INTERNATIONAL ATOMIC ENERGY AGENCY
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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY, CABLE: CENTRATOM TRIESTE

WINTER COLLEGE ON "MULTILEVEL TECHNIQUES IN COMPUTATIONAL PHYSICS"

Physics and Computations with Multiple Scales of Lengths
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H4.SMR 539/17

Computer Simulation of the Liquid-Vapour Phase Transition

M. Rovere
Dipartimento Fisica Teorica
Trieste. Italy

M. ROVERE
DIPARTIMENTO FISICA TEORICA
TRIESTE

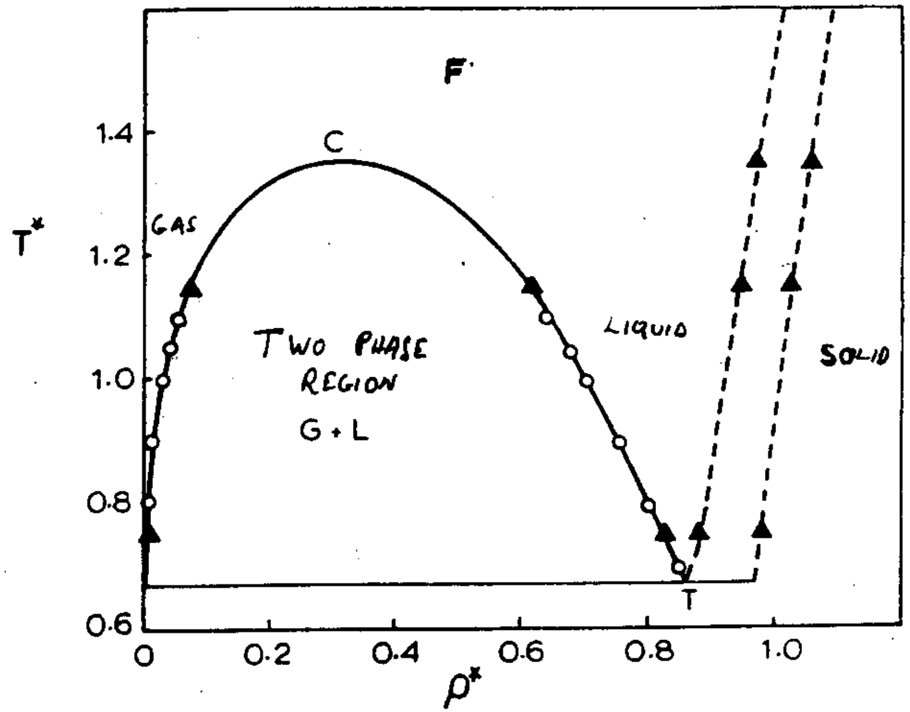
COMPUTER SIMULATION OF
THE LIQUID-VAPOUR PHASE TRANSITION

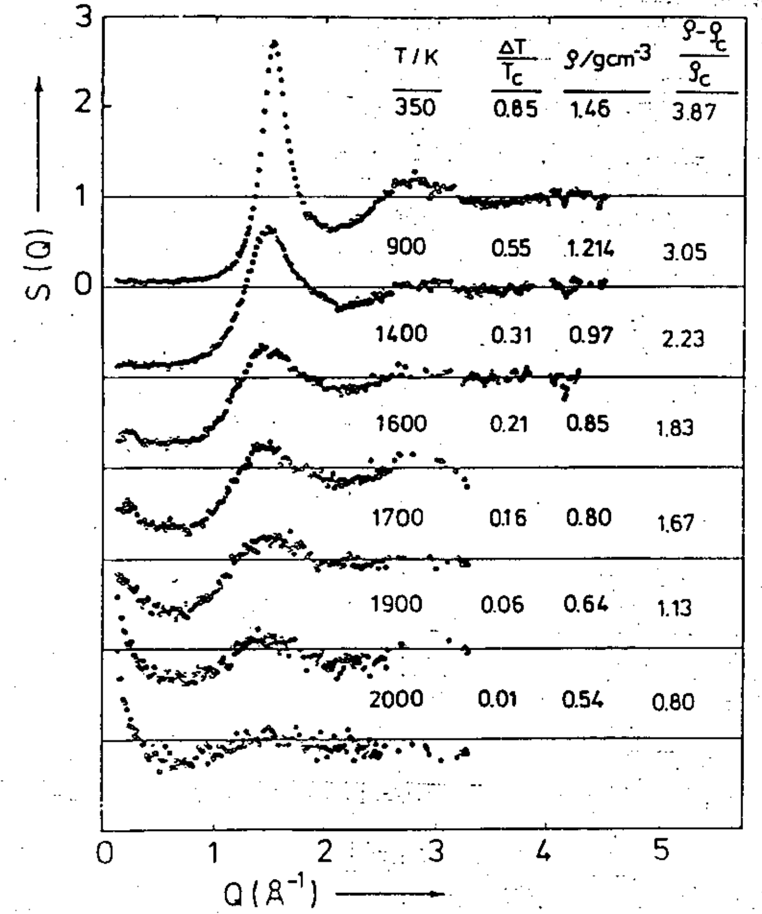
LIQUID-VAPOUR PHASE TRANSITION

OPEN PROBLEMS:

- How critical parameters (P_c, T_c, ρ_c) are related to the microscopic forces ?
- cross-over normal to critical
- dynamical aspects
- metastability in the two phase region
- phase separation in fluid mixtures

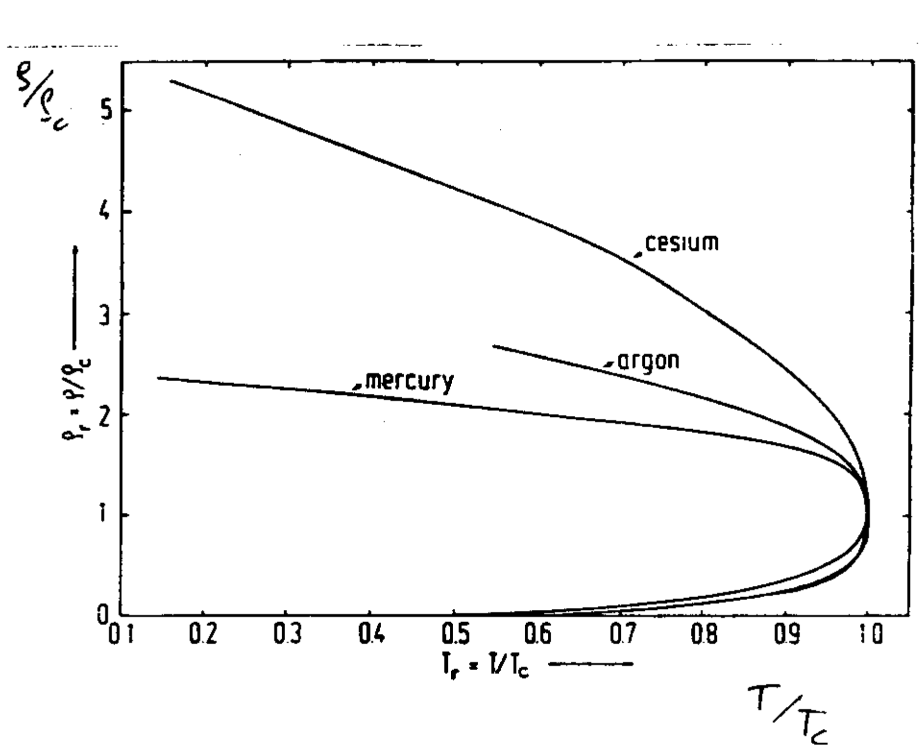
MODEL FOR FLUID Argon



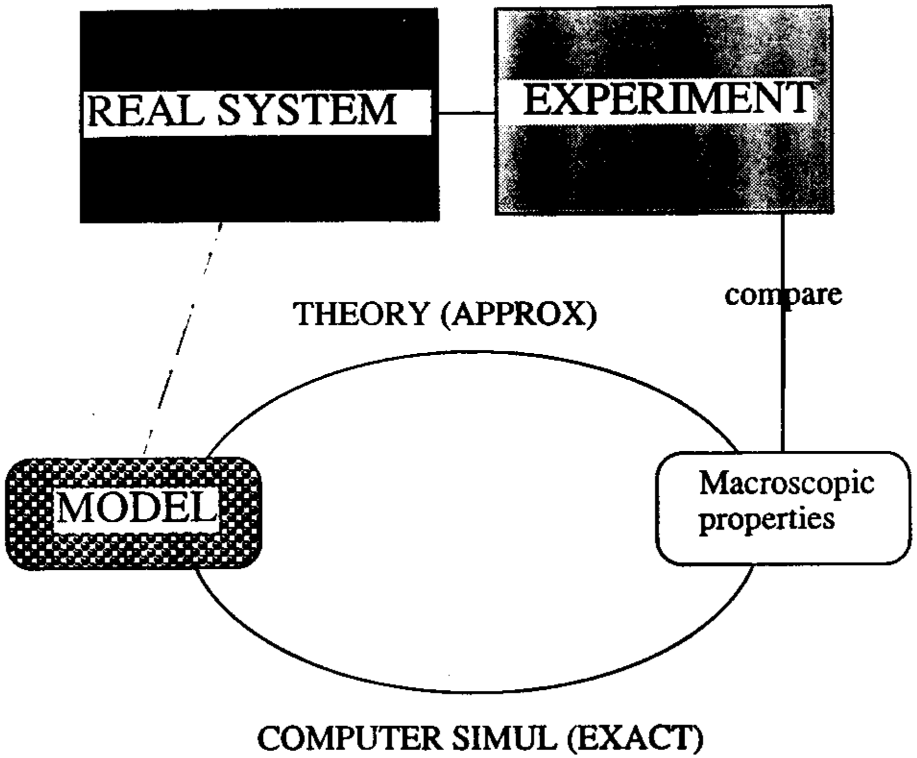


Static structure factor of expanded liquid Rb determined by neutron diffraction (Franz *et al.* 1980).

