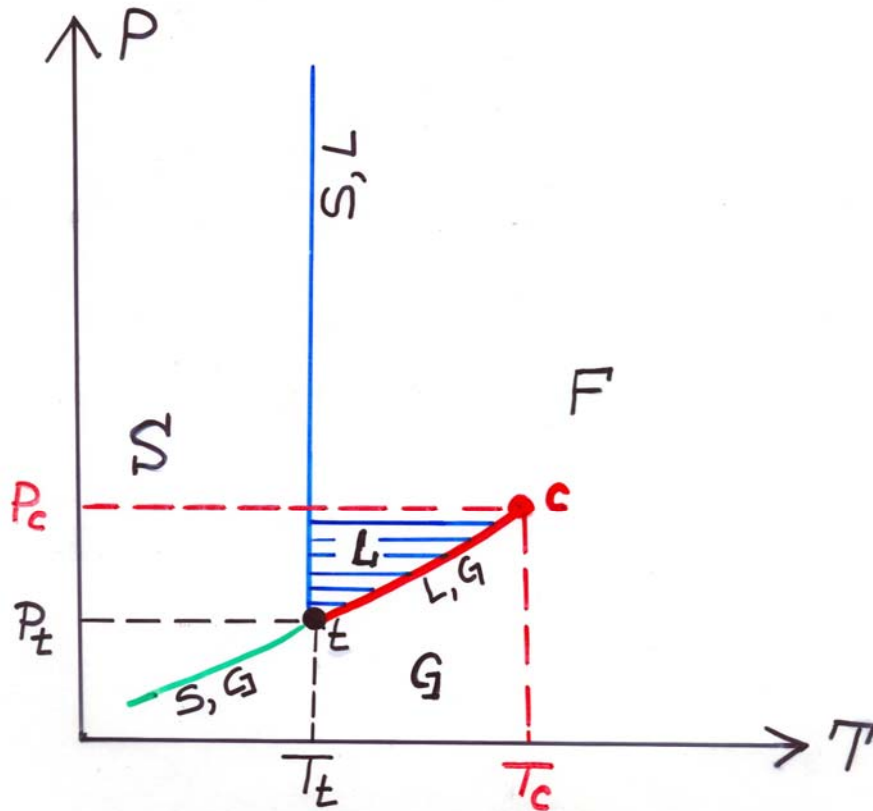


The Program

- Lecture 1: Phase transitions in atomic and molecular systems
- Lecture 2: Colloids as atoms
- Lecture 3: Hard spheres
- Lecture 4: Hard spheres + attraction
- Lecture 5: Rods
- Lecture 6: Platelets

PHASE TRANSITIONS IN SIMPLE ATOMIC (AND MOLECULAR) SYSTEMS



<u>Argon</u>	<u>Critical Point</u>	$T_c = 151 \text{ K}$	$P_c = 48 \text{ atm}$
	<u>Triple Point</u>	$T_t = 85 \text{ K}$	$P_t = 0.8 \text{ atm}$

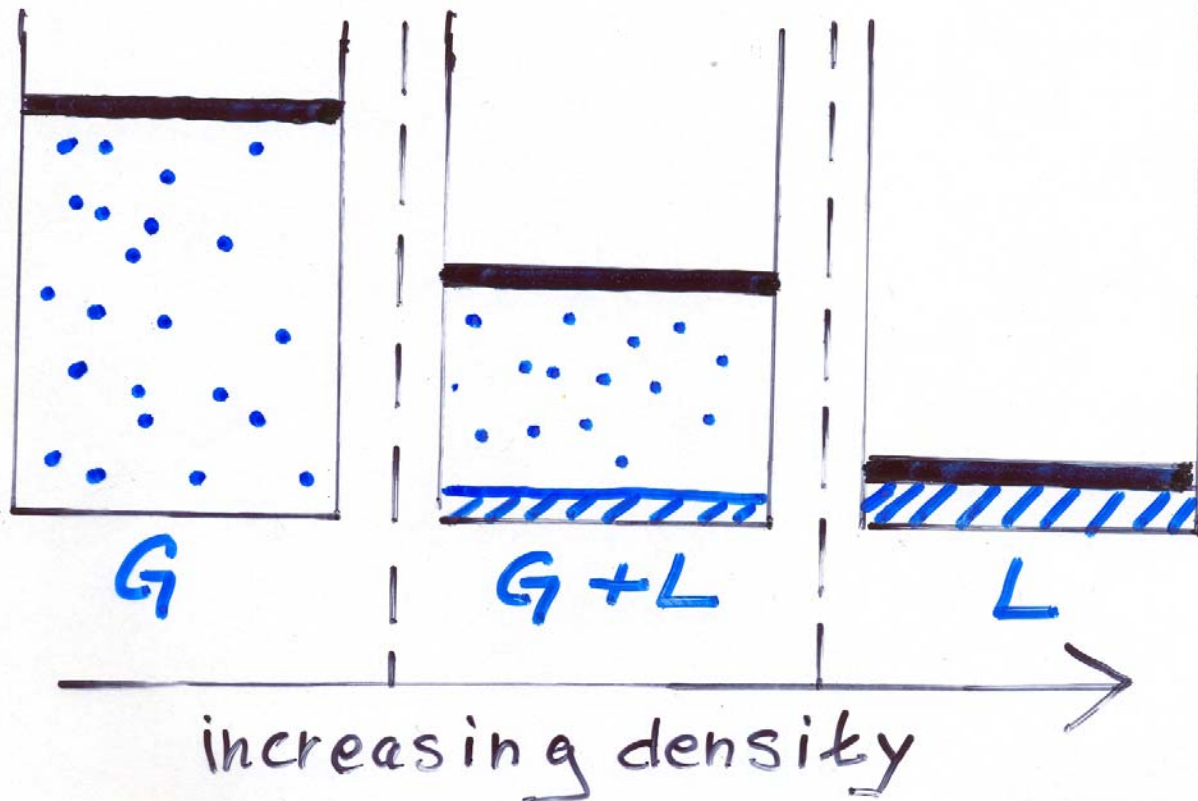
$$T_c / T_t = 1.8$$

<u>Water</u>	<u>Critical Point</u>	$T_c = 647 \text{ K}$	$P_c = 218 \text{ atm}$
	<u>Triple Point</u>	$T_t = 273 \text{ K}$	$P_t = 0.006 \text{ atm}$

$$T_c / T_t = 2.4$$

PHASE TRANSITIONS

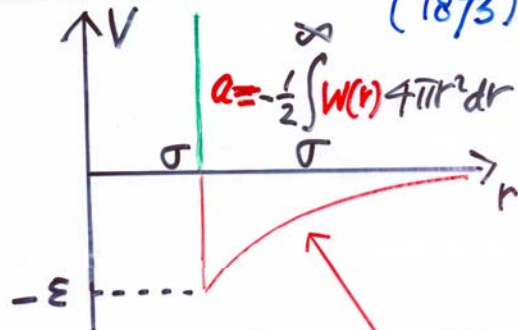
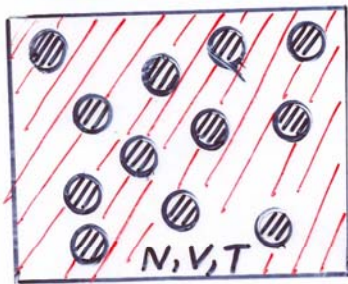
CONDENSATION



CONDENSATION GAS-LIQUID

The essential mechanism of condensation is the competition between the liquid configurations which are favoured by their low energy and gaseous configurations which have a high entropy

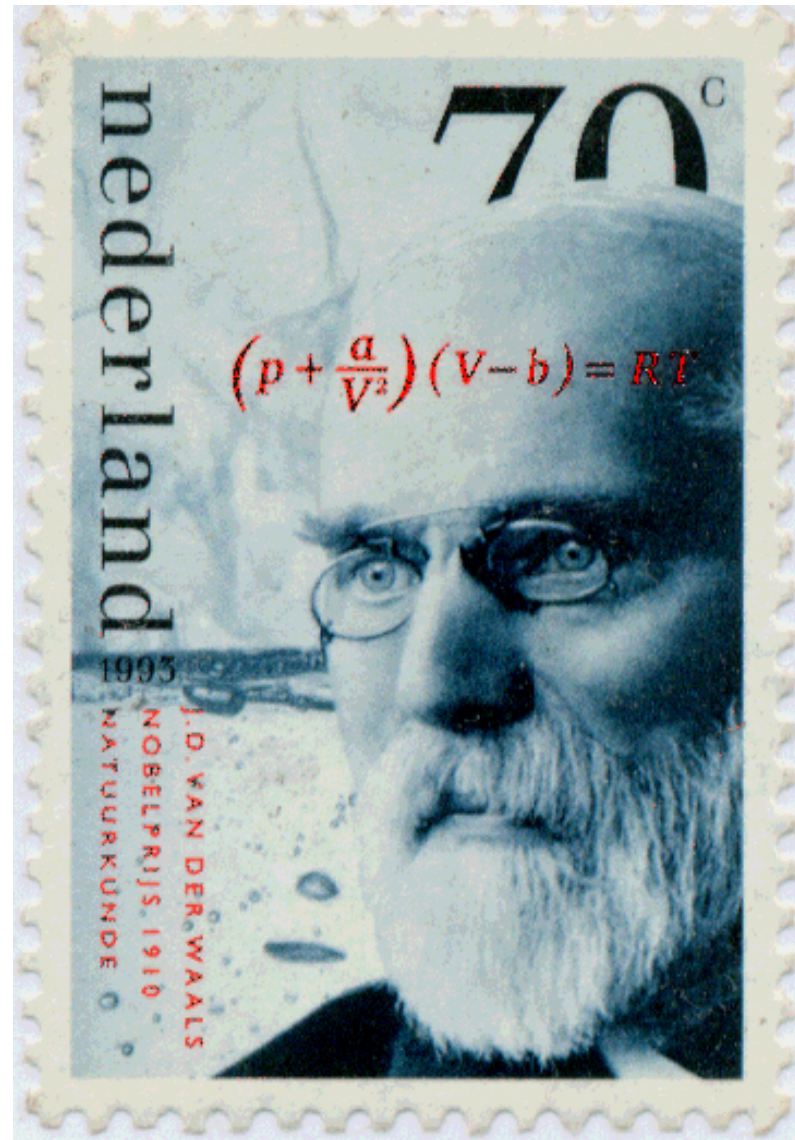
This competition is correctly described by the Van der Waals model (1873)



$$F = F_{HS} + \frac{1}{2} N \psi \quad \psi = -2a \frac{N}{V}$$

$$P = -\frac{\partial F}{\partial V} = P_{HS} - a \left(\frac{N}{V}\right)^2$$
$$\mu = \frac{\partial F}{\partial N} = \mu_{HS} - 2a \frac{N}{V}$$

Van der Waals Mean Field



Hard sphere equation of state - Fluid

Virial Expansion (J.E. Mayer 1930's)

$$\frac{P}{gkT} = 1 + B_2 g + B_3 g^2 + B_4 g^3 + \dots$$

<u>Exact</u>	<u>Approximation</u>
$B_2 = 4 V_0$	$B_{n+1} = (n^2 + 3n) V_0^n$ $4 V_0$
$B_3 = 10 V_0^2$	$10 V_0^2$
$B_4 = 18.36 V_0^3$	$18 V_0^3$
$B_5 = 28.24 V_0^4$	$28 V_0^4$
$B_6 = 39.53 V_0^5$	$40 V_0^5$
$B_7 = 56.52 V_0^6$	$54 V_0^6$
\vdots	\vdots

$$\left(V_0 = \frac{\pi}{6} \sigma^3 \text{ volume hard sphere} \right)$$

$$\frac{P}{gkT} = 1 + \sum_{n=1}^{\infty} (n^2 + 3n) \phi^n$$

$$\frac{P}{gkT} = \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3}$$

Carnahan-Starling
(1969)

VERY ACCURATE!

