Chapter 4 Phase Transitions

4.1. Phenomenology

4.1.1 Basic ideas

Partition function

$$Z = \sum_i e^{-\varepsilon_i/kT}.$$

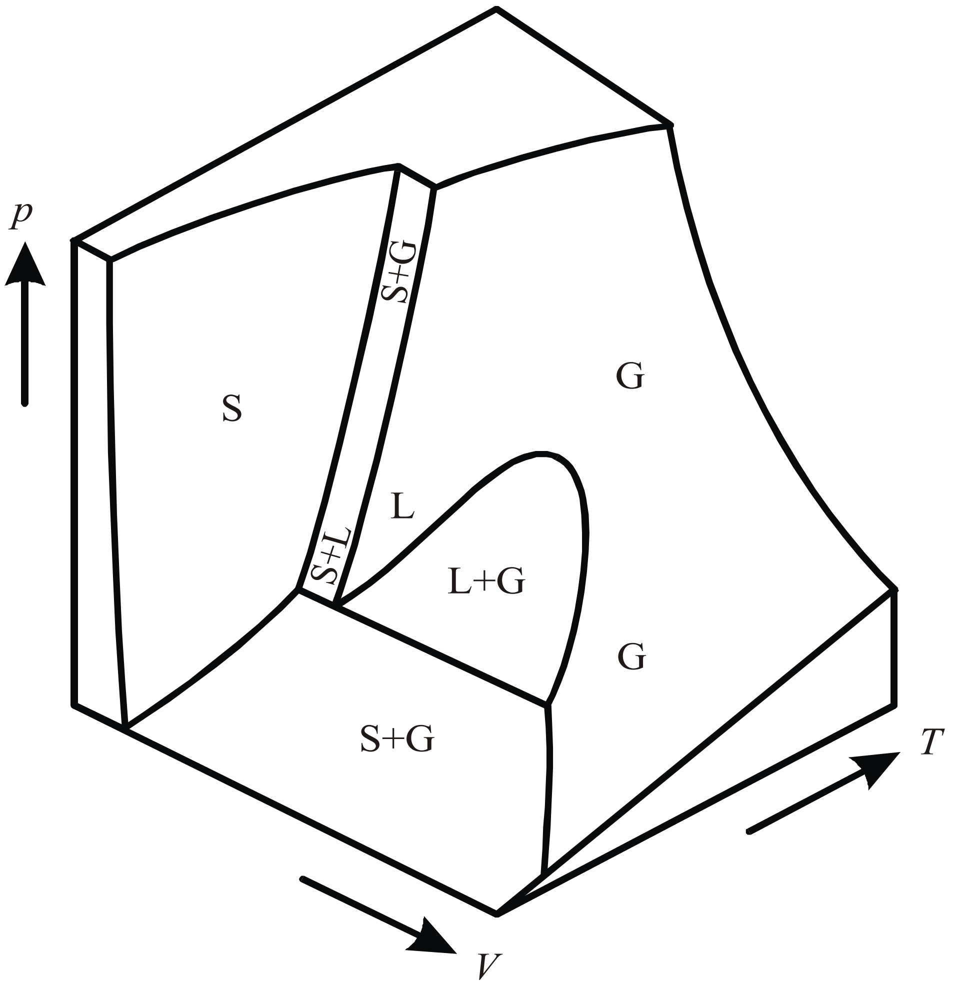
Does Z contain the information about a phase transition?

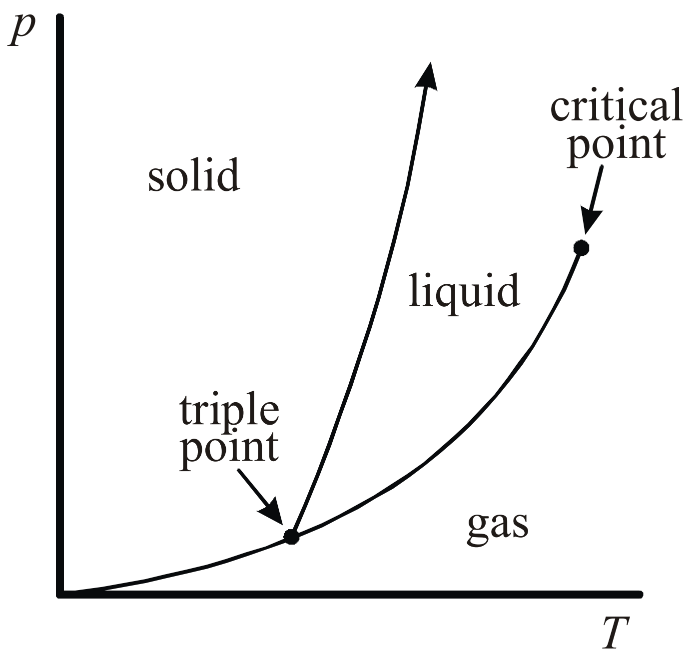
Answer given by H. Kramers around 1937/1938 — Thermodynamic limit

Formal demonstration by Lee and Yang 1952, simplification Fisher 1965.

Our basic problem: diverse range of phenomena, how to find a common language/description. Culmination/unification in Landau theory.