COEXISTENCE CURVES



From: Freyland - Hensel



SIMULATION OF PHASE TRANSITIONS

PROBLEMS:

1. **Finite size**

2. **Finite time**

Critical properties are related to
non analiticity of the free energy
in the therm. limit

$$F(T,V,N) \qquad \left.\begin{matrix} N \\ V \end{matrix}\right\} \longrightarrow \infty \quad , \quad \rho=\text{const}$$

Finite size analysis for simulation
of lattice models

(Ma Swendsen Binder ....)

Extension to "realistic fluids"

in collaboration
K. Binder , D. Heermann (Mainz)

SIMULATION OF THE GAS LIQUID TRANSITION

1- **Introduction and Motivations**

2- **MODEL: 2D-Lennard-Jones**

3- **BLOCK DISTRIBUTION FUNCTION (BDF)**

4- **RESULTS IN THE TWO PHASE REGION**

5- **MOMENTS OF THE BDF**

6- **DETERMINATION OF THE CRITICAL POINT**

7- **DISCUSSION AND FUTURE WORK**

$$C_V \sim \langle \Delta E \, \Delta E \rangle$$

$$K_T \sim \langle \Delta \rho \, \Delta \rho \rangle$$

$$\chi \sim \langle \Delta M \, \Delta M \rangle$$

$$\langle \ldots \rangle \sim \exp(-r/\xi)$$

ξ $\qquad$ $T \gg T_c$

$\xi \rightarrow \infty$ $\qquad$ $T \rightarrow T_c$

$$\xi \sim |T - T_c|^{-\nu}$$

Liquid-Gas

$$C_V \sim |T - T_c|^{-\alpha}$$

$$K \sim |T - T_c|^{-\gamma}$$

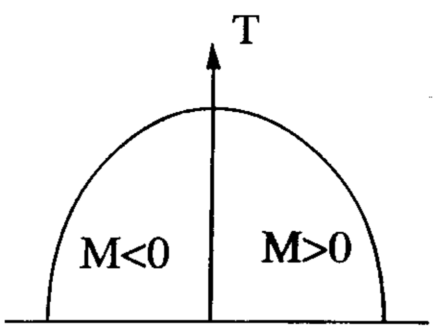
Magnet

$$C_V \sim |T - T_c|^{-\alpha}$$

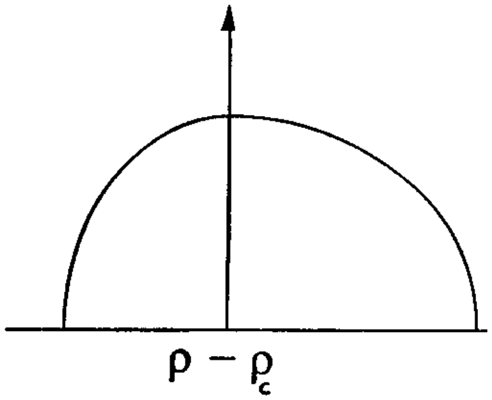
$$\chi \sim |T - T_c|^{-\gamma}$$

	α	γ
liquid-gas	0.08-0.10	1.2
magnet (uniax.)	0.08-0.10	1.15
3D Ising	0.12	1.25
2D Ising	(0)	1.75

ISING



LIQUID-GAS



$T=T_c$: universal properties like Ising model

no information about not univ. prop.

$$\boxed{u(r_{ij}) \longrightarrow \rho_c \;, T_c \,, p_c}$$

$T \to T_c$

influence of the realistic potential

⇒ **Traditional theories of liquids are not adequate**

⇒ **Attempts to combine with R.G.**

Hubbard and Schofield
Van Dieren and Van Leeuween

Parola,Meroni and Reatto

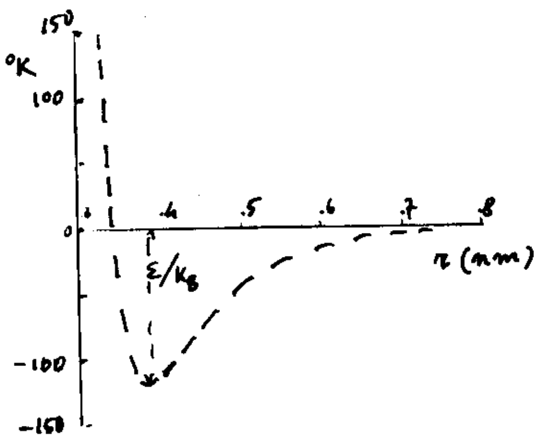
SIMULATION OF "REAL" CLASSICAL FLUIDS

$$H = \sum_i \frac{p_i^2}{2m} + \underline{V(r_1, \ldots, r_N)}$$

$$V = \sum_{i>j} \phi(r_{ij}) + \ldots \simeq \sum_{i>j} \phi^{eff}(r_{ij})$$

EXAMPLE: LENNARD-JONES POTENTIAL

$$\phi^{LJ}(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$



Argon: $\sigma \simeq 0.34$ nm

$\varepsilon / k_B \simeq 120$ °K

COMPUTE AVERAGES IN THE ENSEMBLES

$$\langle A \rangle = \frac{\int d\tau \, A \, e^{-\beta H}}{\int d\tau \, e^{-\beta H}} = \quad (1)$$

$$= \lim_{t_0 \to \infty} \frac{1}{t_0} \int_0^{t_0} A(t)\, dt \quad (2)$$

(1) M.C. USUALLY CANONICAL ENS.

(2) M.D. USUALLY MICROCANONICAL

$$\boxed{\begin{aligned} \dot{X}_i &= p_i \\ \dot{p}_i &= -\frac{\partial V}{\partial X_i} \end{aligned}}$$

average temperature

$$\frac{f}{2} N k_B \langle T \rangle = \langle K \rangle$$

COMPUTER SIMULATION

INITIAL CONFIGURATION

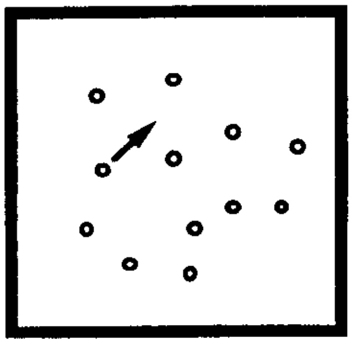
↓ THERMALIZATION

EQUILIBRIUM

M.C. SIMULATION

AVERAGES ON DIFFERENT CONFIGURATIONS

C1 → C2 → C3 → C4 →



$$\mathbf{r}_i \longrightarrow \mathbf{r}_i + \delta$$

$$\Delta E = E_{new} - E_{old}$$

Computer simulation near T_c

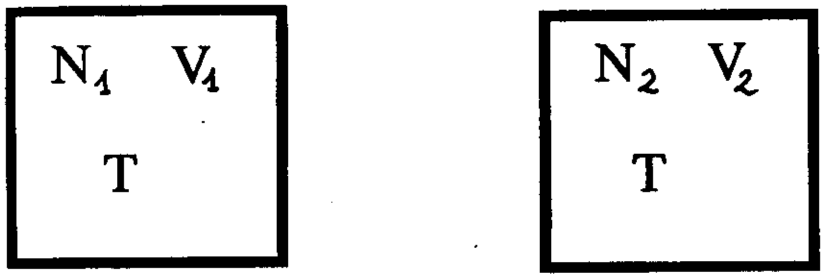
Indirect methods

⇒ **thermodynamic integration**
(free energy)

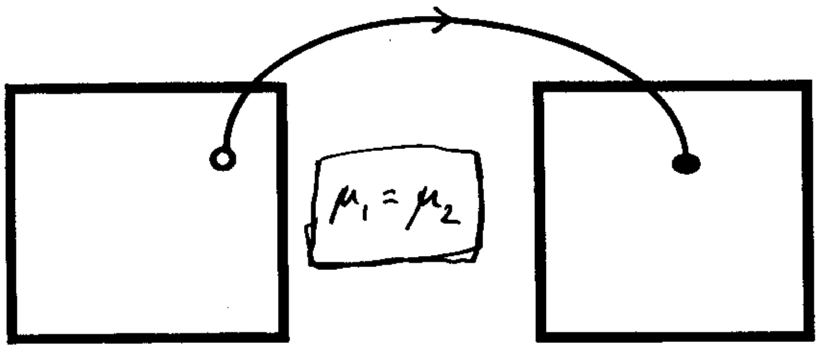
⇒ **umbrella sampling**

⇒ **particle insertion**
(chemical potential)

GIBBS ENSEMBLE (M.C.)



ΔV_1 $\quad \Delta V_2 = -\Delta V_1$ $\quad \boxed{P_1 = P_2}$



EXCHANGE PARTICLES

M.C. simulation of 2D L.J. fluid

Potential

$$\varphi(r) = 4\epsilon\{(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^6\}$$

canonical M.C. with P.B.C.