Hard sphere equation of state - Fluid

$$\begin{aligned}\frac{P}{gkT} &= 1 + \sum_{n=1}^{\infty} (n^2 + 3n)\phi^n \\ &= \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3}\end{aligned}$$

$$S_0 = \sum_{n=1}^{\infty} \phi^n = \frac{\phi}{1 - \phi}$$

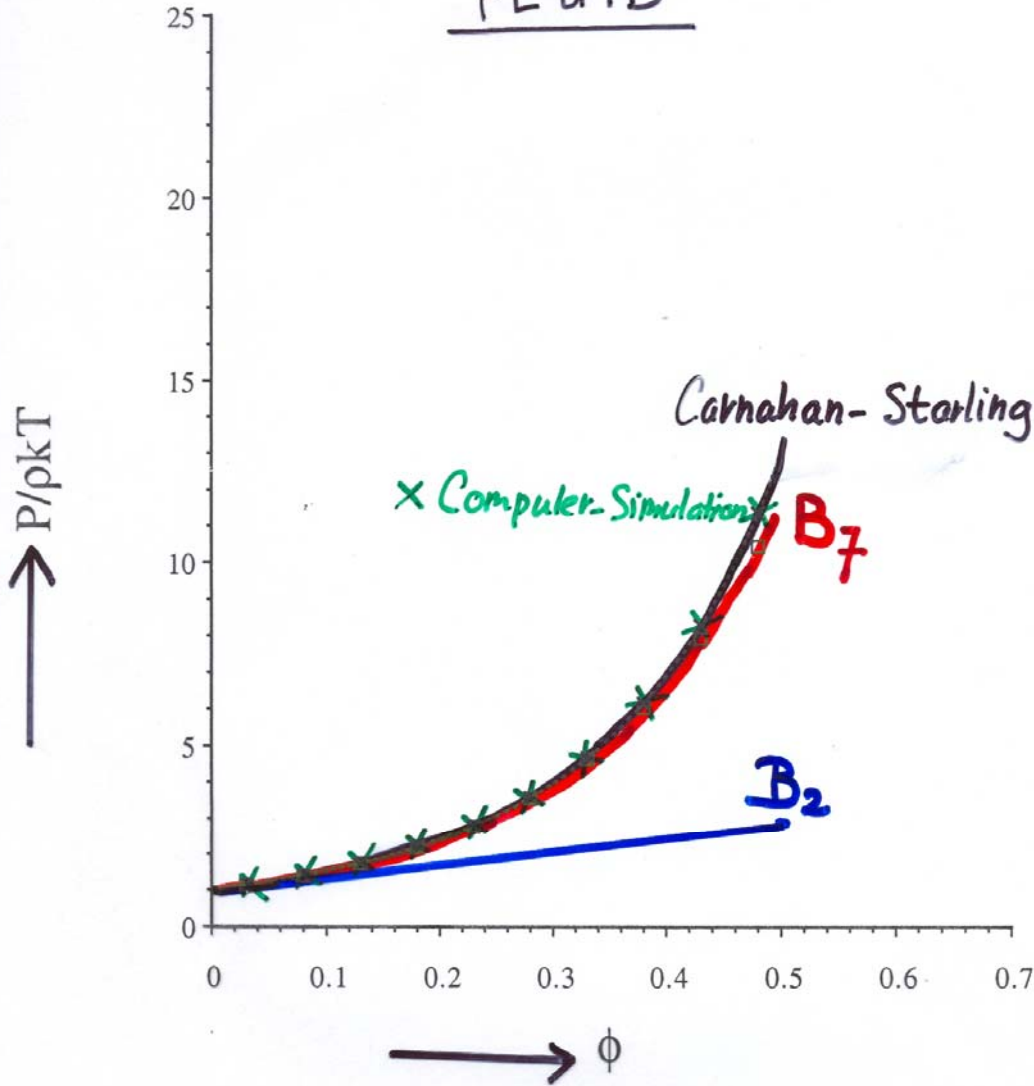
$$S_1 = \sum_{n=1}^{\infty} n \phi^n = \frac{dS_0}{d\phi} - 1 - S_0$$

$$S_2 = \sum_{n=1}^{\infty} n^2 \phi^n = \frac{d^2 S_0}{d\phi^2} + 1 - 3 \frac{dS_0}{d\phi} + S_0$$

$$\begin{aligned}\frac{P}{gkT} &= 1 + 3S_1 + S_2 \\ &= -1 - 2S_0 + \frac{d^2 S}{d\phi^2} \\ &= -1 - \frac{2\phi}{1 - \phi} + \frac{2}{(1 - \phi)^3}\end{aligned}$$

Hard Sphere Equation of State

FLUID



$$\rho = \frac{N}{V} : \text{number density}$$

$$\phi = \frac{N}{V} \frac{\pi}{6} \sigma^3 : \text{volume fraction}$$

Hard sphere equation of state - Fluid

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

Alternative
Route :
Gibbs-Duhem

$$P_{HS} \xrightarrow[\text{integration}]{\text{thermodyn.}} F_{HS}$$

$$V dP = N d\mu \quad (T \text{ const.})$$

$$\mu = \left(\frac{\partial F}{\partial N} \right)_{V, T}$$

$$\left(\frac{\partial \mu}{\partial P} \right)_T = \frac{1}{\rho}$$

$$F_{HS} \longrightarrow \mu_{HS}$$

$$\frac{\mu_{HS}}{kT} = \text{const} + \ln \phi + \frac{(8 - 9\phi + 3\phi^2)\phi}{(1 - \phi)^3}$$

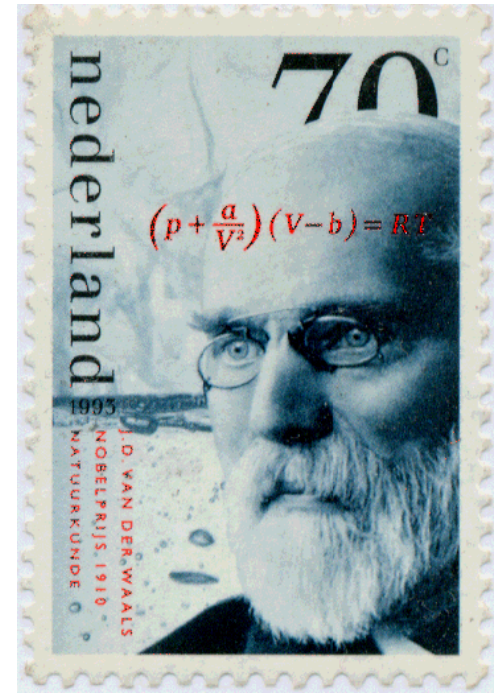
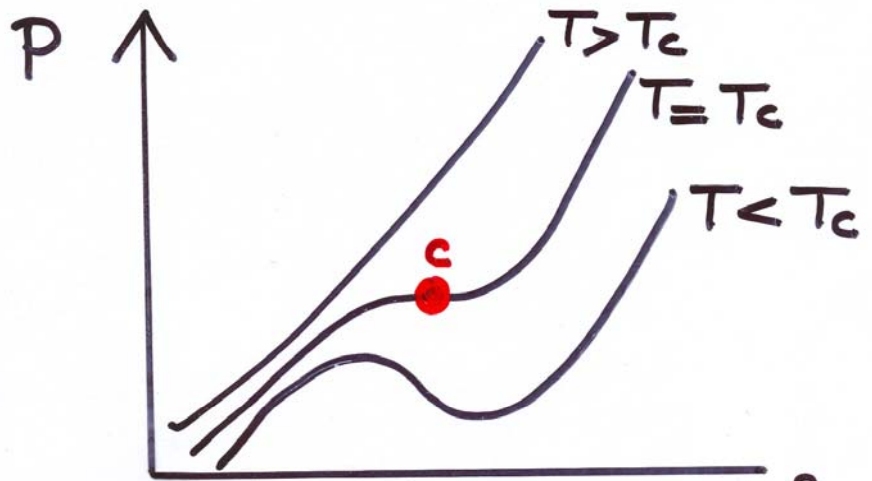
$$P = P_{HS} - a \rho^2$$

$$\mu = \mu_{HS} - 2a \rho$$

VanderWaals Theory

$$REP \leftrightarrow ATT$$

$$(HS) \leftrightarrow (a)$$



Critical Point $\left(\frac{\partial P}{\partial \rho}\right)_{T=T_c} = 0$ $\left(\frac{\partial^2 P}{\partial \rho^2}\right)_{T=T_c} = 0$