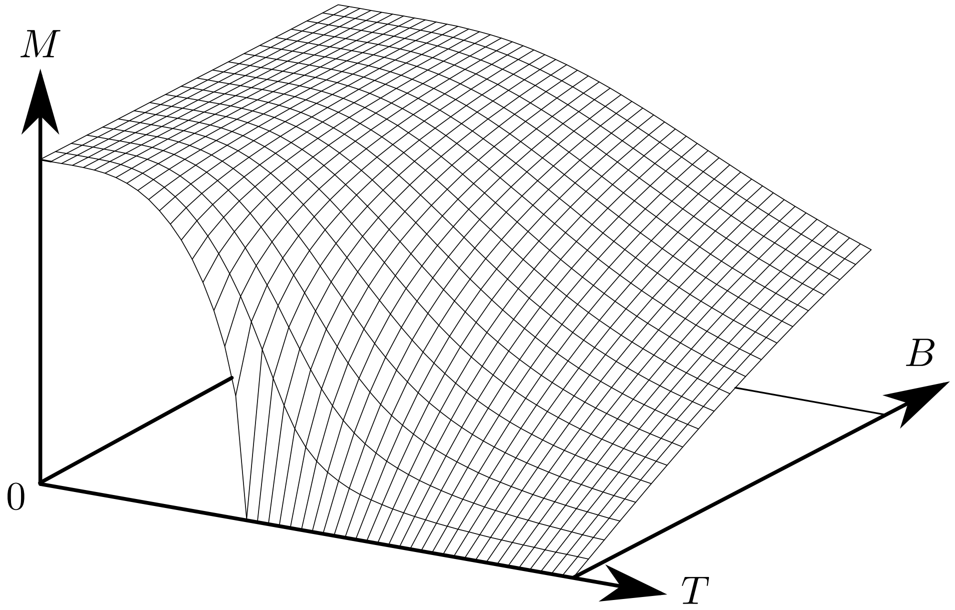
4.1.2 Phase diagrams

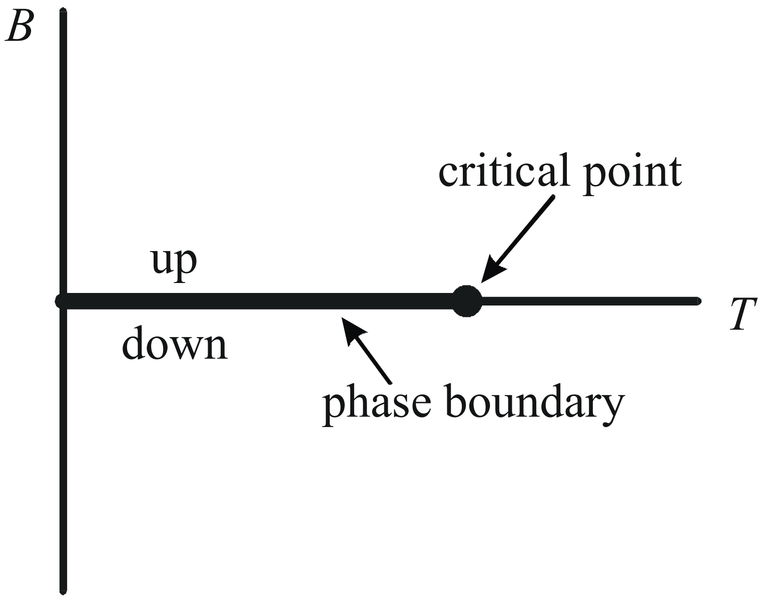




V is the extensive variable

P V T system





M is the extensive variable

magnetic system

4.1.3 Symmetry

• Crystal	Translational symmetry
• Ferromagnet	Rotational (time reversal) symmetry
• Ferroelectric	Inversion symmetry
• Superfluid	Gauge symmetry

4.1.4 Order of phase transitions (1st use of the word "order")

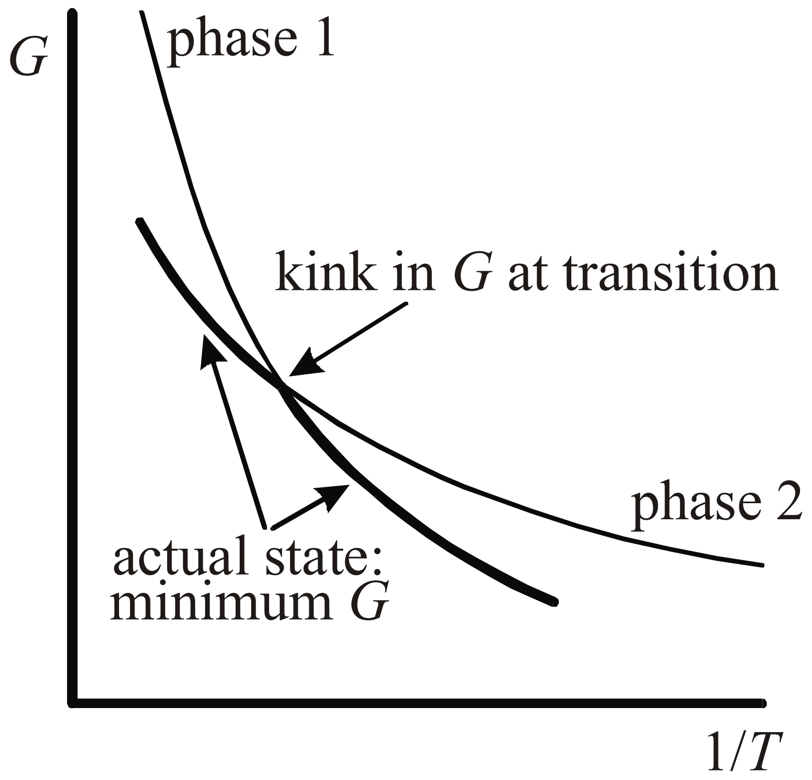
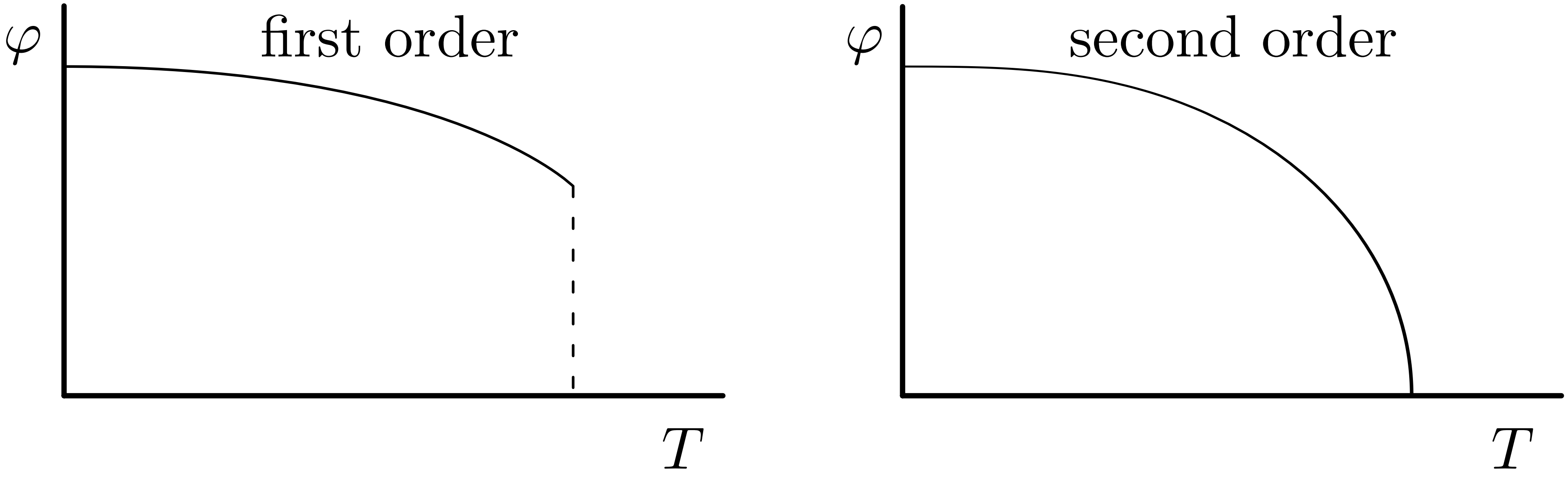