Units:

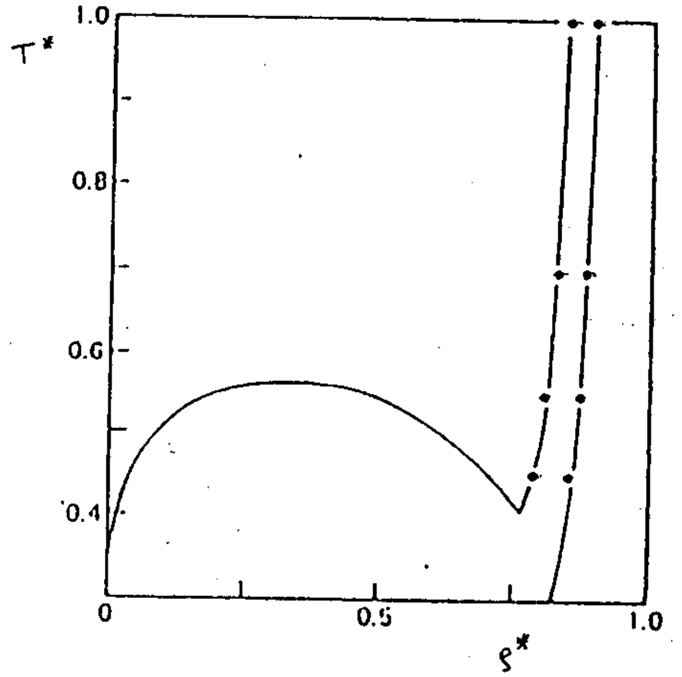
$$T^* = \frac{k_B T}{\epsilon}$$

$$\rho^* = \rho\sigma^2$$

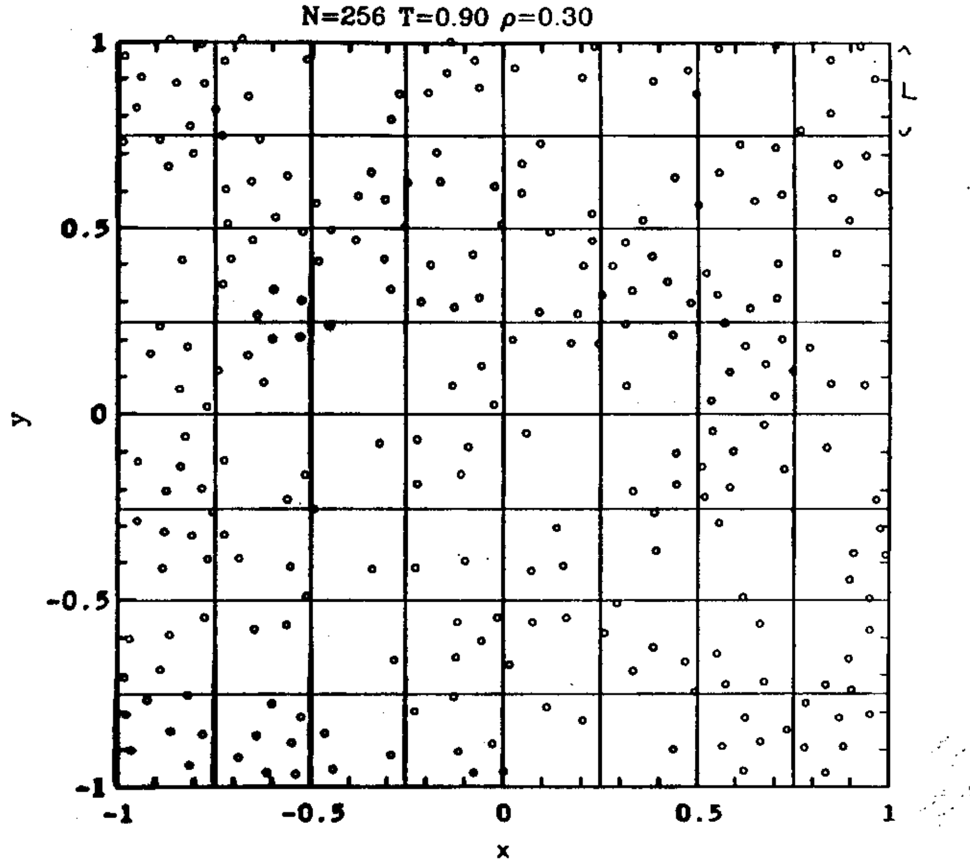
(19)

Estimated critical point (2D L.J.)

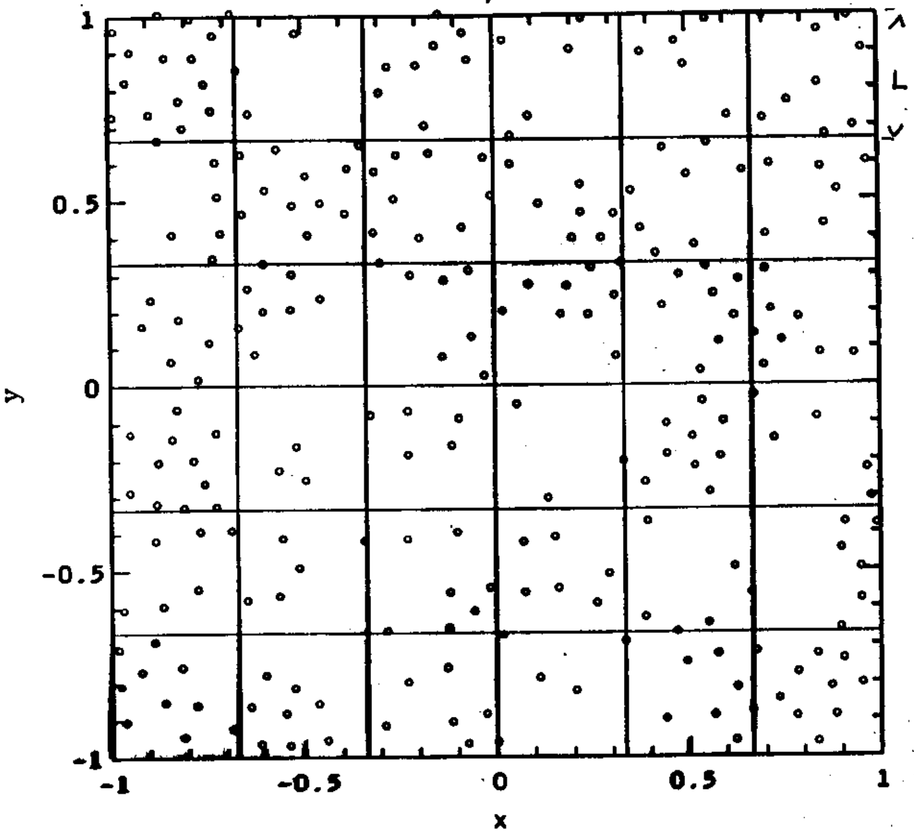
T_c^*	ρ_c^*	
$0.62 \div 0.7$	0.38	*Tsien&Valleau*
0.56	0.32	*Henderson(77)*
0.53	0.33	*Barker&al.(81)*



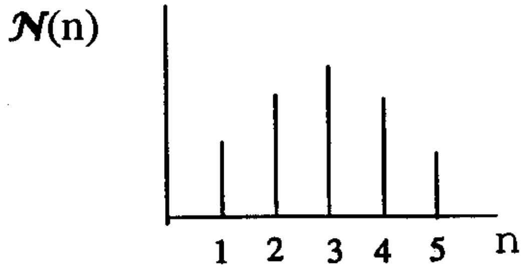
(20)



N=256 T=0.90 ρ=0.30



Block distribution functions



$$\rho = n / L^2 \longrightarrow P_L(\rho)$$

$T \gg T_c$ $\xi \ll L$

$$P_L(\rho) \sim \exp\{-(\rho - \langle\rho\rangle)^2 / \alpha^2\}$$

$$\alpha^2 \sim k_B T \underline{K_T^L} L^{-d}$$

isothermal compress.

(in the therm. limit

$K_T^L \to K_T$)

BLOCK DISTRIBUTION FUNCTIONS

length of the block $L = S/M$

$= 2 \quad M^2$ Blocks

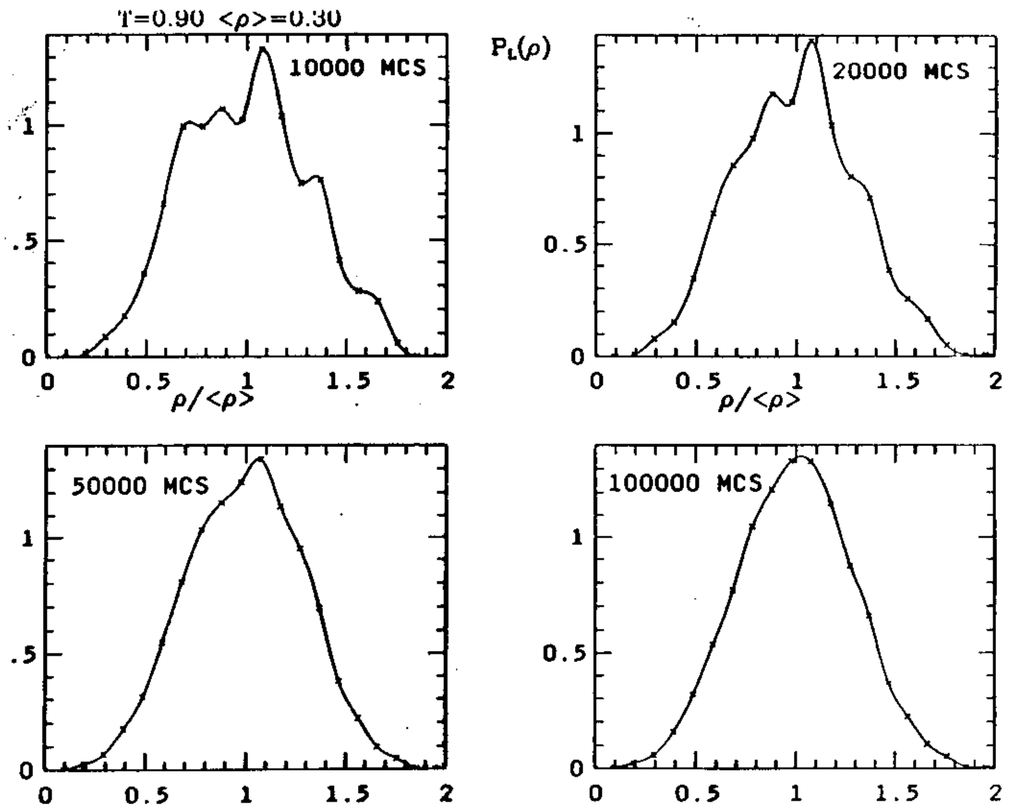
$\mathcal{N}_b(n_b)$ n. of blocks with n_b particles