$$\phi_c = 0.13$$

$$\frac{kT_c}{(a/v_0)} = 0.094$$

$$\frac{P_c v_0}{kT_c} = 0.046$$

Argon

$$P_c = 48 \text{ atm}$$

$$T_c = 151 \text{ K}$$

$$v_0 = \frac{\pi}{6} (0.34)^3 \text{ nm}^3$$

$$\frac{P_c v_0}{kT_c} = 0.047$$

$$P = P_{HS} - a s^2$$

$$\mu = \mu_{HS} - 2a s$$

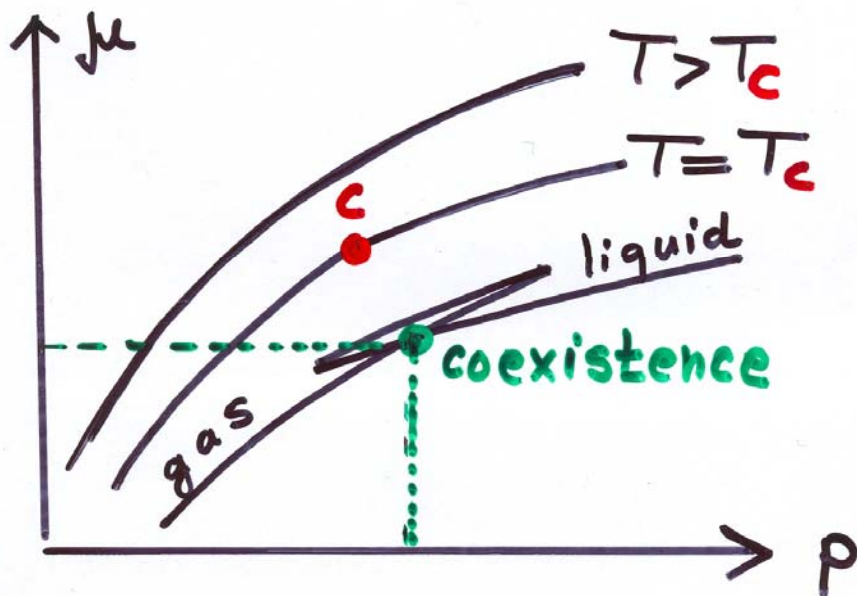
Coexistence gas - liquid

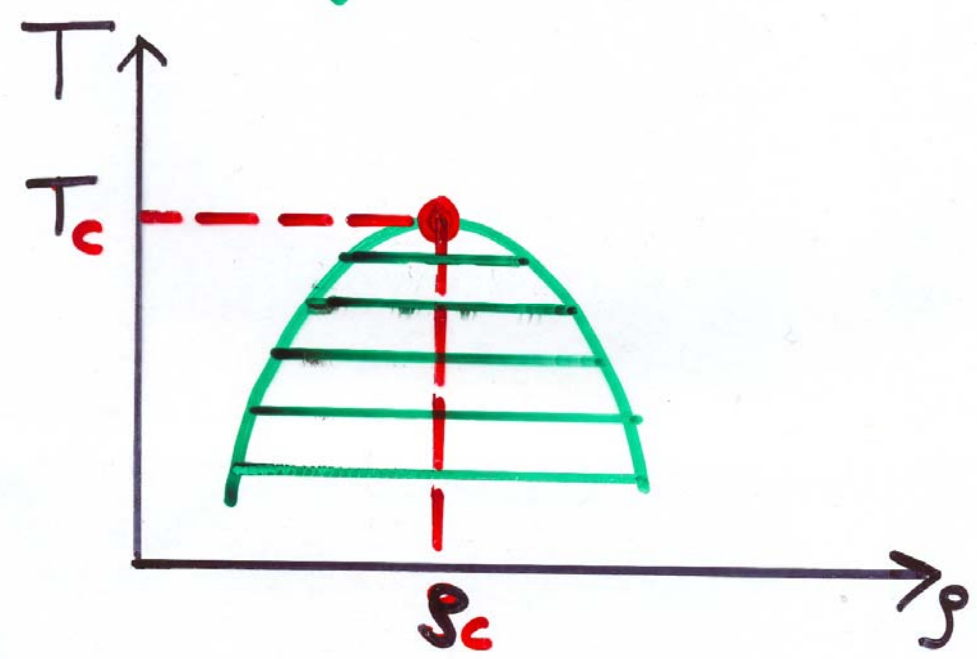
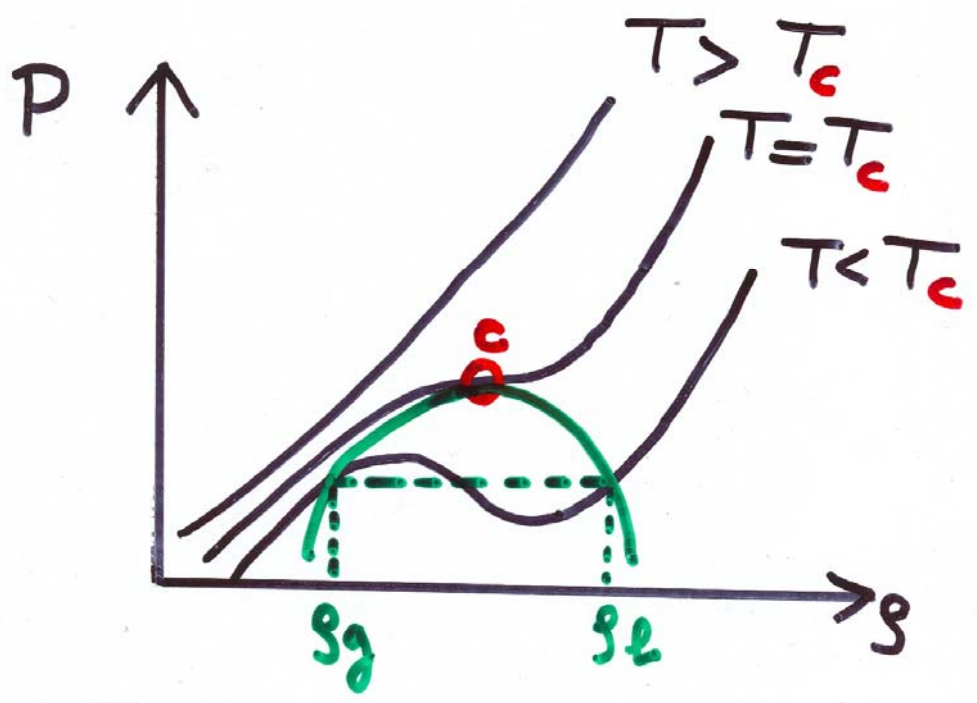
$$P(s_g) = P(s_l)$$

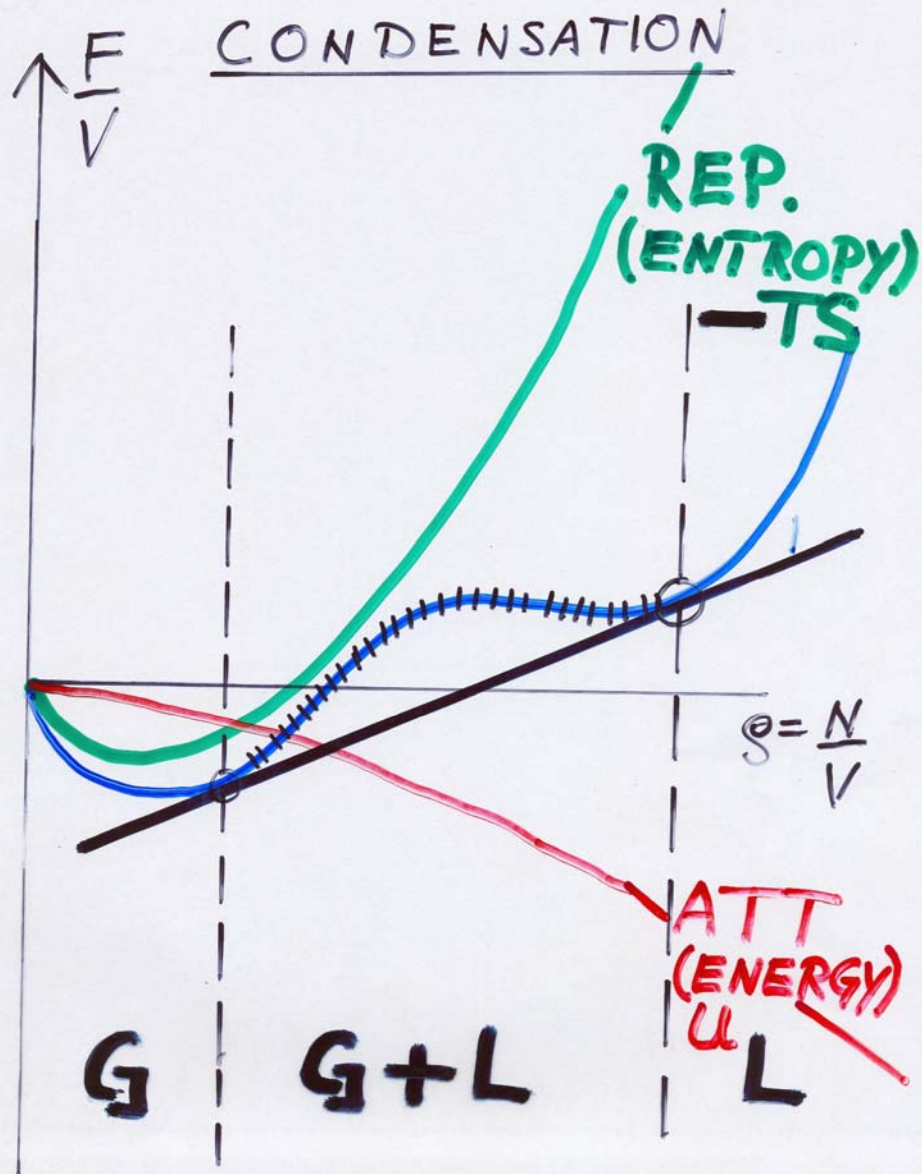
$$\mu(s_g) = \mu(s_l)$$

$T > T_c$ no solution

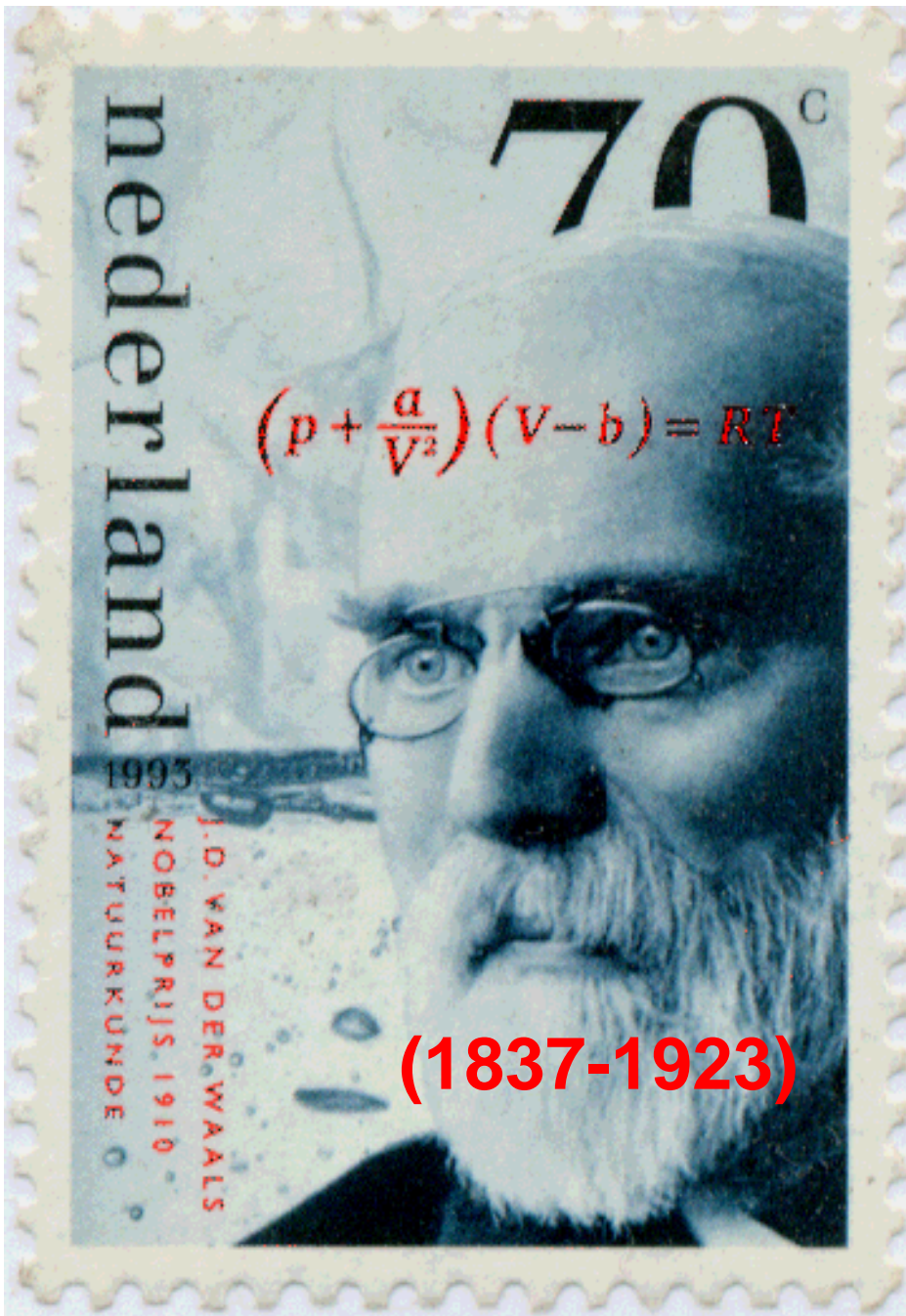
$T < T_c$ s_g, s_l







$$F = U - TS$$



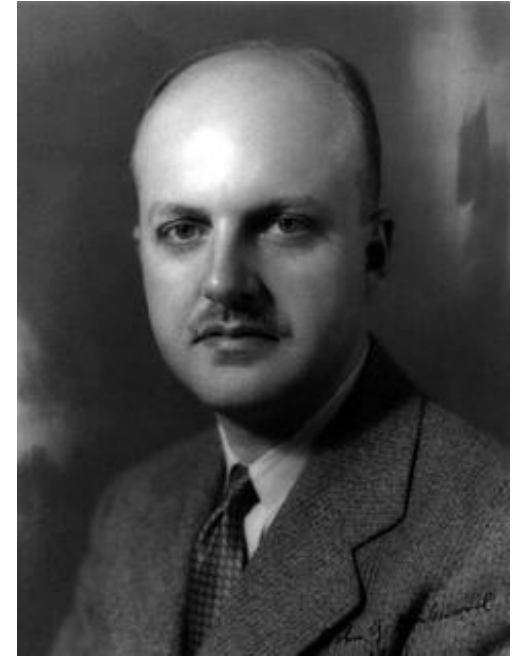
Over
de continuïteit van den gas –
en vloeistofoestand.