Fig. 4.5 Variation of Gibbs free energy for two phases

4.1.5 The order parameter (2nd use of the word "order")

System	*Order parameter*		
● Ferromagnet	magnetisation	$\mathbf{M}$	vector
● Ferroelectric	polarisation along displacement axis	P	Scalar !!!
● Fluid	density difference	$(n - n_c)$	real scalar
● Superfluid ^{4}He	ground state wavefunction	Ψ_0	complex scalar
● Superconductor	pair wavefunction	Ψ_s	complex scalar
● Ising	Ising ‘magnetisation’	m	real scalar
● Binary alloy	species concentration	x	real scalar

In terms of the order parameter . . . . . order order!



Order parameter in first and second order transitions

4.1.6 Conserved and non-conserved order parameters

System	*Order parameter*			*Section*
• Ferromagnet	magnetisation	$\mathbf{M}$	non-cons.	4.3
• Ferroelectric	polarisation	P	non-cons.	4.6
• Fluid	density difference	$(n - n_{\mathrm{c}})$	conserved	4.2
• Superfluid ^{4}He	ground state wavefunction	Ψ_0	non-cons.	
• Superconductor	pair wavefunction	Ψ_{s}	non-cons.	
• Ising	Ising 'magnetisation'	m	non-cons.	4.4
• Binary alloy	species concentration	x	conserved	4.7

4.1.7 Critical exponents

In terms of the reduced temperature

$$t = \frac{T - T_\mathrm{c}}{T_\mathrm{c}}$$

they are defined (using the ferromagnet variables for example) through

$$\text{heat capacity} \quad C \sim |t|^{-\alpha}$$

$$\text{order parameter} \quad M \sim |t|^{\beta}$$

$$\text{susceptibility} \quad \chi \sim |t|^{-\gamma}$$

$$\text{equation of state at } T_\mathrm{c} \quad M \sim |B|^{1/\delta}$$

There are two more critical exponents, which are connected with the spatial variation of fluctuations in the order as the critical point is approached…………

The spatial correlation function for the order parameter is written as

$$\langle M(r)M(0)\rangle \sim r^{-p}e^{-r/l}$$

where M (in the ferromagnetic case) is the magnetisation per unit volume. From this we obtain two more exponents, ν and η. These describe the divergence in the correlation length l and the power law decay p that remains at $t = 0$, when l has diverged. The exponents are defined through

correlation length $l \sim |t|^{-\nu}$

power law decay at T_c $p = d - 2 + \eta$

where d is the dimensionality of the system.