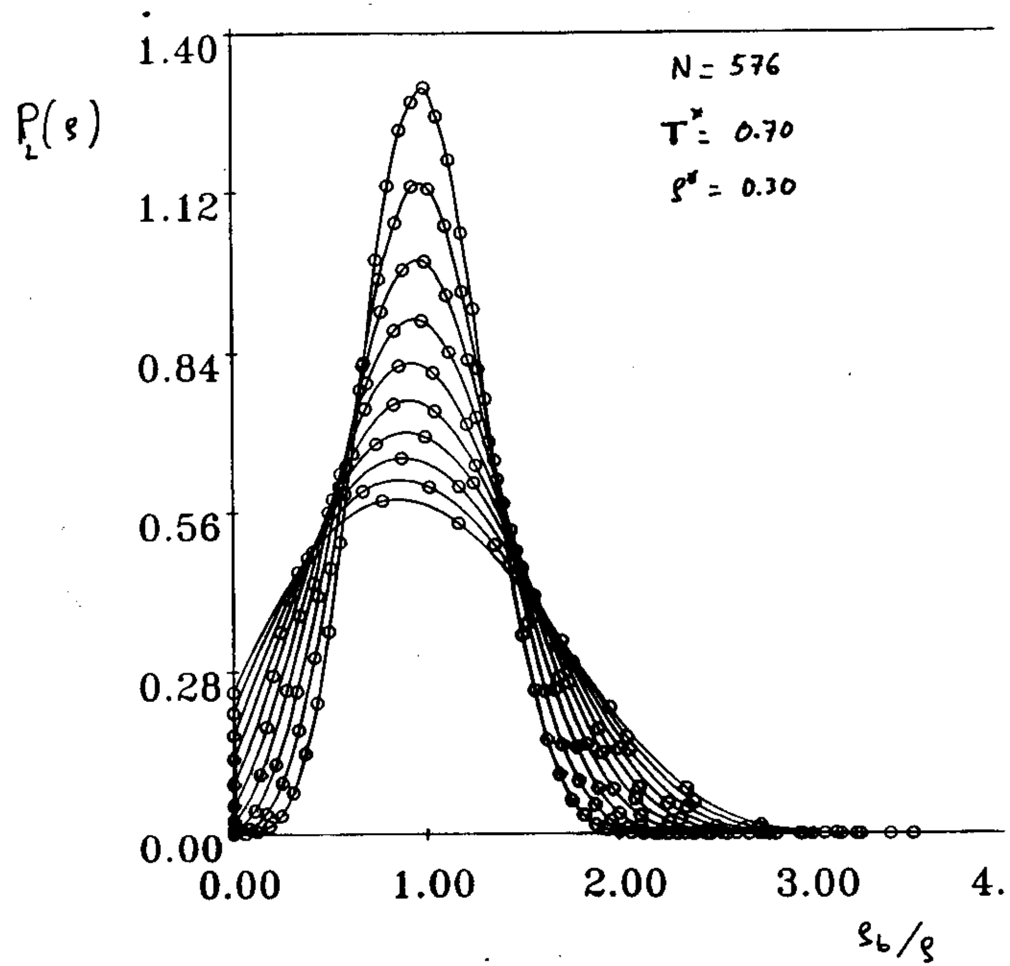
SUM RULES

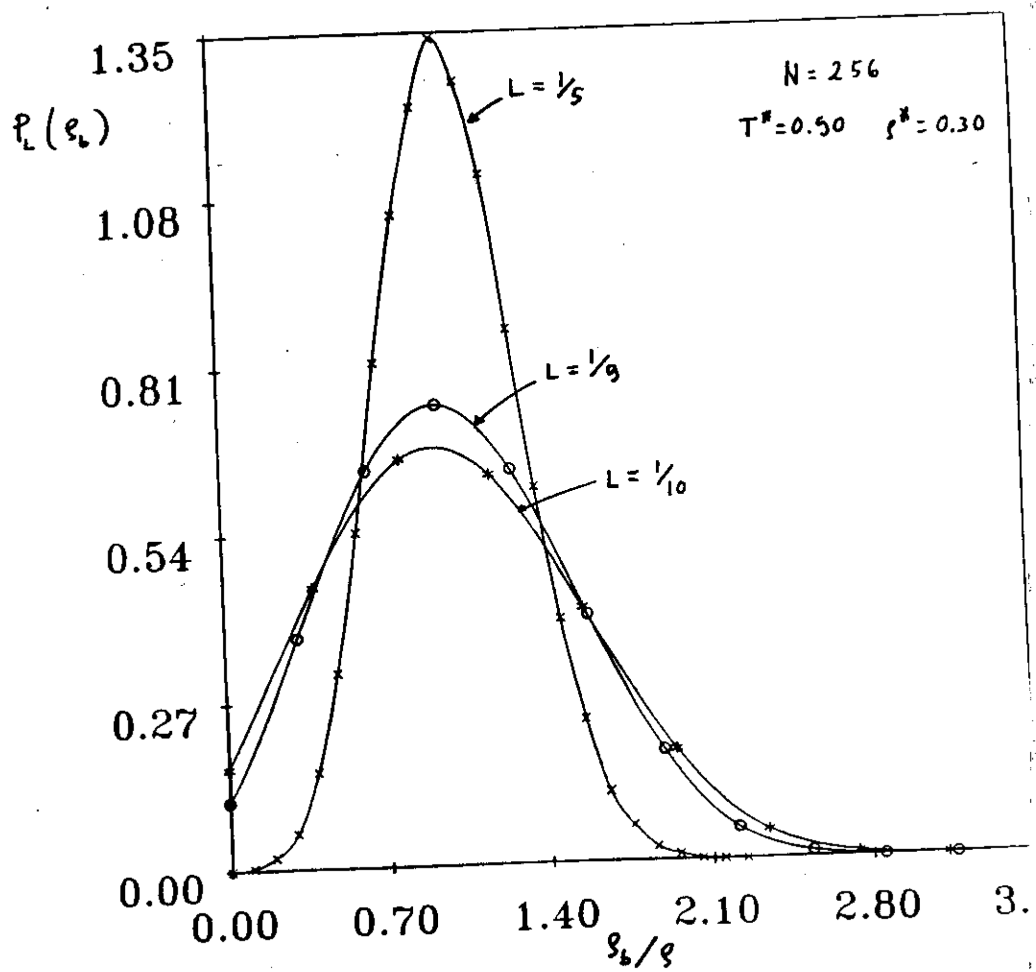
$$\sum_{n_b} \mathcal{N}_b(n_b) = M^2$$

$$\sum_{n_b} \mathcal{N}_b(n_b) \cdot n_b = N$$

$$n_b \rightarrow \rho_b = n_b / L^2 \quad : \quad P_L(\rho)$$

