = \frac{2}{3}\pi\sigma^3 + \frac{2\pi}{kT}\int_\sigma^\infty dr r^2 u_1(r)$$

A plot of the isotherms of the Van der Waals equation of state is shown below:
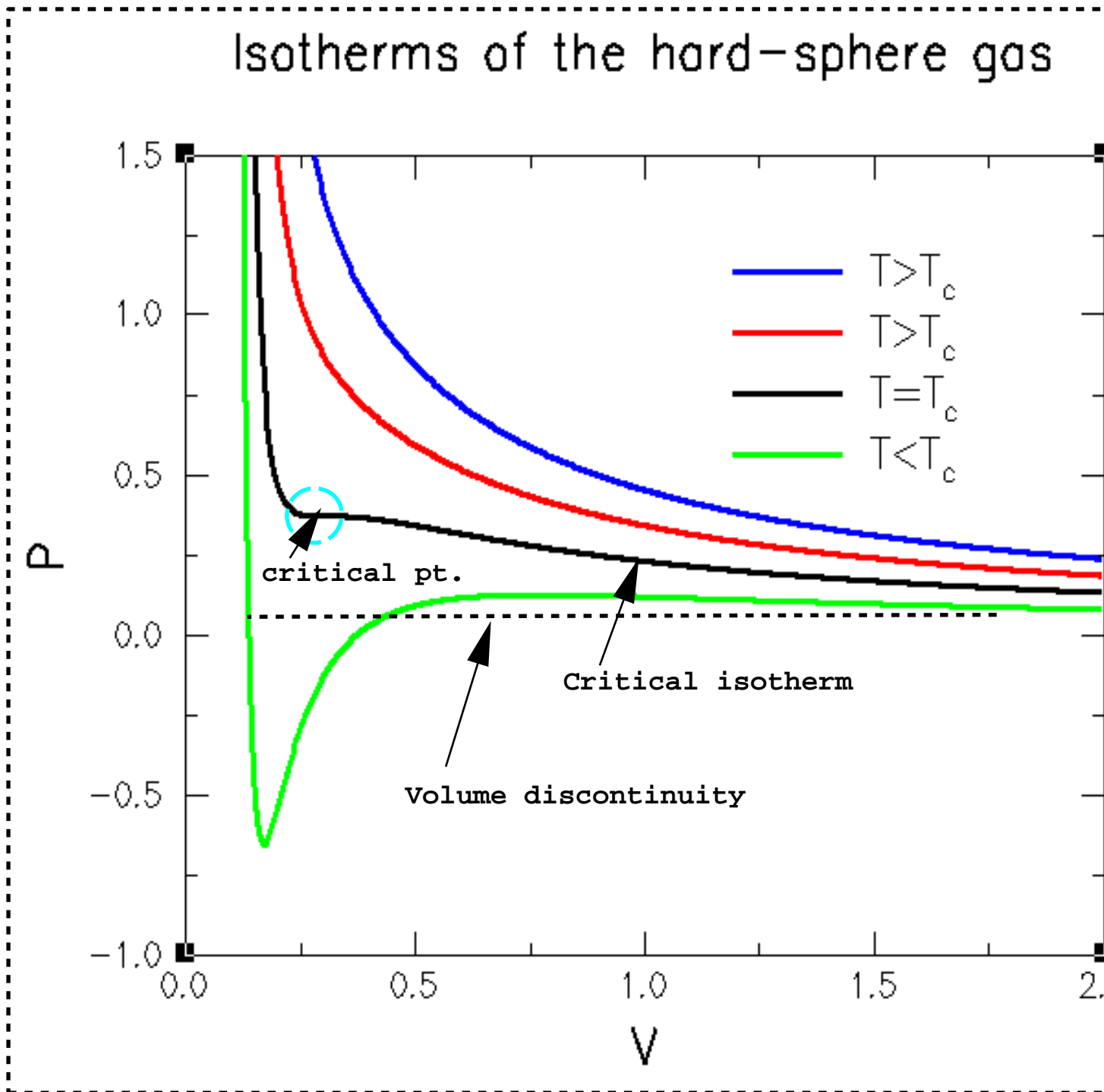
FIG. 4.

The red and blue isotherms appear similar to those of an ideal gas, i.e., there is a monotonic decrease of pressure with increasing volume. The black isotherm exhibits an unusual feature not present in any of the ideal-gas isotherms - a small region where the curve is essentially horizontal (flat) with no curvature. At this point, there is no change in pressure as the volume changes. Below this isotherm, the Van der Waals starts to exhibit unphysical behavior. The green isotherm has a region where the pressure decreases with decreasing volume, behavior that is not expected on physical grounds. What is observed experimentally, in fact, is that at a certain pressure, there is a dramatic, discontinuous change in the volume. This dramatic jump in volume signifies that a phase transition has occurred, in this case, a change from a gaseous to a liquid state. The dotted line shows this jump in the volume. Thus, the small

flat neighborhood along the black isotherm becomes larger on isotherms below this one. The black isotherm just represents a boundary between those isotherms along which no such phase transition occurs and those that exhibit phase transitions in the form of discontinuous changes in the volume. For this reason, the black isotherm is called the critical isotherm, and the point at which the isotherm is flat and has zero curvature is called a critical point.