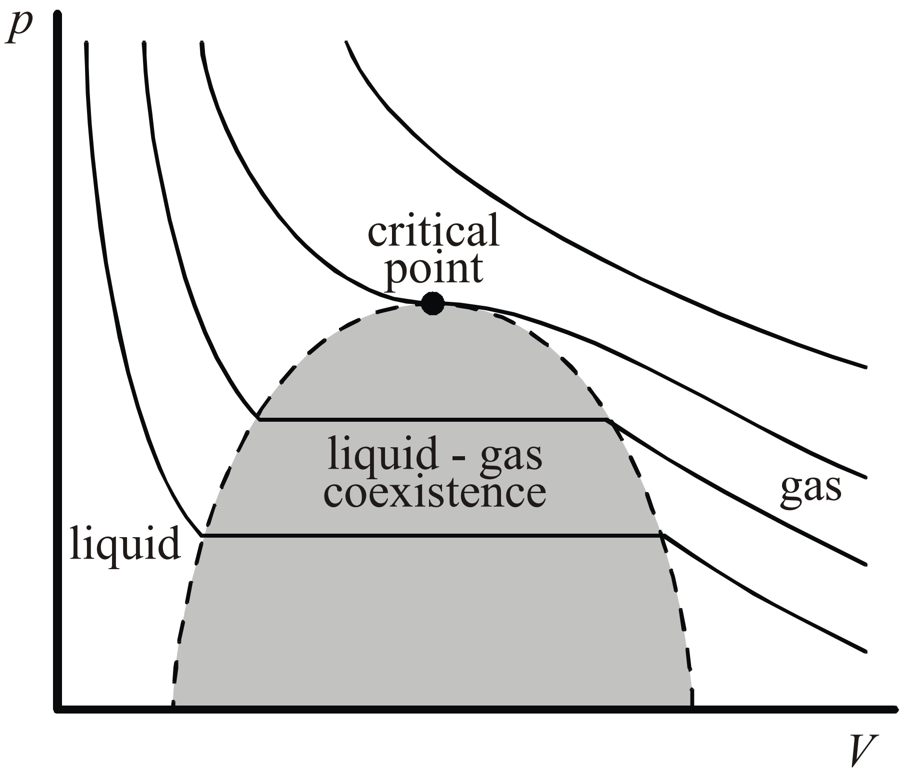
4.1.8 Scaling theory

$\gamma=\nu\left(2-\eta\right)$	Fisher law
$\alpha+2\beta+\gamma=2$	Rushbrooke law
$\gamma=\beta\left(\delta-1\right)$	Widom law
$\nu d=2-\alpha$	Josephson law

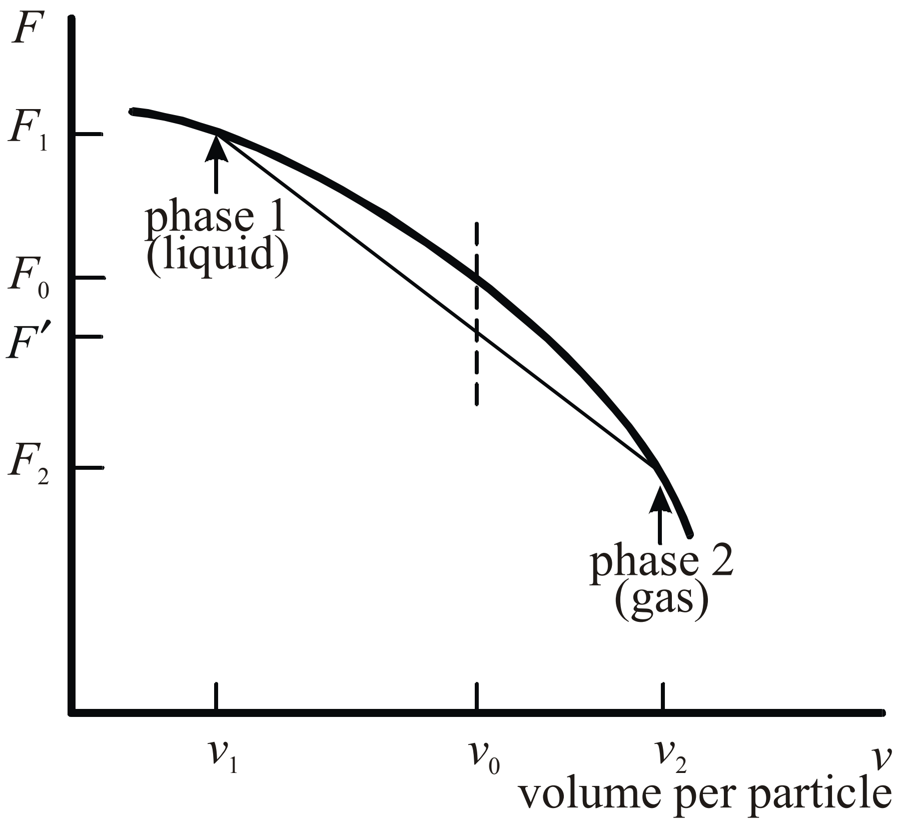
The experimental verification of these results is strong evidence in favour of the scaling hypothesis. Thus it would appear that the correlation length *is* the only length of importance in the vicinity of the critical point. A consequence of the hypothesis is that only two critical exponents need be calculated for a specific system. Note the Josephson law is the only one to make explicit mention of the spatial dimensionality d.

4.2 First order transition – an example

4.2.1 Coexistence



Coexistence region, showing p-V isotherms for liquid–gas system



Helmholtz free energy curve

Thus if a fraction α_1 of the particles is in regions of specific volume v_1 and a fraction $\alpha_2 = 1 - \alpha_1$ in regions of specific volume v_2 then

$$v_1\alpha_1 + v_2\alpha_2 = v_0$$

so that the fractions are given by

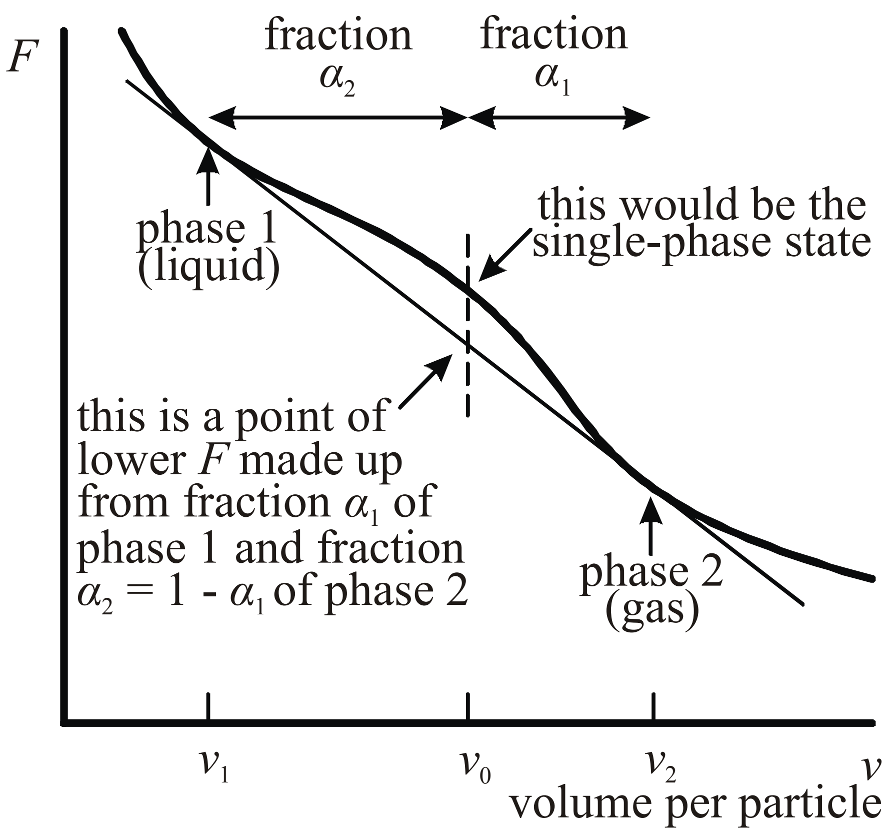
$$\alpha_1 = \frac{v_2 - v_0}{v_2 - v_1}, \qquad \alpha_2 = \frac{v_0 - v_1}{v_2 - v_1}.$$