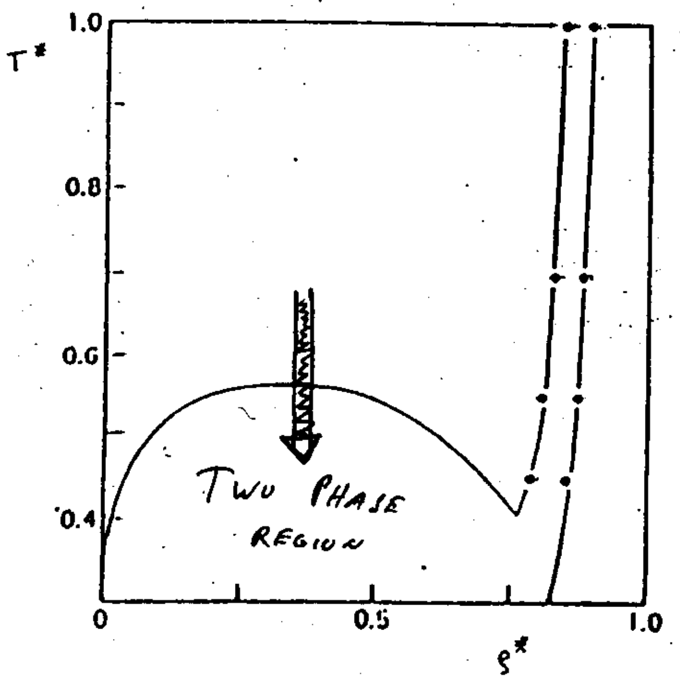






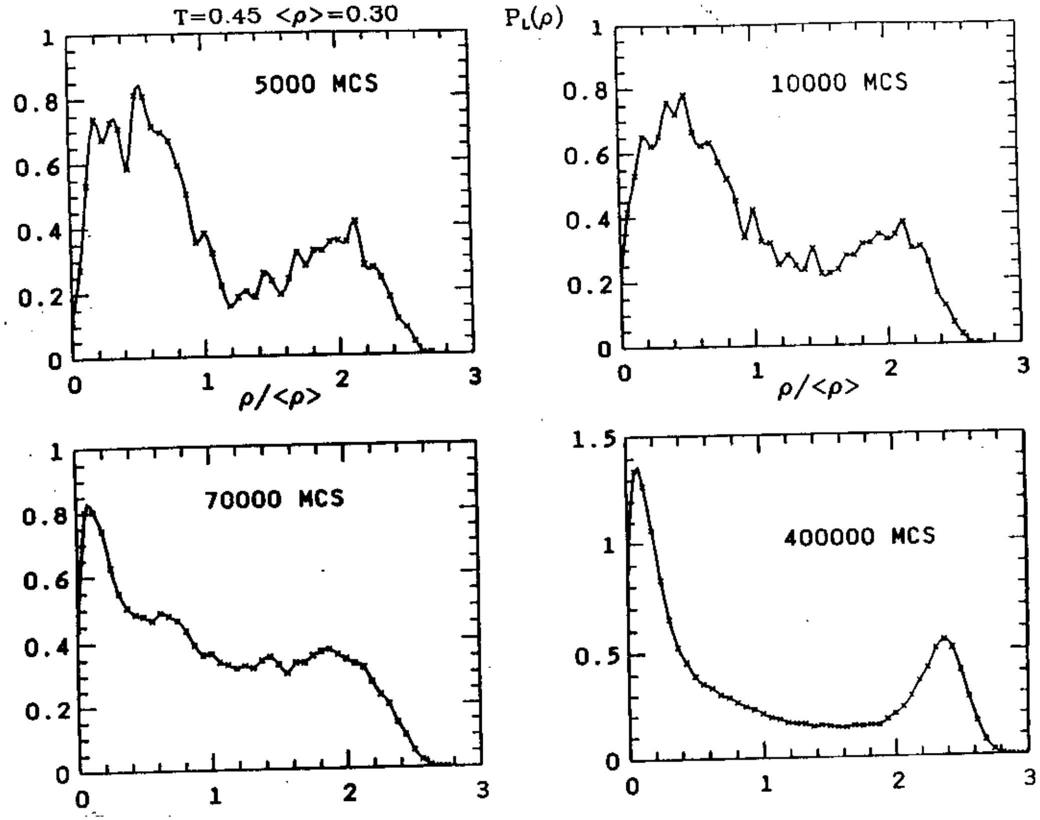
$T_c \approx 0.55-0.50$

(27)

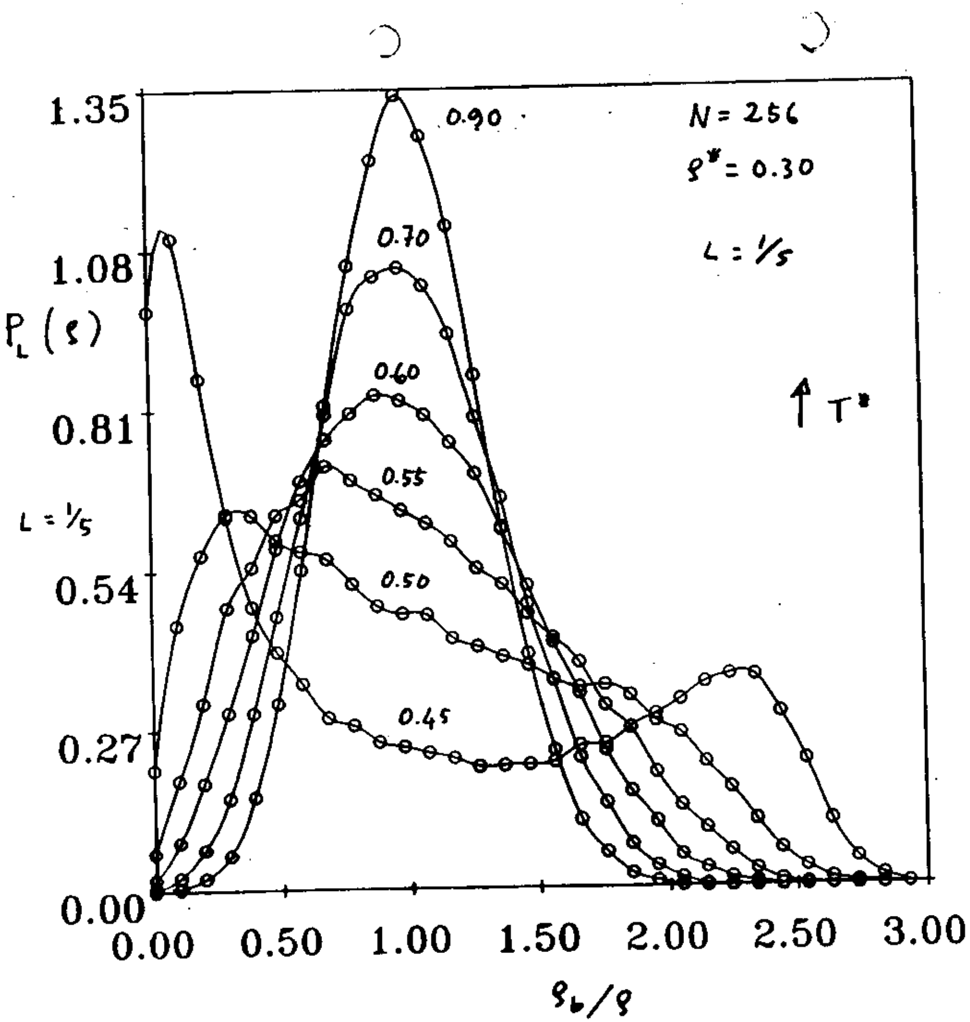


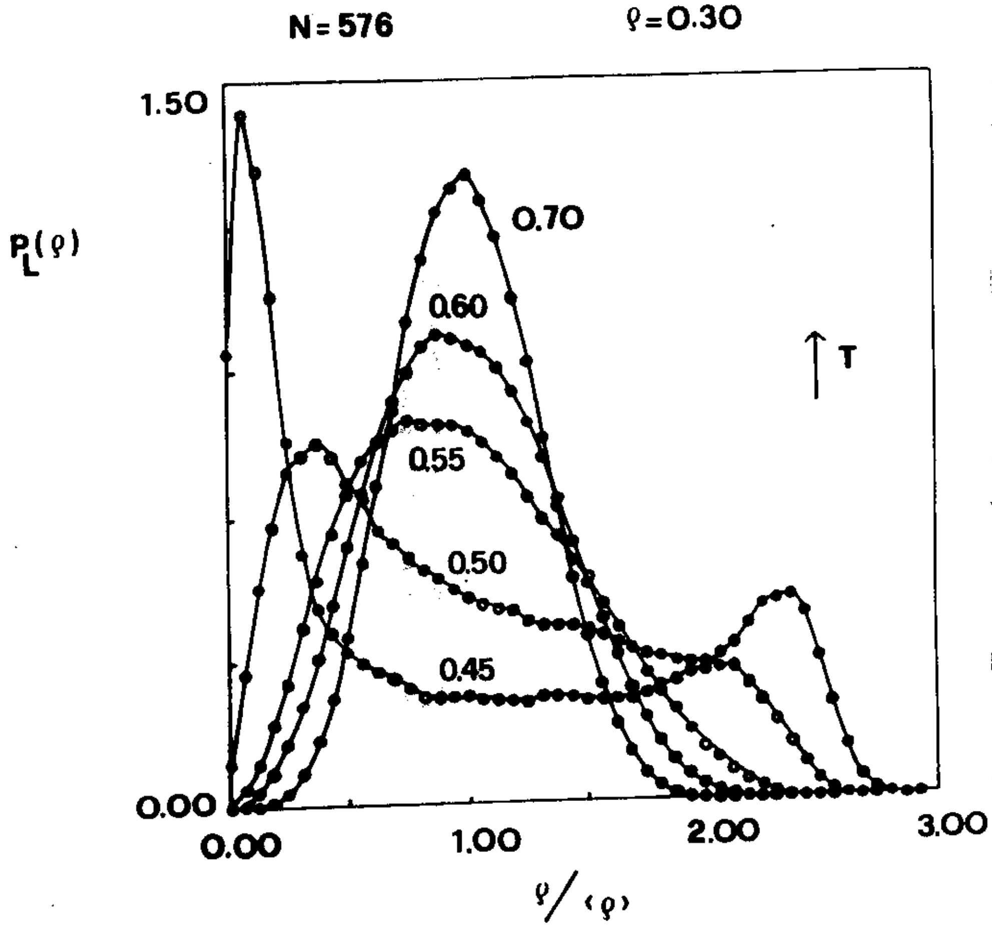
T*
1.0
0.8
0.6
0.4
0
0.5
1.0
ρ*
TWO PHASE
REGION

(28)