Proefschrift Leiden, 1873.

Condensatie vereist
attractie en repulsie

maar kristallisatie...

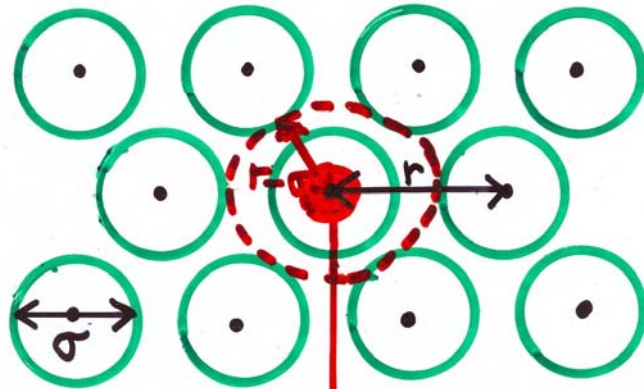
“I think it is quite **unnecessary** to have an **attractive force** to achieve a crystalline phase and one can produce simple intuitive arguments for that.”



John G. Kirkwood
(1907-1959)

Hard sphere equation of state - Solid

Free volume or cell model (Lennard-Jones + Devonshire (1937))



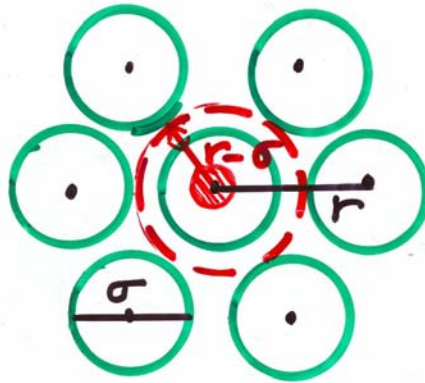
Free Volume $v^* = \frac{4\pi}{3} (r - \sigma)^3$
(Spherical Approximation)

$$Z_N = (v^*)^N$$

$$F = -kT \ln Z_N$$

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

Hard Sphere Equation of State - SOLID



Free volume $V^* = \frac{4\pi}{3}(r-\sigma)^3$

At close packing ($\phi_{cp} = \frac{\pi}{3\sqrt{2}} = 0.74$)

$r = \sigma \rightarrow V^* = 0$

Scaling

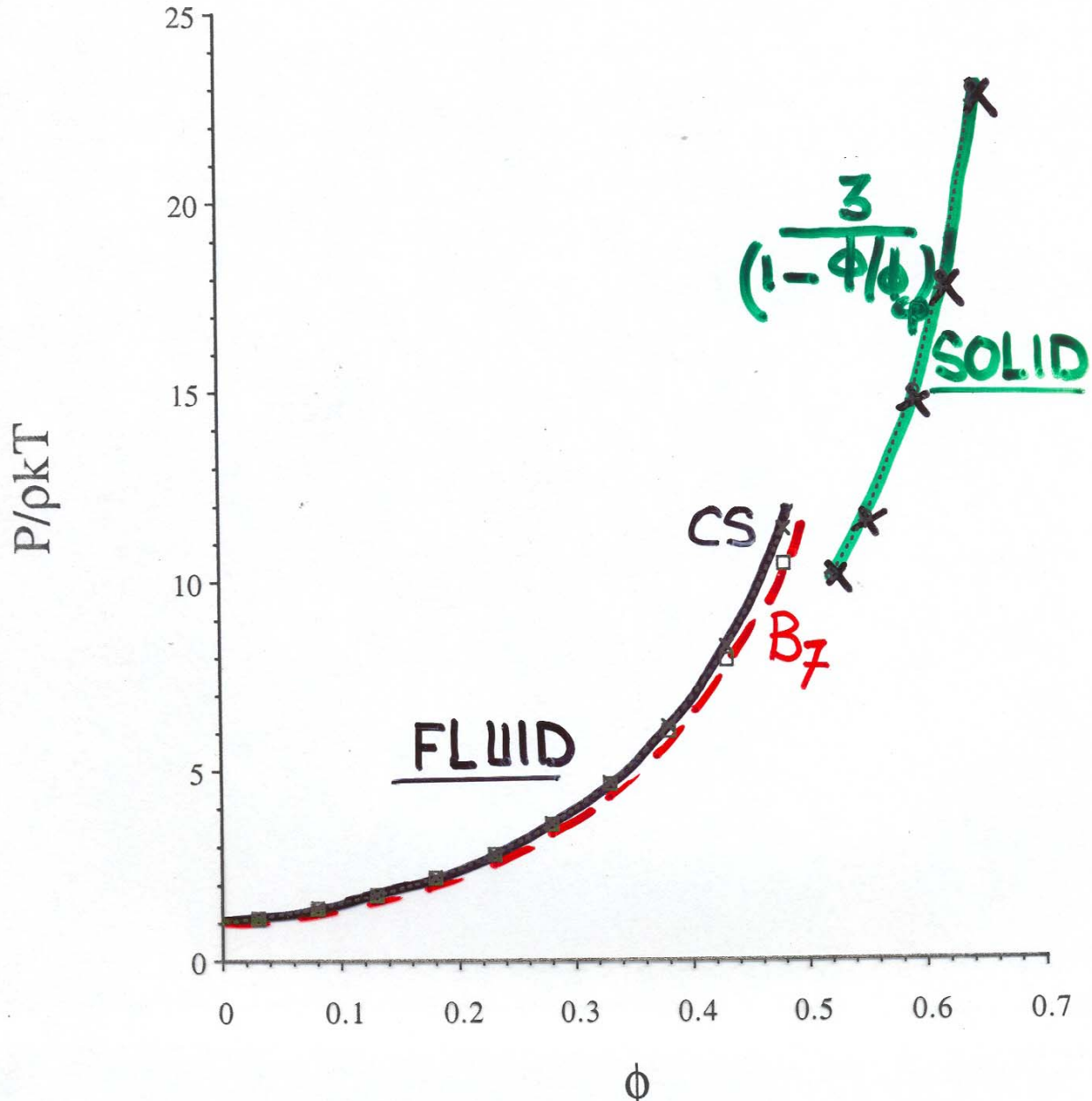
$\phi r^3 = \phi_{cp} \sigma^3$

$$V^* = \frac{4\pi\sigma^3}{3} \left(\left(\frac{\phi_{cp}}{\phi} \right)^{1/3} - 1 \right)^3$$

$$\frac{p}{gkT} = \frac{3}{1 - \phi/\phi_{cp}}$$

Very Accurate!

Hard Sphere Equation of State



Hard Sphere Equation of State Solid

$$P_{HS} \xrightarrow[\text{integration}]{\text{thermodynamic}} F_{HS}$$

$$\mu_{HS} = - \left(\frac{\partial F_{HS}}{\partial N} \right)_{V, T}$$

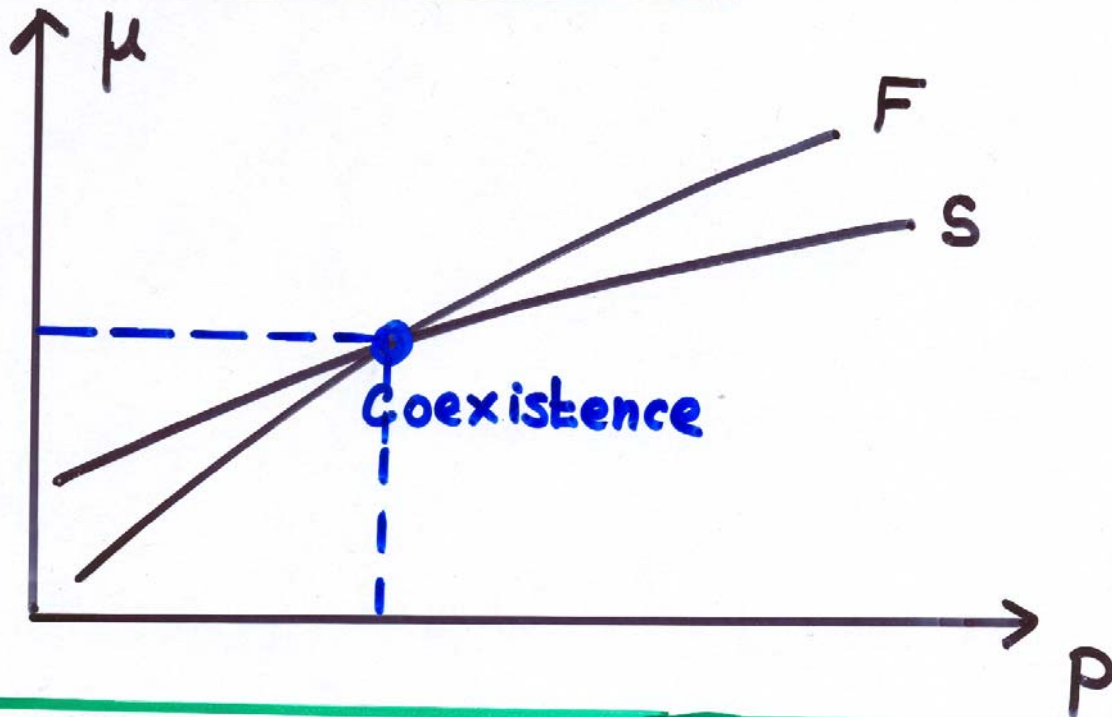
$$\frac{P_{HS}}{gkT} = \frac{3}{(1 - \phi/\phi_{cp})}$$

$$\frac{\mu_{HS}}{kT} = \text{const} + 3 \ln \frac{\phi}{1 - \phi/\phi_{cp}} + \frac{3}{1 - \phi/\phi_{cp}}$$

cell model : $\text{const} = \ln \frac{27}{8} - 3 \ln \phi_{cp} = 2.12$

computer simulation : $\text{const} = 2.13$
(Frenkel+Ladd 1984)

CRYSTALLIZATION OF AN ASSEMBLY OF HARD SPHERES continuation



FLUID

$$\frac{P_{HS}}{gkT} = \frac{1 + \phi + \phi^2 - \phi^3}{(1 - \phi)^3}$$

$$\frac{\mu_{HS}}{kT} = \ln \phi + \frac{(8 - 9\phi + 3\phi^2)\phi}{(1 - \phi)^3}$$

SOLID

$$\frac{P_{HS}}{gkT} = \frac{3}{(1 - \phi/\phi_{cp})}$$

$$\frac{\mu_{HS}}{kT} = 2.13 + 3 \ln \frac{\phi}{1 - \phi/\phi_{cp}}$$

MOLECULAR PHYSICS 8.549 (1964)