Then the free energy of the inhomogeneous system will be given by

$$\begin{aligned} F &= \alpha_1 F_1 + \alpha_2 F_2 \\ &= \frac{v_2 F_1 - v_1 F_2}{v_2 - v_1} - \frac{F_1 - F_2}{v_2 - v_1} v_0. \end{aligned}$$

v_1, v_2 fixed

linear in v_0



Double tangent construction for phase coexistence

$$\mathrm{d}F = -S\mathrm{d}T - p\mathrm{d}V$$

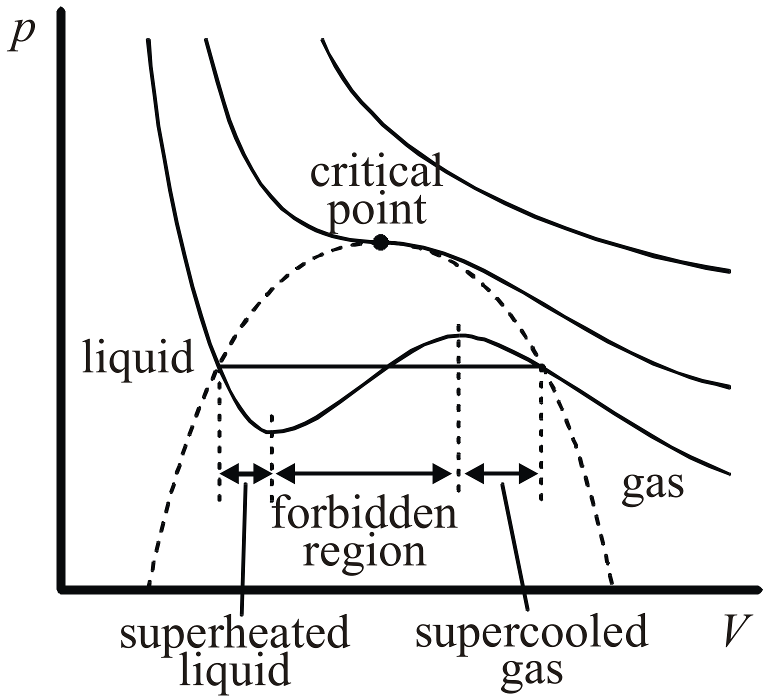
so that

$$p = -\left.\frac{\partial F}{\partial V}\right|_T;$$

equality of pressure.