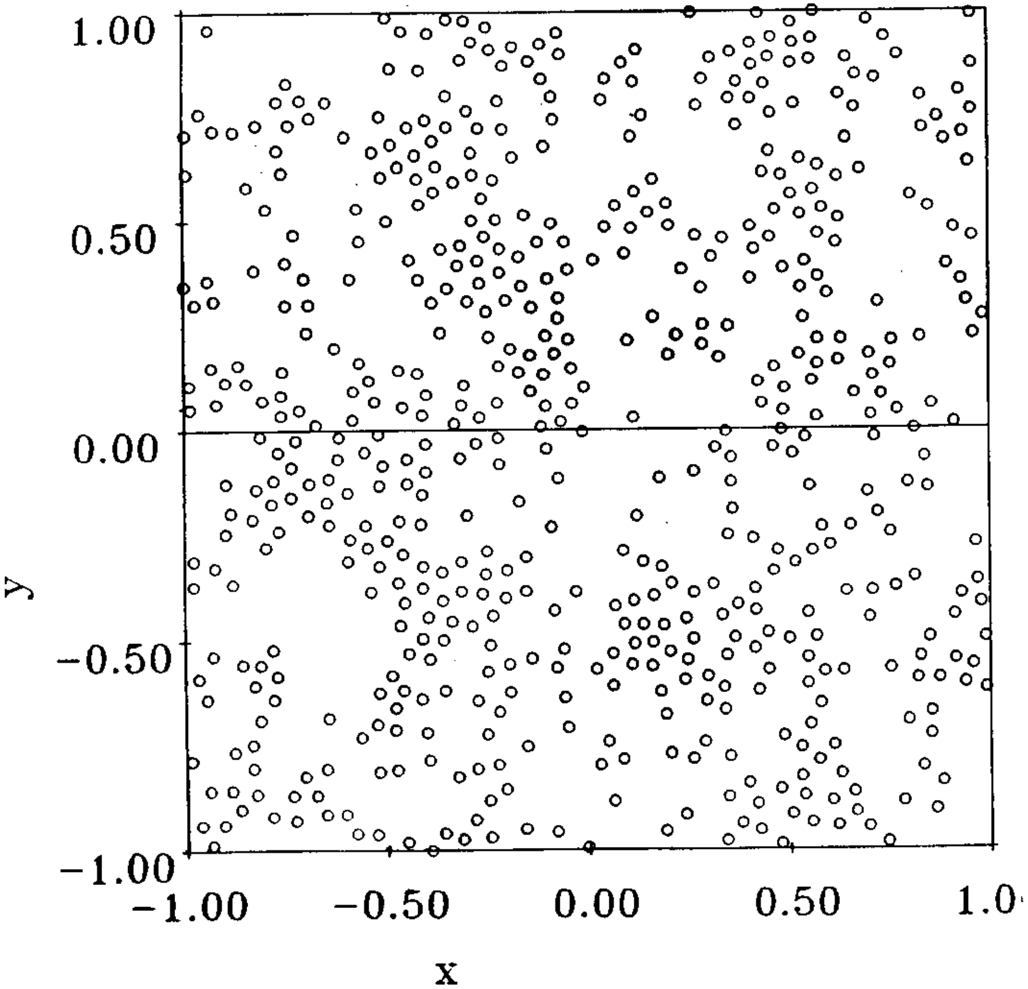


T=0.45 <ρ>=0.30
P_L(ρ)
5000 MCS
10000 MCS
70000 MCS
400000 MCS
ρ/<ρ>
ρ/<ρ>

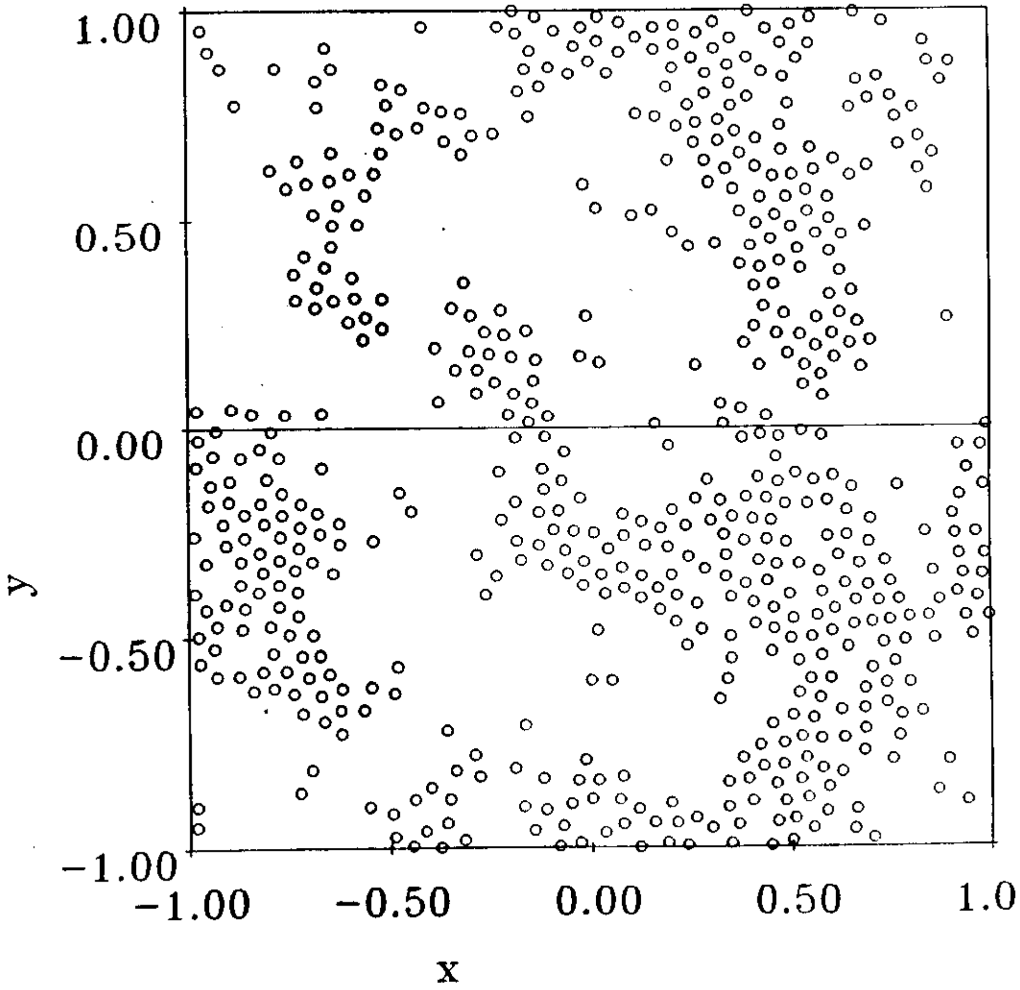

1.35
1.08
0.81
0.54
0.27
0.00
$P_L(\rho)$
$L = 1/5$
0.90
0.70
0.60
0.55
0.50
0.45
$N = 256$
$\rho^* = 0.30$
$L = 1/5$
$\uparrow T^*$
0.00 0.50 1.00 1.50 2.00 2.50 3.00
ρ_L/ρ


N=576
ρ=0.30
1.50
0.00
$P_L(\rho)$
0.70
0.60
0.55
0.50
0.45
$\uparrow$ T
0.00 1.00 2.00 3.00
$\rho/\langle\rho\rangle$