A rigid sphere model for the melting of argon

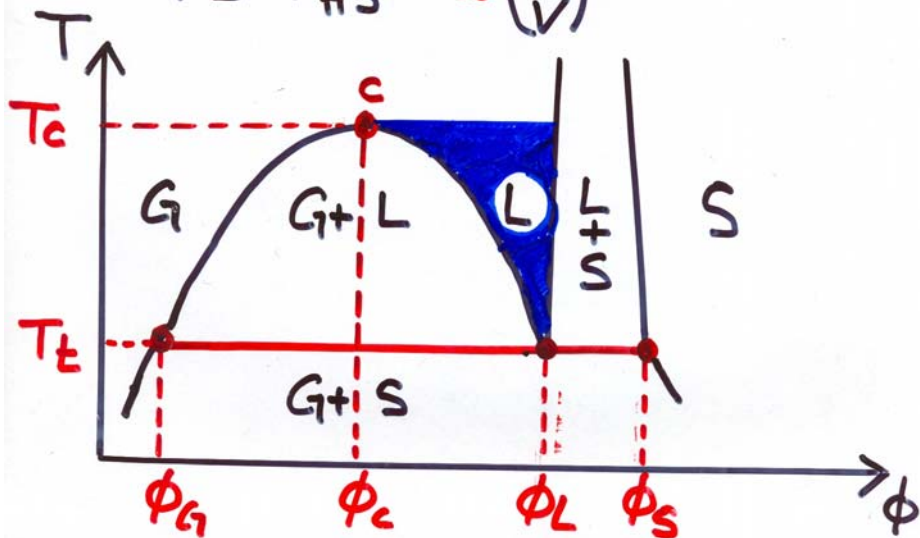
by H. C. LONGUET-HIGGINS† and B. WIDOM
 Department of Chemistry, Cornell University, Ithaca, N.Y., U.S.A.

† Department of Theoretical Chemistry, University Chemical
 Laboratory, Cambridge, England.

"VANDERWAALS I U M"

$$\mu = \mu_{HS} - 2a \frac{N}{V}$$

$$P = P_{HS} - a \left(\frac{N}{V} \right)^2$$



CRITICAL POINT

$$\frac{kT_c}{a/v_0} = 0.094 \quad \phi_c = 0.13$$

TRIPLE POINT

$$\frac{kT_t}{a/v_0} = 0.040 \quad \phi_t = 0.49$$

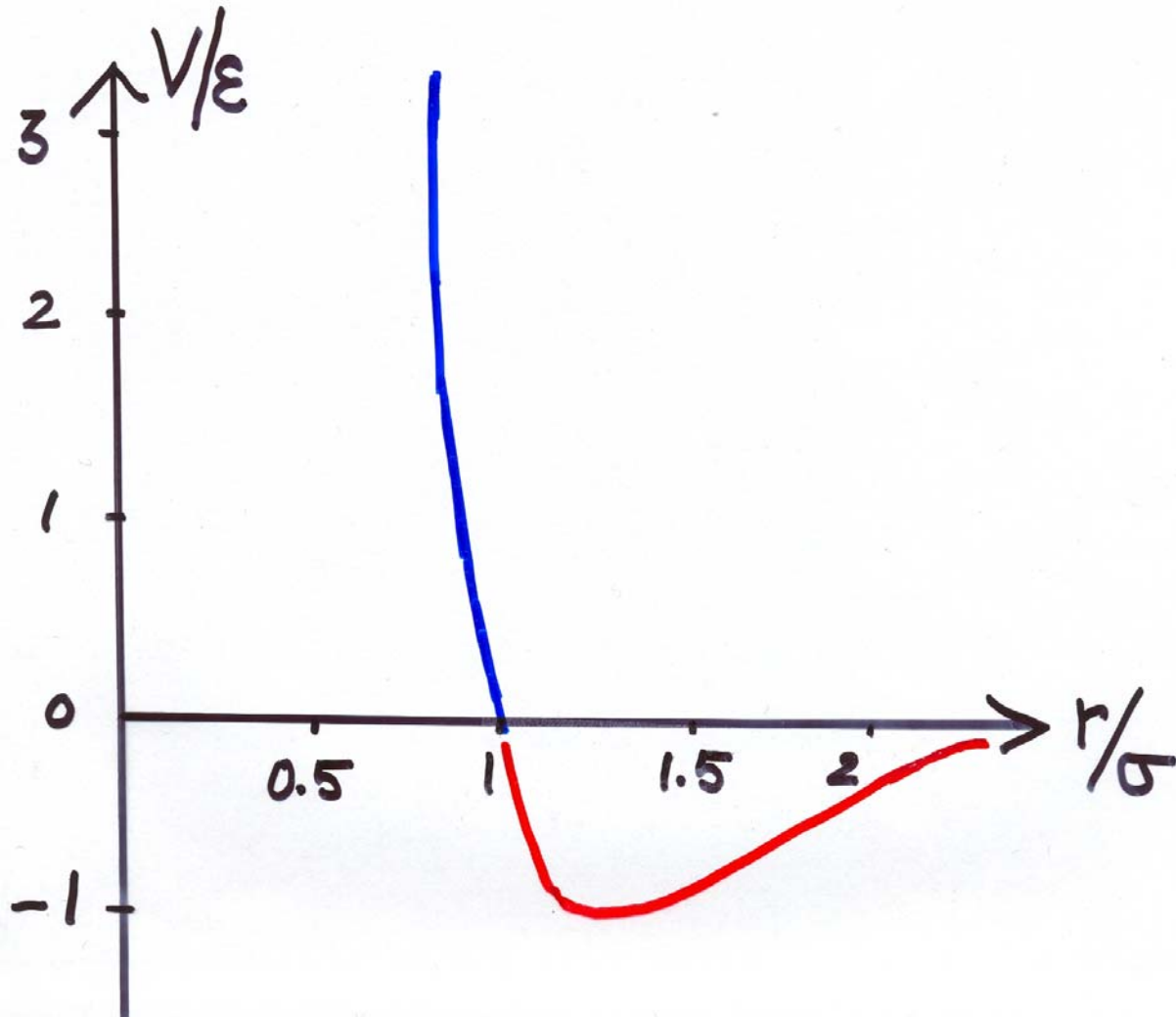
$$T_c/T_t = 2.4$$

$$\phi_L = 0.60$$

PHASE TRANSITIONS IN ATOMIC SYSTEMS

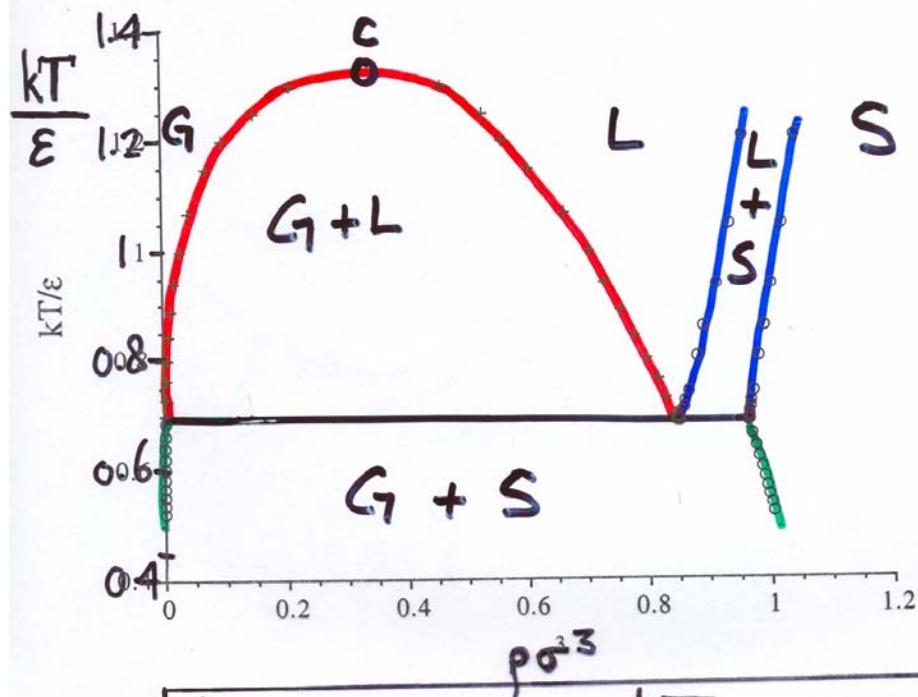
Lennard-Jones Potential

$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$



J.-P. Hansen + L. Verlet, Phys. Rev. 184, 151 (1969)

Phasediagram 12-6 Lennard Jones system



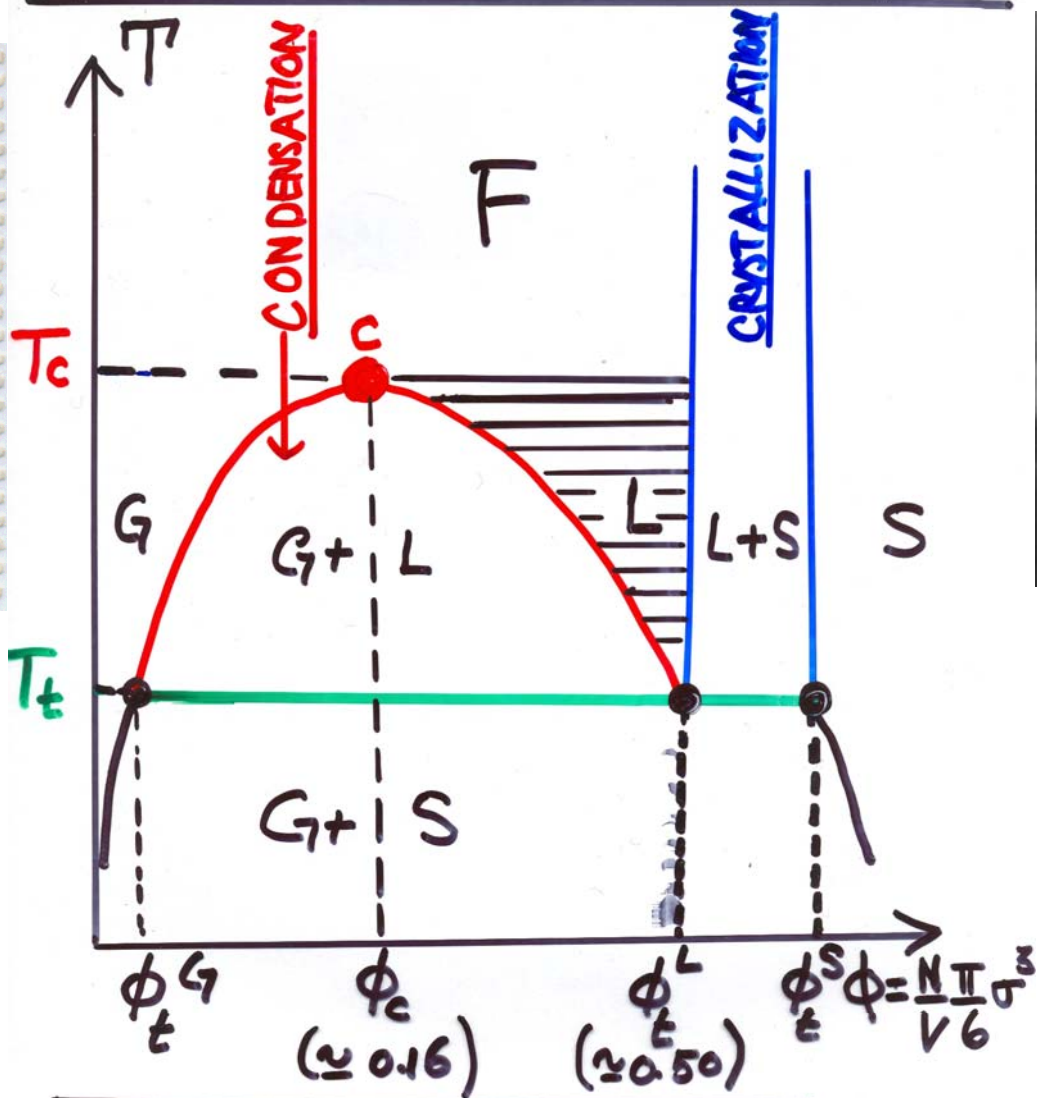
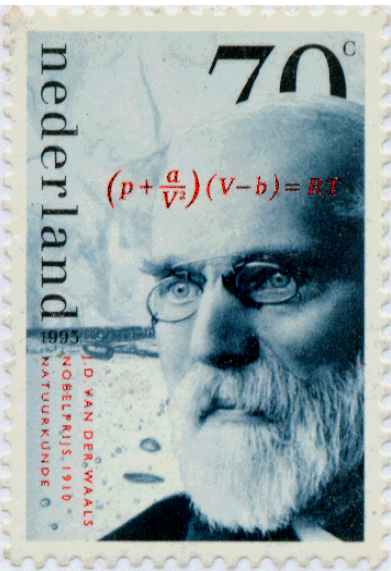
$\phi_c = 0.16$	$\frac{kT_c}{\epsilon} = 1.316$
$\phi_l = 0.45$	$\frac{kT_t}{\epsilon} = 0.69$
triple point	$T_c/T_t = 1.9$