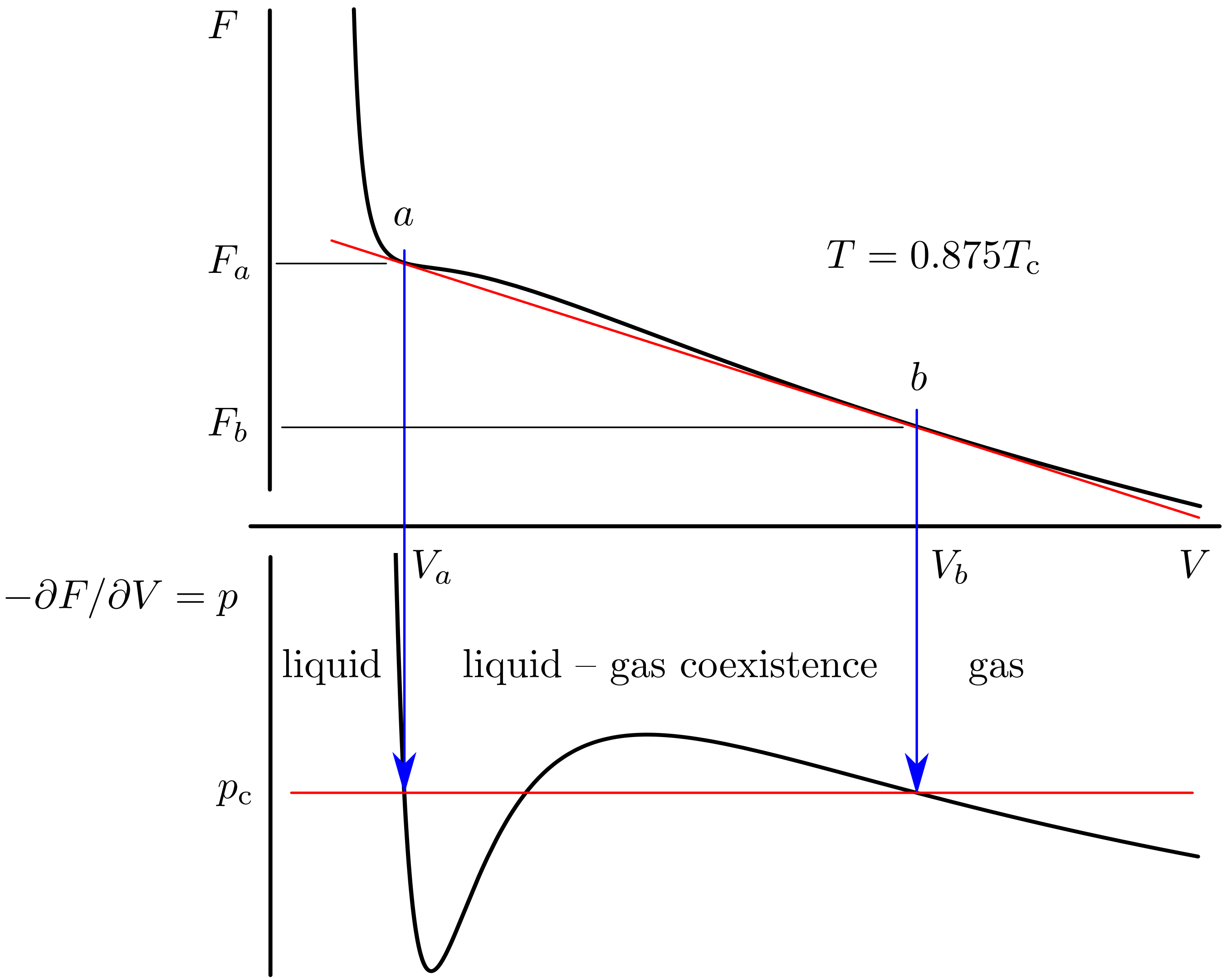
4.2.2 Van der Waals fluid

$$\left(p+\frac{aN^2}{V^2}\right)(V-Nb)=NkT$$



Isotherms of the van der Waals equation

4.2.3 The Maxwell construction



$$F_b = F_a + \int_{V_a}^{V_b} \left.\frac{\partial F}{\partial V}\right|_T \mathrm{d}V$$

$$= F_a - \int_{V_a}^{V_b} p\,\mathrm{d}V.$$

Integral independent of path:

$$\int_{V_a}^{V_b} p\,\mathrm{d}V = \int_{V_a}^{V_b} p\,\mathrm{d}V.$$

so that

4.2.4 The critical point

$$\left.\frac{\partial p}{\partial V}\right|_T = 0 \quad \text{and} \quad \left.\frac{\partial^2 p}{\partial V^2}\right|_T = 0 \, .$$

$$V_\mathrm{c} = 3Nb, \qquad p_\mathrm{c} = \frac{a}{27b^2}, \qquad kT_\mathrm{c} = \frac{8a}{27b} \, .$$

-- Elegant derivation of Stanley.

4.2.5 Corresponding states

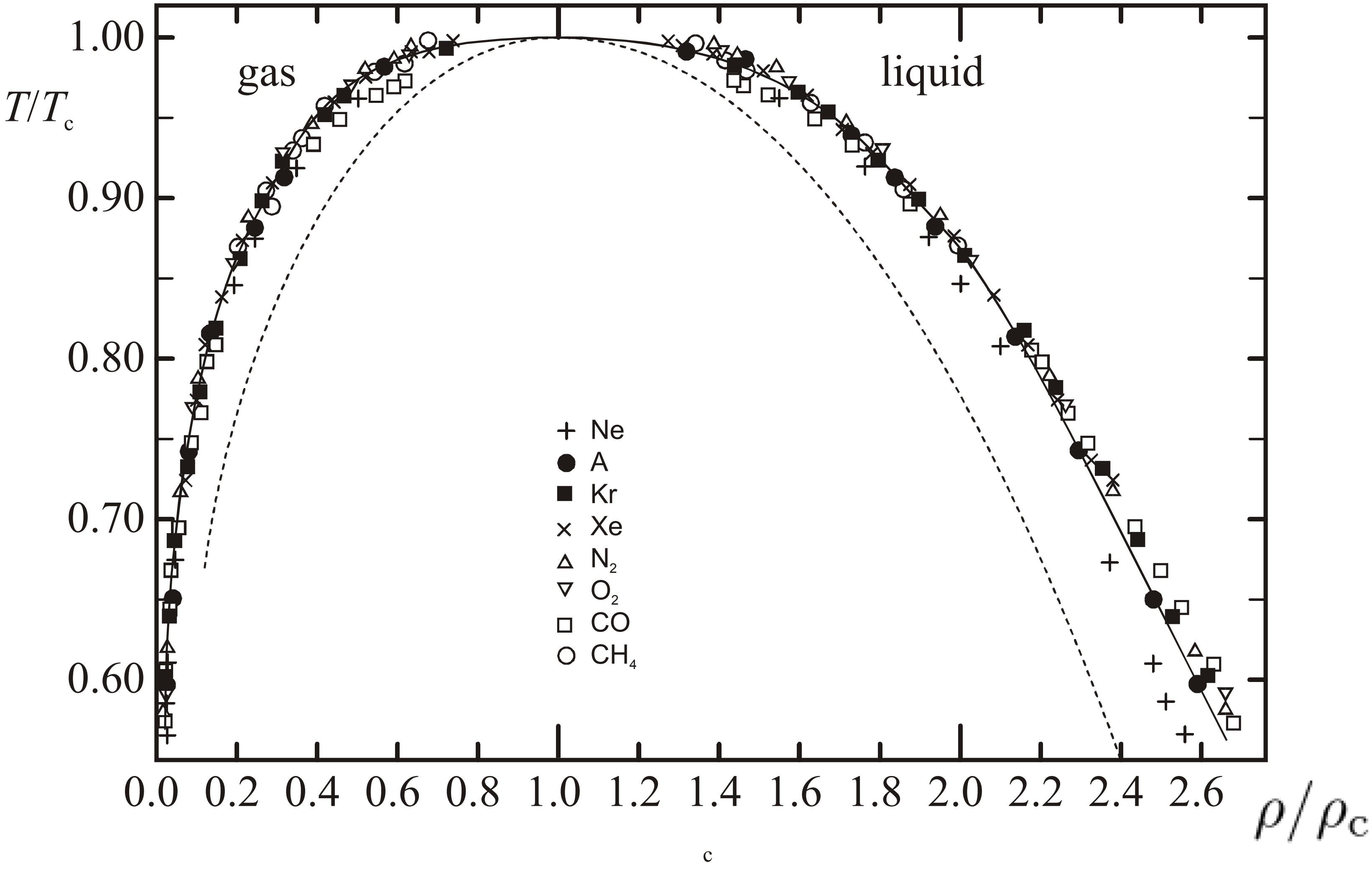
$$v = \frac{V}{V_\mathrm{c}}, \qquad \pi = \frac{p}{p_\mathrm{c}}, \qquad t = \frac{T}{T_\mathrm{c}}$$