N = 576 $\rho^* = 0.30$ $T^* = 0.70$

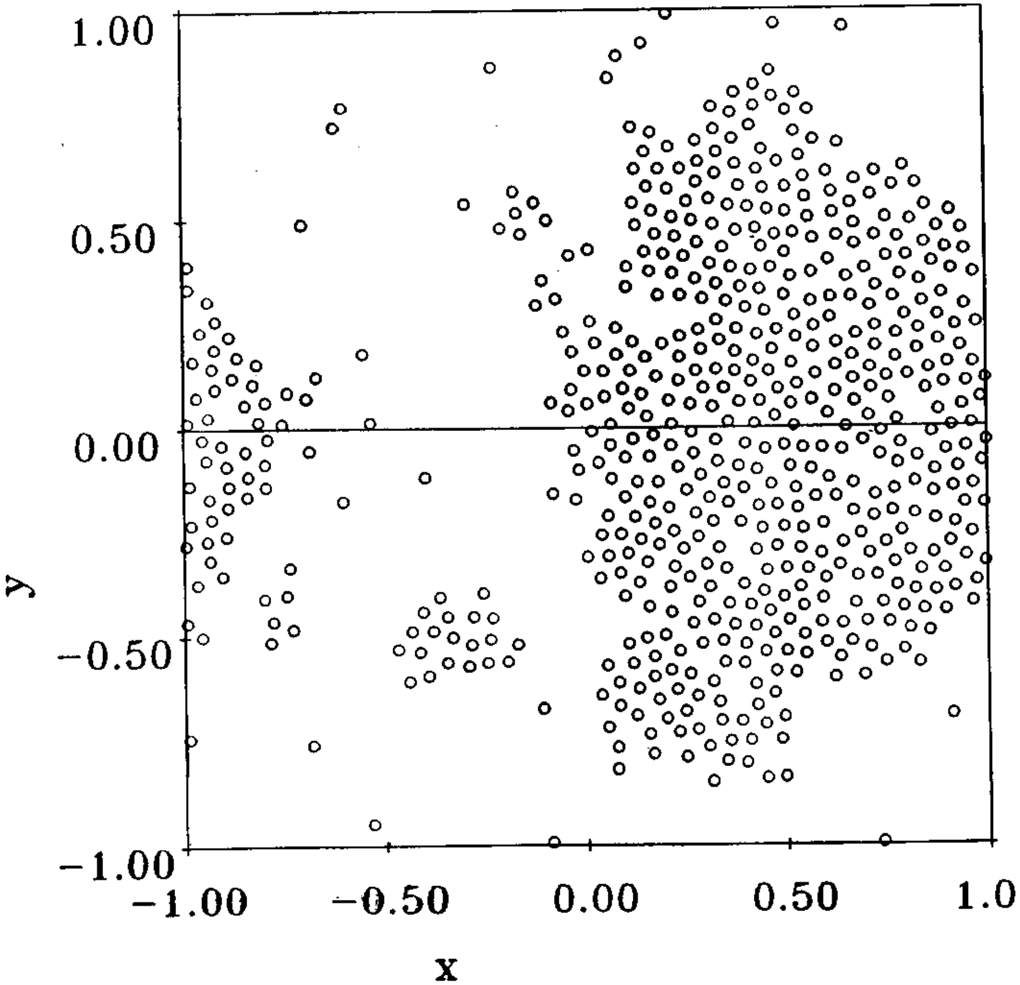


N = 576 $\rho^* = 0.30$ $T^* = 0.50$



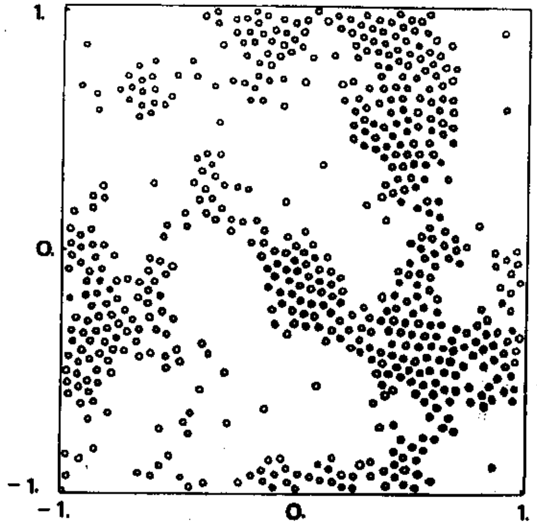
~ 10^6 MCS

$N = 576$ $\rho^* = 0.30$ $T^* = 0.45$

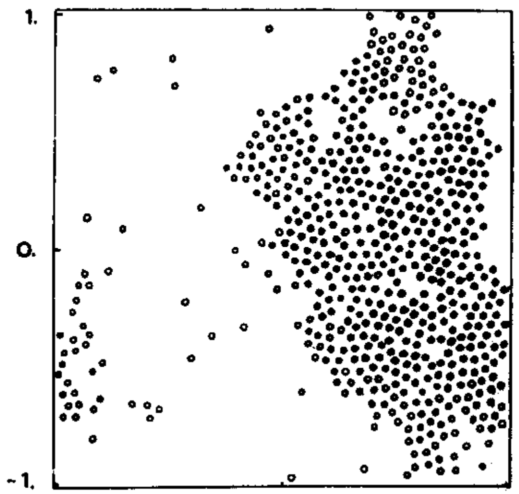


$\sim 10^6$ MCS

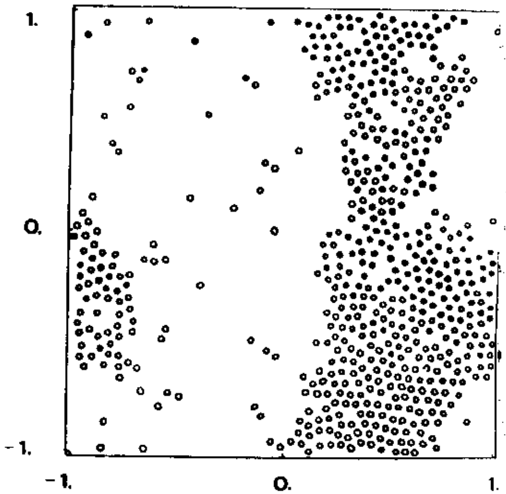
N=576 T=0.45 ρ=0.30 MCS=10.000

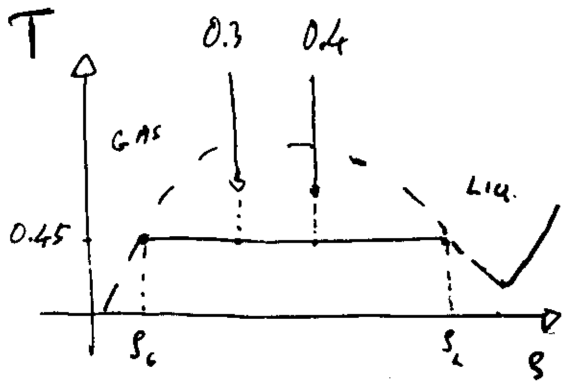


N=576 T=0.45 ρ=0.30 MCS=900.000

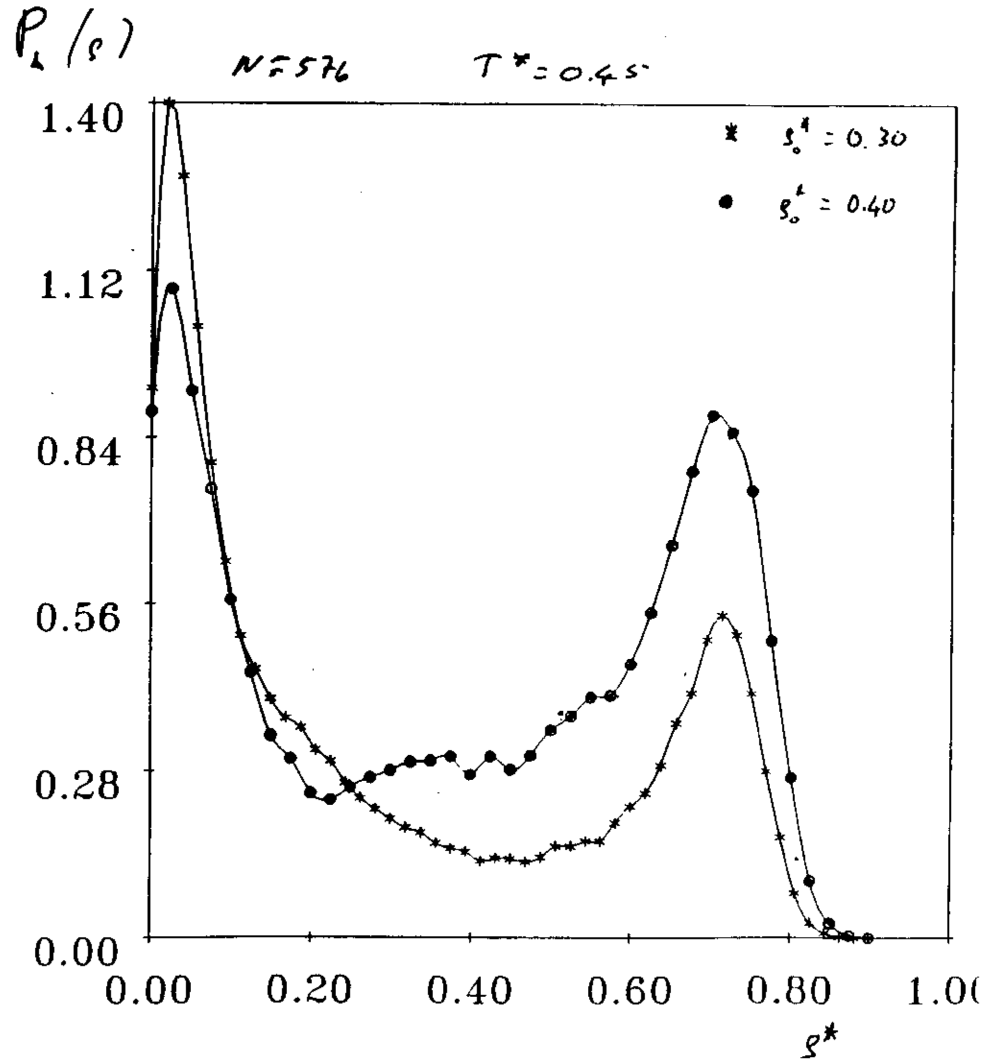


N=576 T=0.45 ρ=0.30 MCS=480

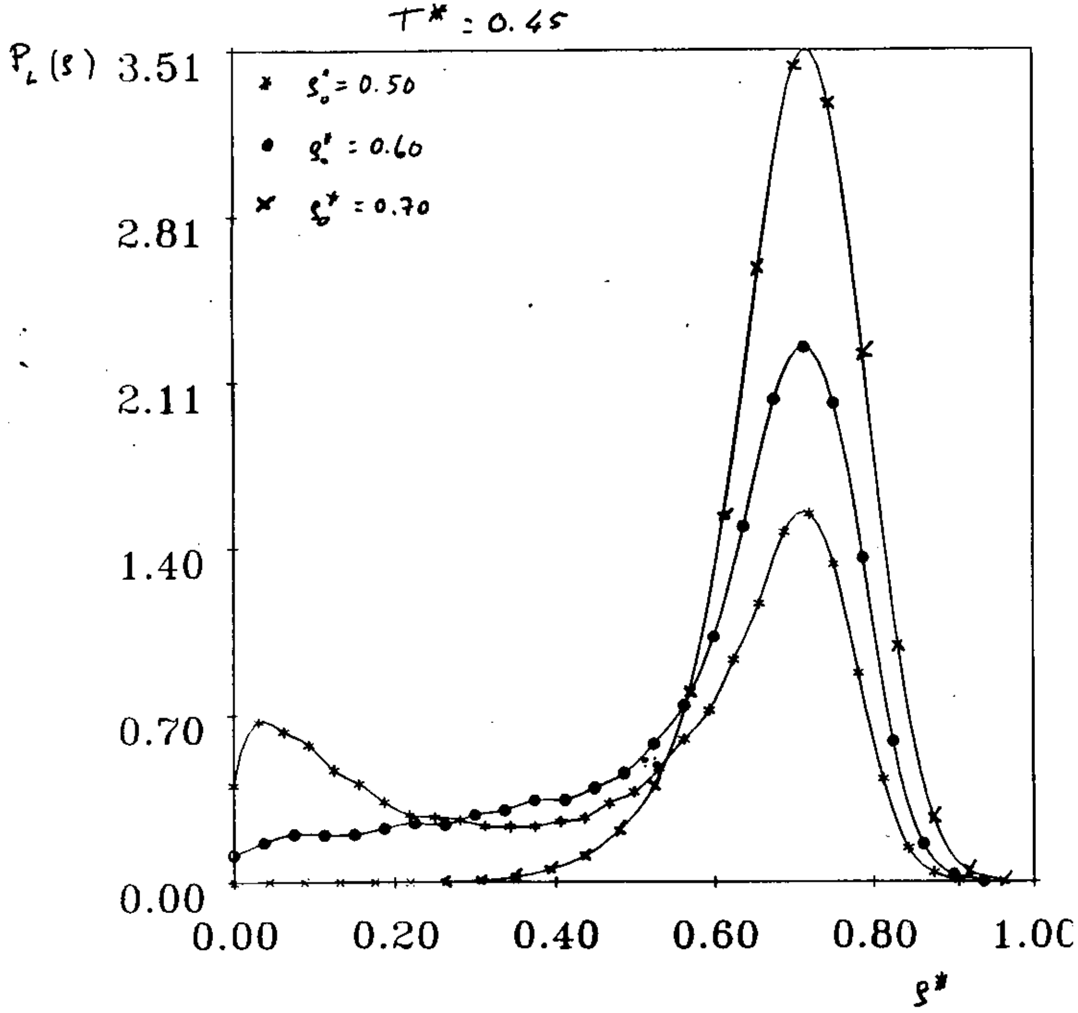


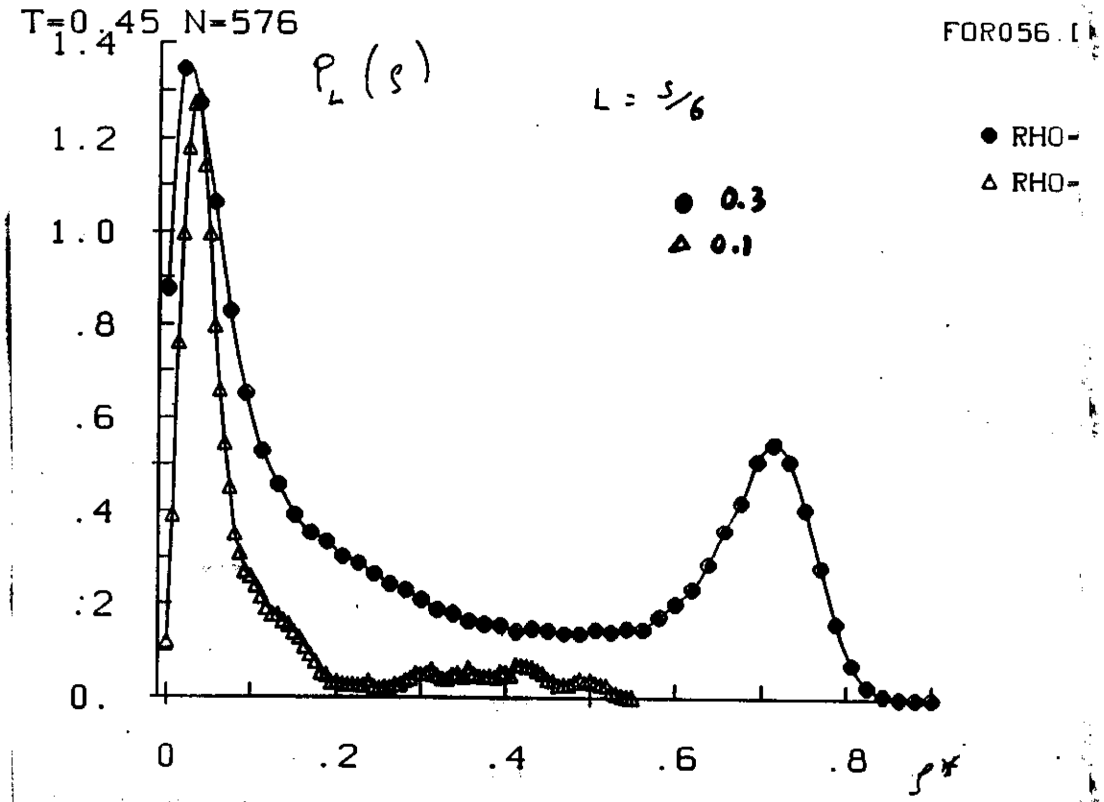


T
0.3
0.4
GAS
LIQ.
0.45
ρ_G
ρ_L
ρ



$P_L(\rho)$
N=576
$T^*=0.45$
$\rho_0^* = 0.30$
$\rho_0^* = 0.40$
1.40
1.12
0.84
0.56
0.28
0.00
0.00
0.20
0.40
0.60
0.80
ρ^*


$T^* = 0.45$
$P_L(\rho)$