THE LIQUID RANGE: T_c / T_t

VAN DER WAALS IUM: 2.4

	T_c (K)	T_t (K)	
Ne	44.5	24.6	1.8
Ar	151.5	83.8	1.8
Kr	209.4	115.8	1.8
Xe	289.8	161.4	1.8
F ₂	144.1	53.5	2.7
Cl ₂	416.9	171.6	2.4
Br ₂	588	265.9	2.2
I ₂	819	386.8	2.1
N ₂	126.2	63.2	2.0
O ₂	154.6	54.4	2.8
CO ₂	304.1	216.6	1.4
CH ₄	190.5	90.7	2.1
HF	461	189.8	2.4
HCl	324.7	159.0	2.0
H ₂ O	647.1	273.15	2.4

PHASE TRANSITIONS IN ATOMIC SYSTEMS



John G. Kirkwood

$\frac{T_c}{T_t} \approx 2$	$\frac{\phi_c}{\phi_t} \approx \frac{1}{3}$
-----------------------------	---

BEN WIDOM



That in a liquid near its triple-point the correlations due to the short-ranged repulsive forces are more significant than those due to the longer-ranged attractive forces, and that in a fluid near its critical point precisely the opposite is true, may be viewed as inevitable consequences of the fact that at the triple-point the density of a liquid is close to that of the corresponding solid, while typically the critical density is only one-third that. Nevertheless, the extreme sharpness with which the distinction appears is most striking and unexpected.

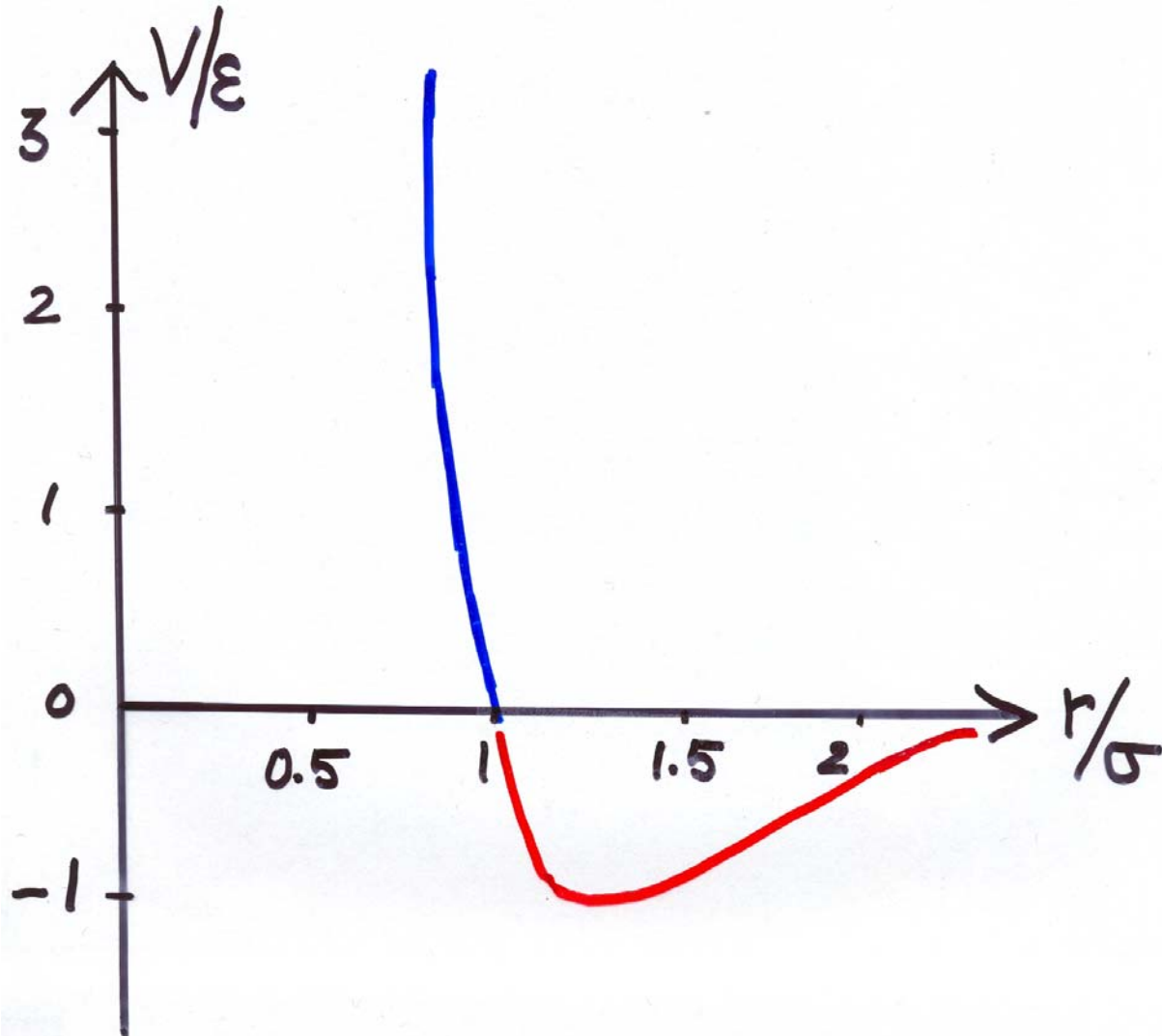
*Intermolecular Forces and the Nature of the Liquid State, Science 157
(1967) 375*

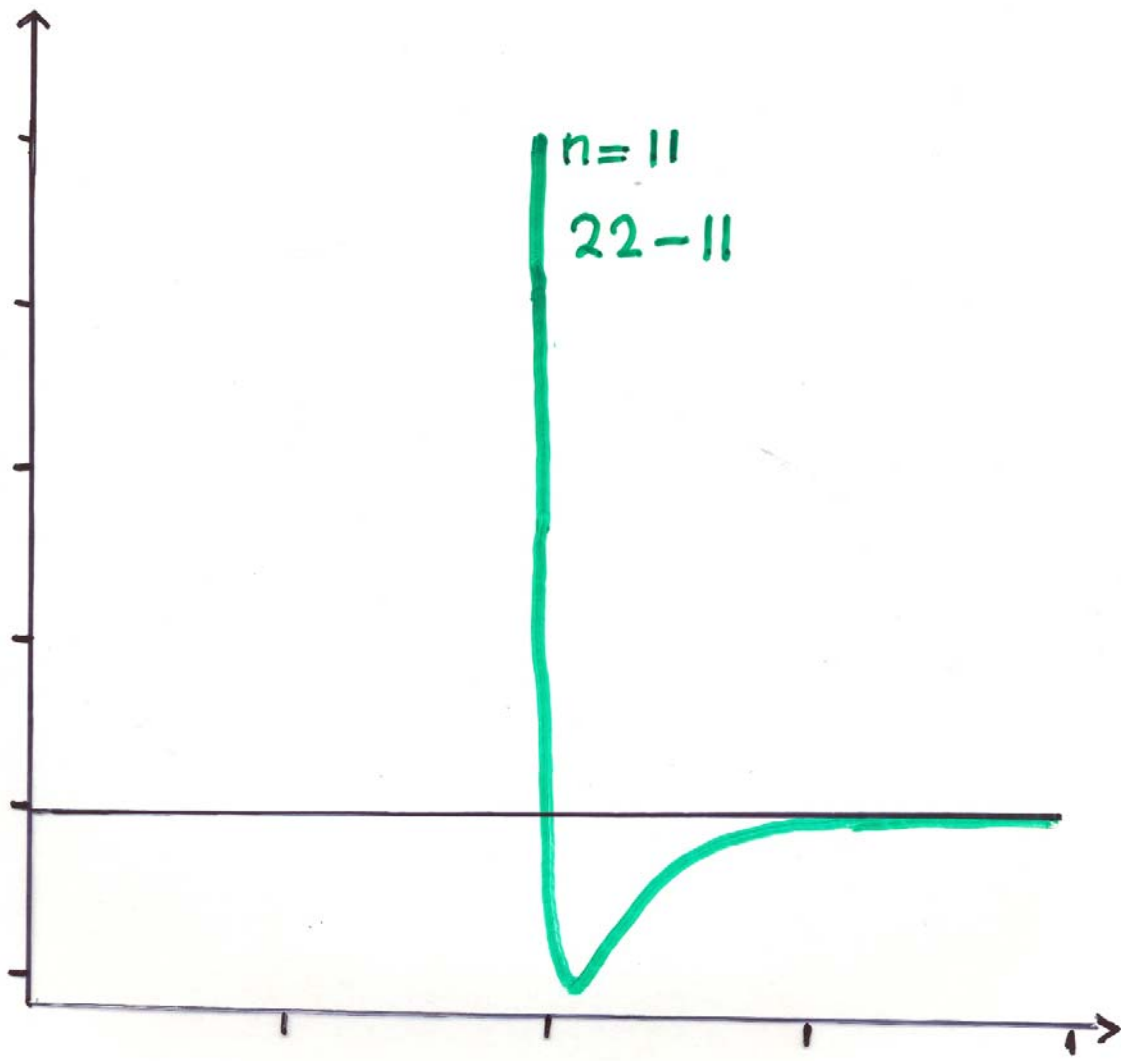
"DECLARATION OF THE RIGHTS ^{OF THE EXISTENCE} OF ALIQUID"