then the van der Waals equation takes on the *universal* form:

$$\left(\pi + \frac{3}{v^2}\right)\left(v - \frac{1}{3}\right) = \frac{8t}{3}\,.$$

'Critical compressibility ratio' $z_\mathrm{c} = p_\mathrm{c}V_\mathrm{c} / NkT_\mathrm{c}$ is predicted to have the universal value 3/8 = 0.375 for all liquid–gas systems.

	^{4}He	Ne	A	Kr	Xe	N_2	O_2	CO	CH_4
$p_\mathrm{c}V_\mathrm{c}/NkT_\mathrm{c}$	0.308	0.305	0.290	0.291	0.290	0.291	0.292	0.294	0.290



Liquid - gas coexistence

Guggenheim's formula Solid line

$$\frac{\rho_\mathrm{l}-\rho_\mathrm{c}}{\rho_c}=\frac{7}{4}\left(1-\frac{T}{T_\mathrm{c}}\right)^{1/3}+\frac{3}{4}\left(1-\frac{T}{T_\mathrm{c}}\right)$$

$$\frac{\rho_\mathrm{c}-\rho_\mathrm{g}}{\rho_c}=\frac{7}{4}\left(1-\frac{T}{T_\mathrm{c}}\right)^{1/3}-\frac{3}{4}\left(1-\frac{T}{T_\mathrm{c}}\right)$$

Order parameter
critical exponent
$\beta = 1/3$

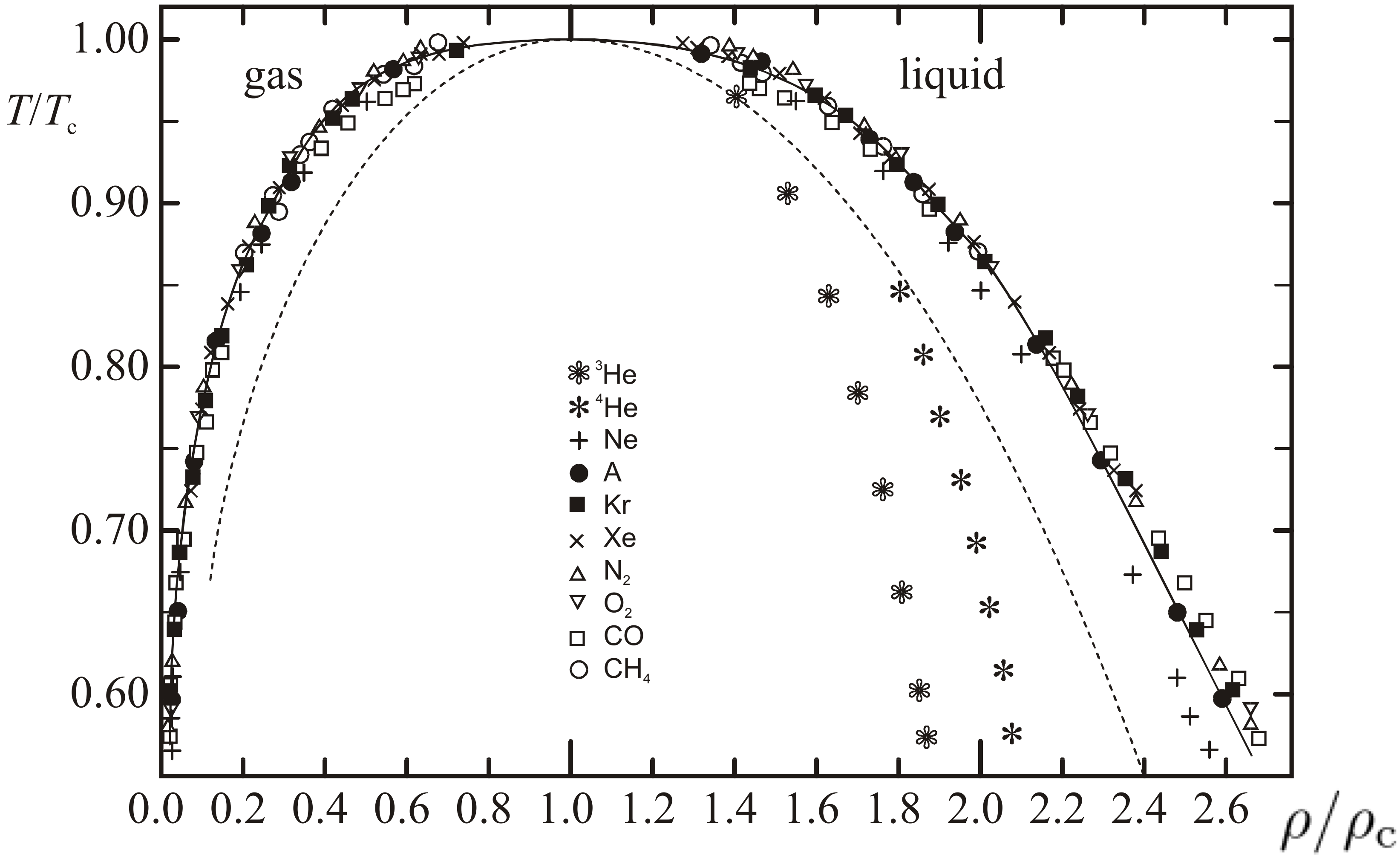
From van der Waals equation (Maxwell construction) Dashed line