A critical point is a point at which

$$\frac{\partial P}{\partial V} = 0, \qquad \frac{\partial^2 P}{\partial V^2} = 0$$

Using these two conditions, we can solve for the critical volume V_c and critical temperature T_c:

$$V_c = 3Nb \qquad kT_c = \frac{8a}{27b}$$

and the critical pressure is therefore

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

Using these values for the critical pressure, temperature and volume, we can show that the isothermal compressibility, given by

$$\kappa_{\mathrm{T}} = \frac{1}{V}\frac{\partial V}{\partial P}$$

diverges as the critical point is approached. To see this, note that

$$\left.\frac{\partial P}{\partial V}\right|_{V=V_c} = -\frac{NkT}{2N^2b^2} + \frac{2aN^2}{27N^3b^3} = -\frac{kT}{4Nb^2} + \frac{2a}{27Nb^3} = \frac{1}{4Nb^2}\left(\frac{8a}{27b} - kT\right) \sim (T - T_c)$$

Thus,

$$\kappa_{\mathrm{T}} \sim (T - T_c)^{-1}$$

It is observed that at a critical point, κ_{T} diverges, generally, as $|T - T_c|^{-\gamma}$. To determine the heat capacity, note that

$$Q(N, V, T) = e^{-\beta A(N,V,T)} = \frac{(V - Nb)^N}{N!\lambda^{3N}}e^{\beta aN^2/V}$$

so that

$$\begin{aligned}
E &= -\frac{\partial}{\partial \beta}\ln Q(N, V, T)\\
&= -\frac{\partial}{\partial \beta}\left[N\ln(V - Nb) - \ln N! - 3N\ln\lambda + \frac{\beta aN^2}{V}\right]\\
&= \frac{3N}{\lambda}\frac{\partial\lambda}{\partial\beta} + \frac{aN^2}{V}\\
&= \frac{3N}{\lambda}\frac{\lambda}{2\beta} + \frac{aN^2}{V}\\
&= \frac{3}{2}NkT + \frac{aN^2}{V}
\end{aligned}$$

Then, since

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

it follows that

$$C_V = \frac{3}{2}Nk \sim |T - T_c|^0$$

The heat capacity is observed to diverge as $|T - T_c|^{-\alpha}$. Exponents such as α and γ are known as *critial exponents*.

Finally, one other exponent we can easily determine is related to how the pressure depends on density near the critical point. The exponent is called δ, and it is observed that

$$\frac{P}{kT} \sim \text{const} + C(\rho - \rho_c)^\delta$$

What does our theory predict for δ? To determine δ we expand the equation of state about the critical density and temperature:

$$\frac{P}{kT} = \frac{P_c}{kT_c} + \frac{1}{kT_c}\left.\frac{\partial P}{\partial \rho}\right|_{\rho=\rho_c}(\rho - \rho_c) + \frac{1}{2kT_c}\left.\frac{\partial^2 P}{\partial \rho^2}\right|_{\rho=\rho_c}(\rho - \rho_c)^2 + \frac{1}{6kT_c}\left.\frac{\partial^3 P}{\partial \rho^3}\right|_{\rho=\rho_c}(\rho - \rho_c)^3 + \cdots$$

$$= \frac{P_c}{kT_c} + \frac{1}{kT_c}\left.\frac{\partial P}{\partial V}\frac{\partial V}{\partial \rho}\right|_{\rho=\rho_c}(\rho - \rho_c) + \frac{1}{2kT_c}\left[\frac{\partial^2 P}{\partial V^2}\left(\frac{\partial V}{\partial \rho}\right)^2 + \frac{\partial P}{\partial V}\frac{\partial^2 V}{\partial \rho^2}\right]\Bigg|_{\rho=\rho_c}(\rho - \rho_c)^2 + \frac{1}{6kT_c}\left.\frac{\partial^3 P}{\partial \rho^3}\right|_{\rho=\rho_c}(\rho - \rho_c)^3 + \cdots$$

The second and third terms vanish by the conditions of the critical point. The third derivative term can be worked out straightforwardly and does not vanish. Rather

$$\frac{1}{kT_c}\left.\frac{\partial^3 P}{\partial \rho^3}\right|_{\rho=\rho_c} = \frac{243}{8}b^2 \neq 0$$

Thus, we see that, by the above expansion, $\delta = 3$.

The behavior of these quantities near the critical temperature determine three critical exponents. To summarize the results, the Van der Waals theory predicts that

$$\alpha = 0 \qquad \gamma = 1 \qquad \delta = 3$$

The determination of critical exponents such as these is an active area in statistical mechanical research. The reason for this is that such exponents can be grouped into *universality classes* – groups of systems with exactly the same sets of critical exponents. The existence of universality classes means that very different kinds of systems exhibit essentially the same behavior at a critical point, a fact that makes the characterization of phase transitions via critical exponents quite general. The values obtained above for α, γ and δ are known as the *mean-field* exponents and shows that the Van der Waals theory is really a mean field theory. These exponents do not agree terribly well with experimental values ($\alpha = 0.1, \gamma = 1.35, \delta = 4.2$). However, the simplicty of mean-field theory and its ability to give, at least, qualitative results, makes it, nevertheless, useful. To illustrate universality classes, it can be shown that, within mean field theory, the Van der Waals gas/liquid and a magnetic system composed of spins at particular lattice sites, which composes the so called Ising model, have exactly the same mean field theory exponents, despite the completely different nature of these two systems.

Another problem with the Van der Waals theory that is readily apparent is the fact that it predicts $\partial P/\partial V > 0$ for certain values of the density ρ. Such behavior is unstable. Possible ways of improving the approximations used are the following:

1. Improve the approximation to $g_0(r)$.

2. Choose a better zeroth order potential $U_0(\mathbf{r}_1, ..., \mathbf{r}_N)$.

3. Go to a higher order in perturbation theory.

Barker and Henderson have shown that going to second order in perturbation theory (see discussion in McQuarrie's book, chapter 14), yields well converged results for a square well fluid, compared to "exact" results from a molecular dynamics simulation.