*IS BEN WIDOM ALWAYS RIGHT?
THIS*

Lennard-Jones Potential

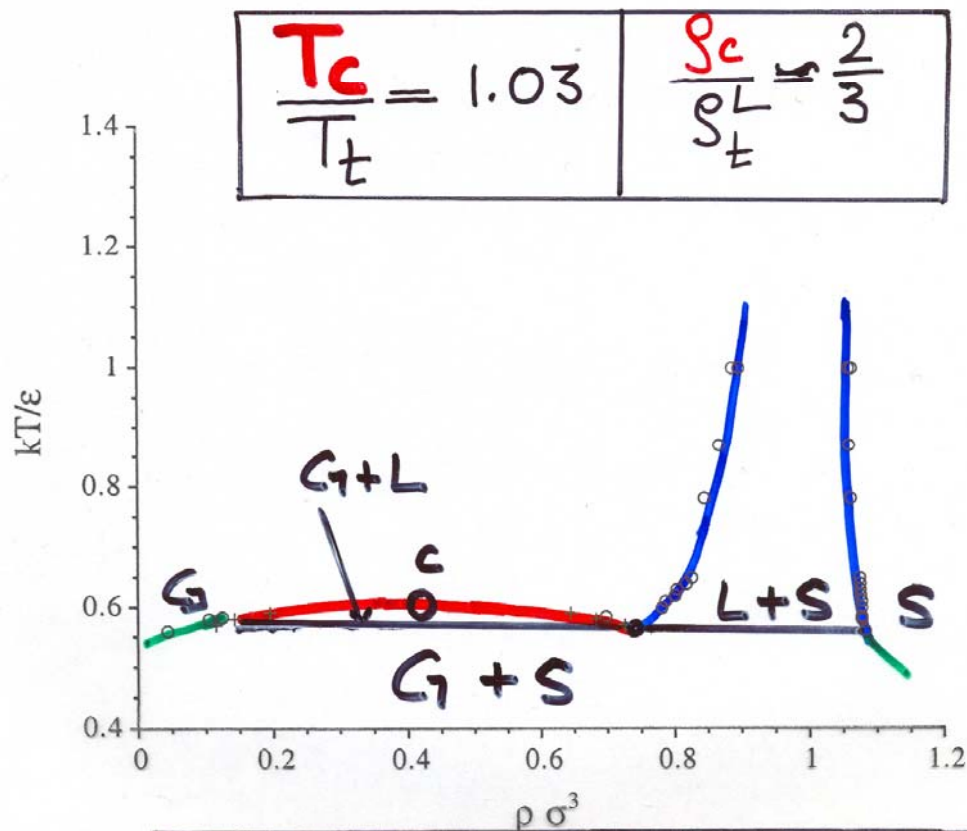
$$V(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$




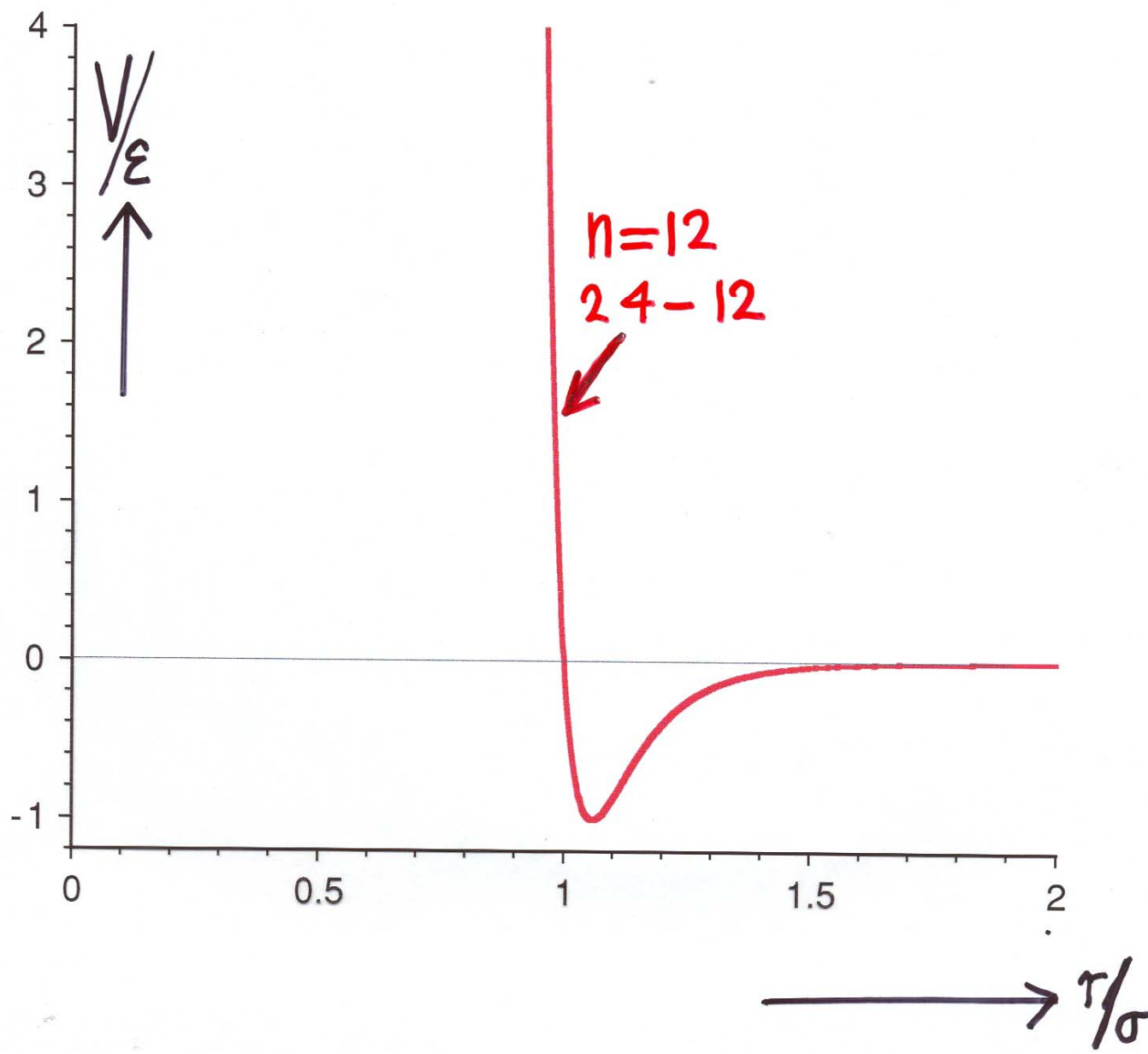


Phase diagram 22-11 Lennard Jones system

(G.A. Vliegenthart, J.F.M. Lodge, HNWL)
(Physica A 263, 378 (1999))



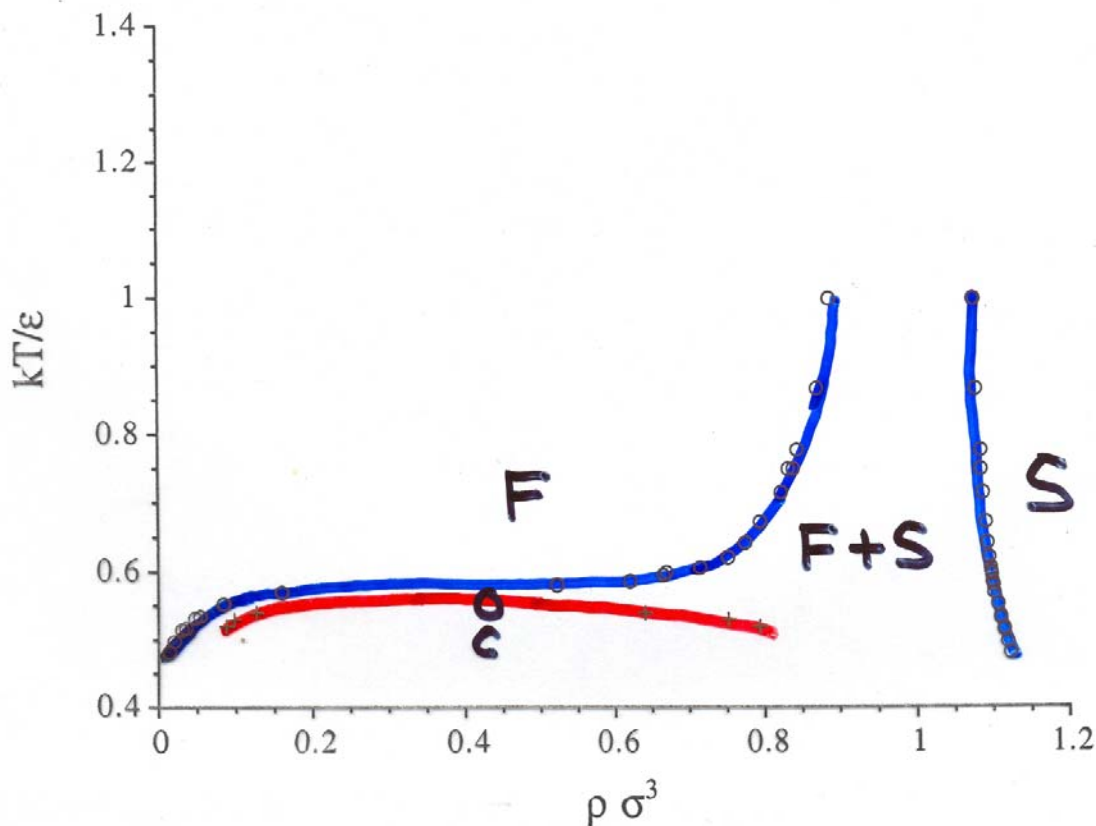
$\phi_c = 0.22$	$\frac{kT_c}{\epsilon} = 0.60$
$\phi_l = 0.35$	$\frac{kT_t}{\epsilon} = 0.58$
triple point $\phi_c / \phi_l = 0.63$	$\frac{T_c}{T_t} = 1.03$ 



Phasediagram 24-12 Lennard Jones system

$$kT_c/\epsilon=0.557, \rho_c \sigma^3=0.42$$

(METASTABLE)