$$\frac{\rho_\mathrm{l}-\rho_\mathrm{c}}{\rho_c}=2\left(1-\frac{T}{T_\mathrm{c}}\right)^{1/2}+\frac{2}{5}\left(1-\frac{T}{T_\mathrm{c}}\right)+\ldots$$

$$\frac{\rho_\mathrm{c}-\rho_\mathrm{g}}{\rho_c}=2\left(1-\frac{T}{T_\mathrm{c}}\right)^{1/2}-\frac{2}{5}\left(1-\frac{T}{T_\mathrm{c}}\right)+\ldots$$

Order parameter
critical exponent
$\beta = 1/2$

4.2.7 Quantum mechanical effects



Liquid - gas coexistence including data for helium

De Boer parameter - measure of “quantum-ness”

The breakdown of Corresponding States occurs as a consequence of quantum effects; this happens when the deBroglie wavelength λ becomes larger than the size of the particles. Then it is no longer appropriate to treat the particles as classical objects since their “extent” is determined by quantum mechanics.

A particle of mass m and energy ε has a momentum $p = \sqrt{2m\varepsilon}$ and a de Broglie wavelength $\lambda = h/\sqrt{2m\varepsilon}$. This is compared with the particle’s size σ. The ratio (apart from a factor of $\sqrt{2}$) is known as the de Boer parameter Λ^*:

$$\Lambda^* = \frac{h}{\sigma\sqrt{m\varepsilon}} .$$

When $\Lambda^* \ll 1$ the particles are “classical”.

When $\Lambda^* \gtrsim 1$ the particles are “quantum”.

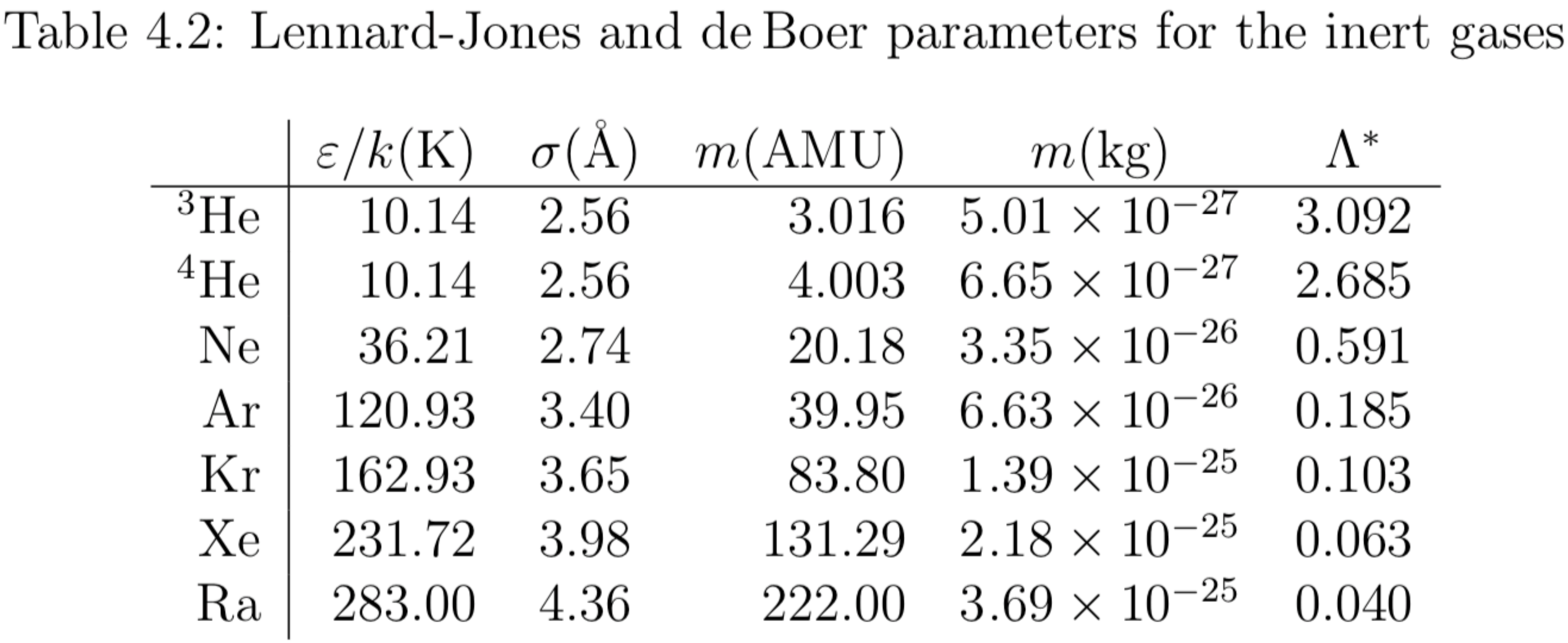


Table 4.2: Lennard-Jones and de Boer parameters for the inert gases

	ε/k(K)	σ(Å)	m(AMU)	m(kg)	Λ^*
^{3}He	10.14	2.56	3.016	5.01×10^{-27}	3.092
^{4}He	10.14	2.56	4.003	6.65×10^{-27}	2.685
Ne	36.21	2.74	20.18	3.35×10^{-26}	0.591
Ar	120.93	3.40	39.95	6.63×10^{-26}	0.185
Kr	162.93	3.65	83.80	1.39×10^{-25}	0.103
Xe	231.72	3.98	131.29	2.18×10^{-25}	0.063
Ra	283.00	4.36	222.00	3.69×10^{-25}	0.040