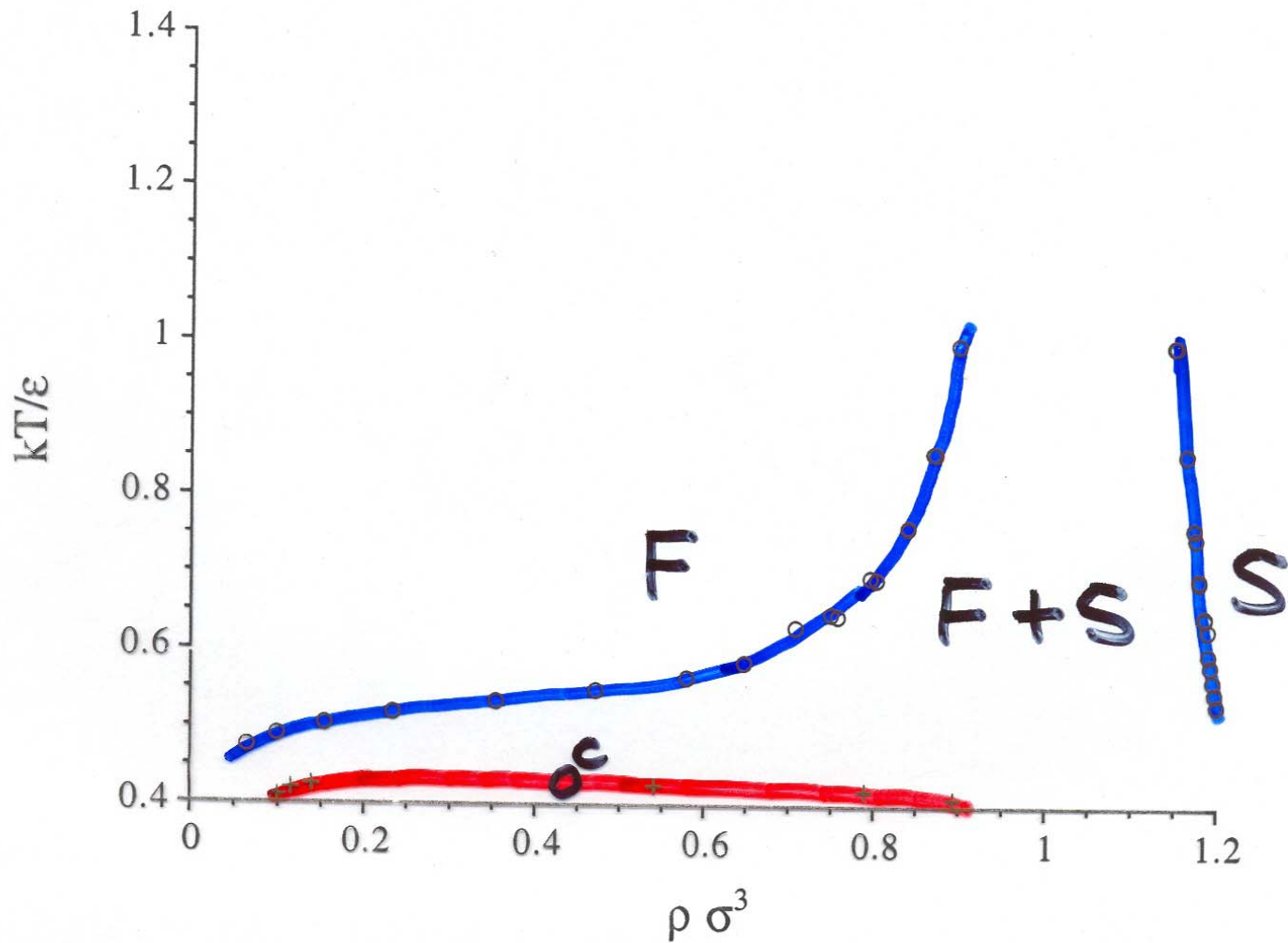


GAS-LIQUID TRANSITION
METASTABLE

Phasediagram 36-18 Lennard Jones system

$$kT_c/\epsilon = 0.425, \rho_c \sigma^3 = 0.43$$

(METASTABLE)

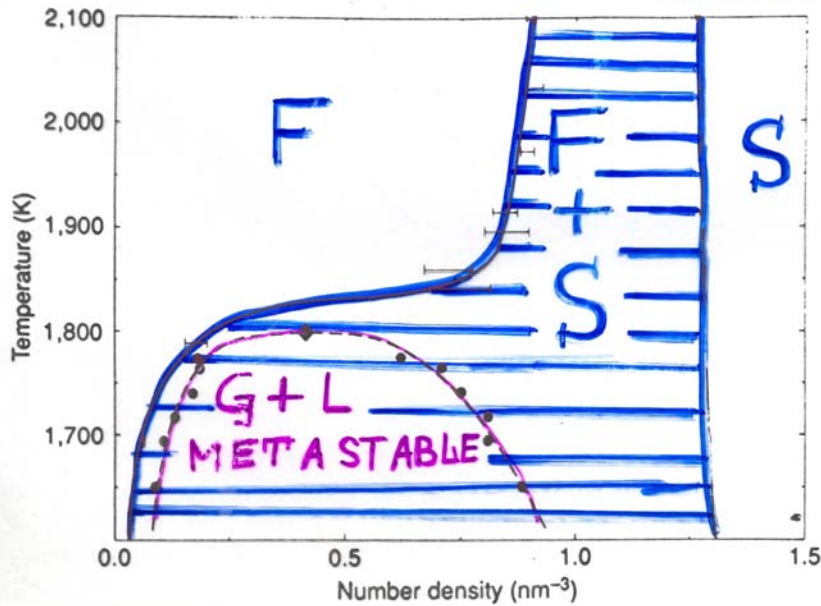
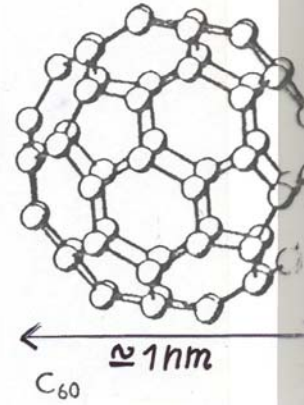
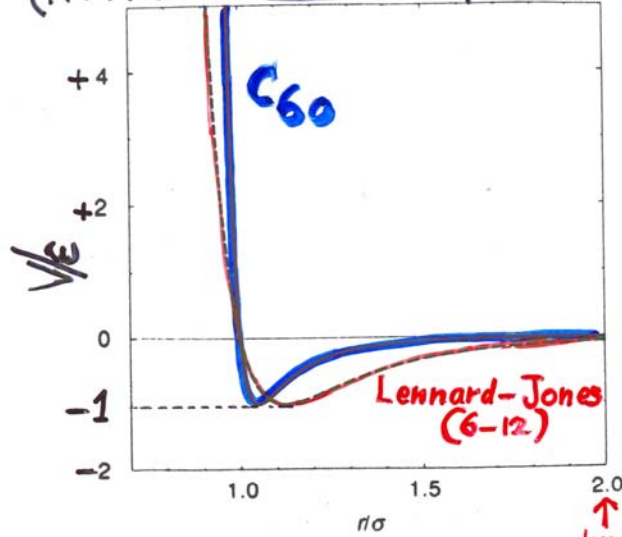


LETTERS TO NATURE

Does C₆₀ have a liquid phase?

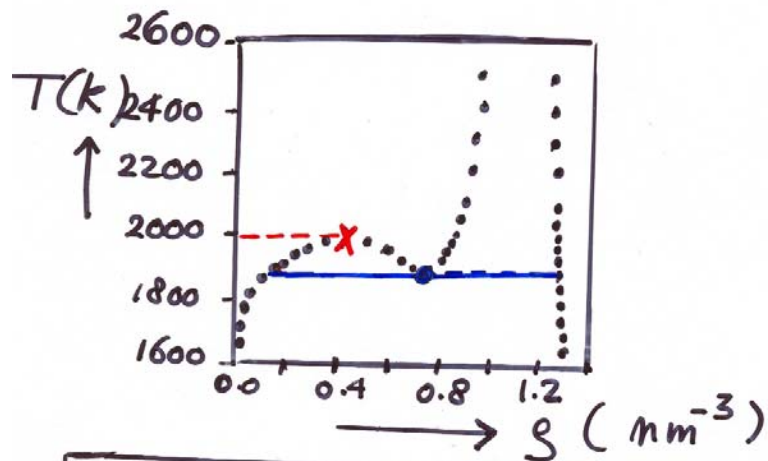
M. H. J. Hagen*, E. J. Meljer*, G. C. A. M. Moolj*,
D. Frenkel** & H. N. W. Lekkerkerker‡

(NATURE 365, 30 September 1993 p425)



M. Hasegawa, K Ohno, J. Chem. Phys. III, 5955
(1999)

Monte Carlo simulation study of the high-temp.
phase diagram of model C₆₀ molecules

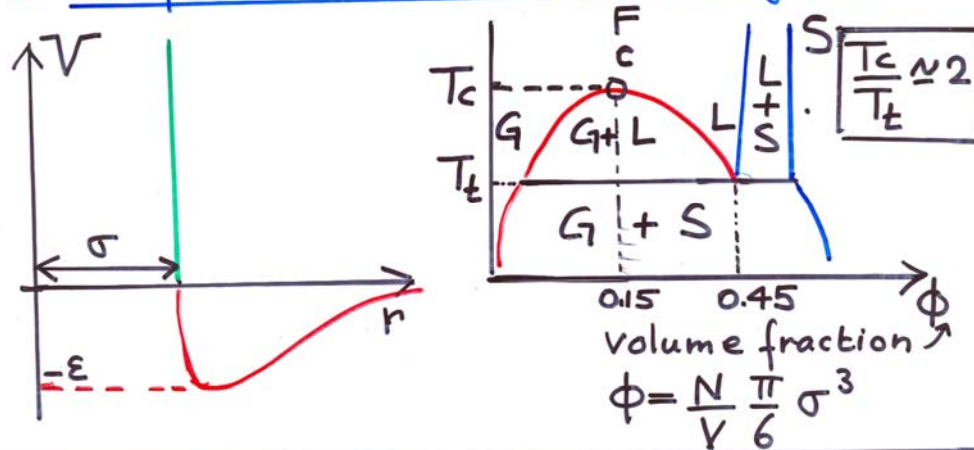


Based on the
same Girifalco
potential as
Hagen et al. but
not truncated at
 $r = 2\sigma$

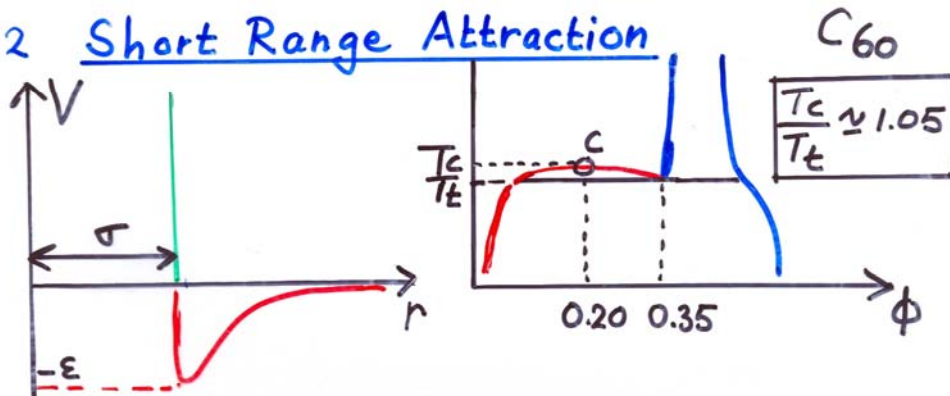
$\times T_c = 1980 \text{ K}$	$\rho_c = 0.44 \text{ nm}^{-3}$	$\phi_c = \frac{\pi \sigma^3}{6} \rho_c = 0.20$
$T_t = 1880 \text{ K}$	$\rho_t^l = 0.74 \text{ nm}^{-3}$	$\phi_t^l = 0.34$
$T_c / T_t = 1.05$	$\rho_t^l / \rho_c = 1.7$	

SUMMARY LECTURE 1

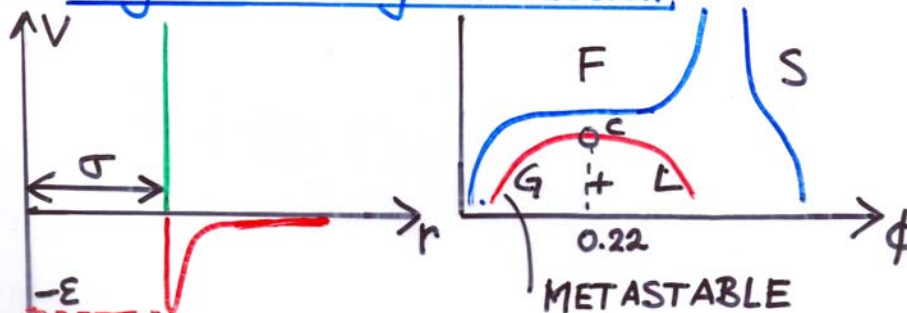
1. Simple Atomic and Molecular Systems



2. Short Range Attraction



3. Very Short Range Attraction



The end of lecture 1