3.51
2.81
2.11
1.40
0.70
0.00
0.00
0.20
0.40
0.60
0.80
1.00
ρ^*
$\rho_0^* = 0.50$
$\rho_0^* = 0.60$
$\rho_0^* = 0.70$


T=0.45 N=576
FOR056.D
$P_L(\rho)$
L = 5/6
● RHO=
△ RHO=
● 0.3
△ 0.1
1.4
1.2
1.0
.8
.6
.4
.2
0.
0
.2
.4
.6
.8
ρ^*

MOMENTS

$$\langle \rho^n \rangle_L = \int d\rho \; P_L(\rho) \; \rho^n$$

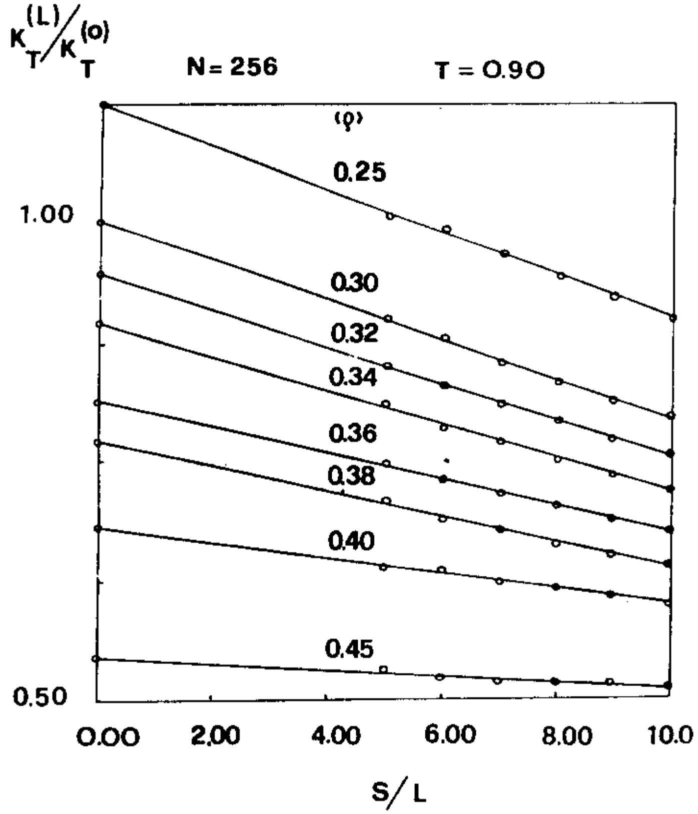
1-ST $\quad \langle \rho \rangle_L$ = av. density of the block

2-nd $\quad$ is related to the isothermal compressibility

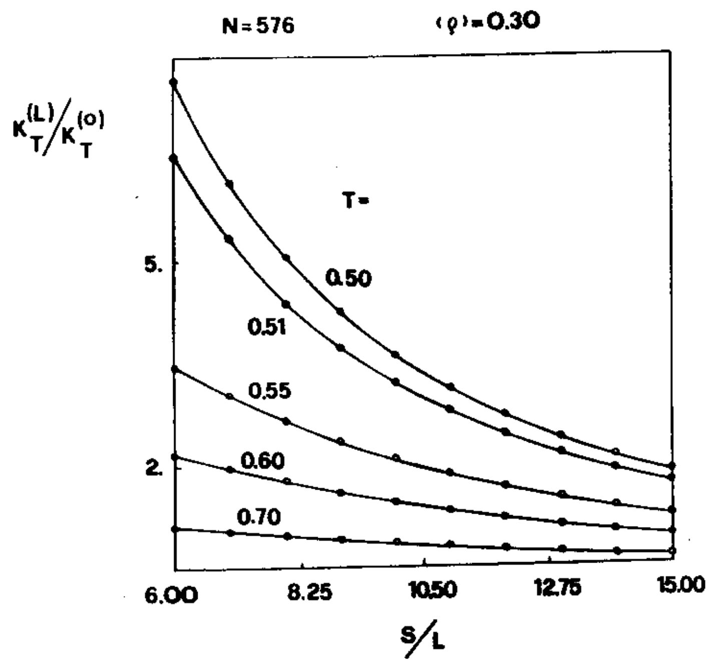
$$L^{-d} \langle \rho \rangle_L^2 \; k_B T \; \underline{K_T^{(L)}} = \langle (\rho - \langle \rho \rangle_L)^2 \rangle_L$$

$T >> T_c$

$$K_T^{(L)} \sim K_T + c L^{-1}$$



(41)



(4

For a state in the two phase region

$$T \ll T_c \qquad L \gg \xi$$

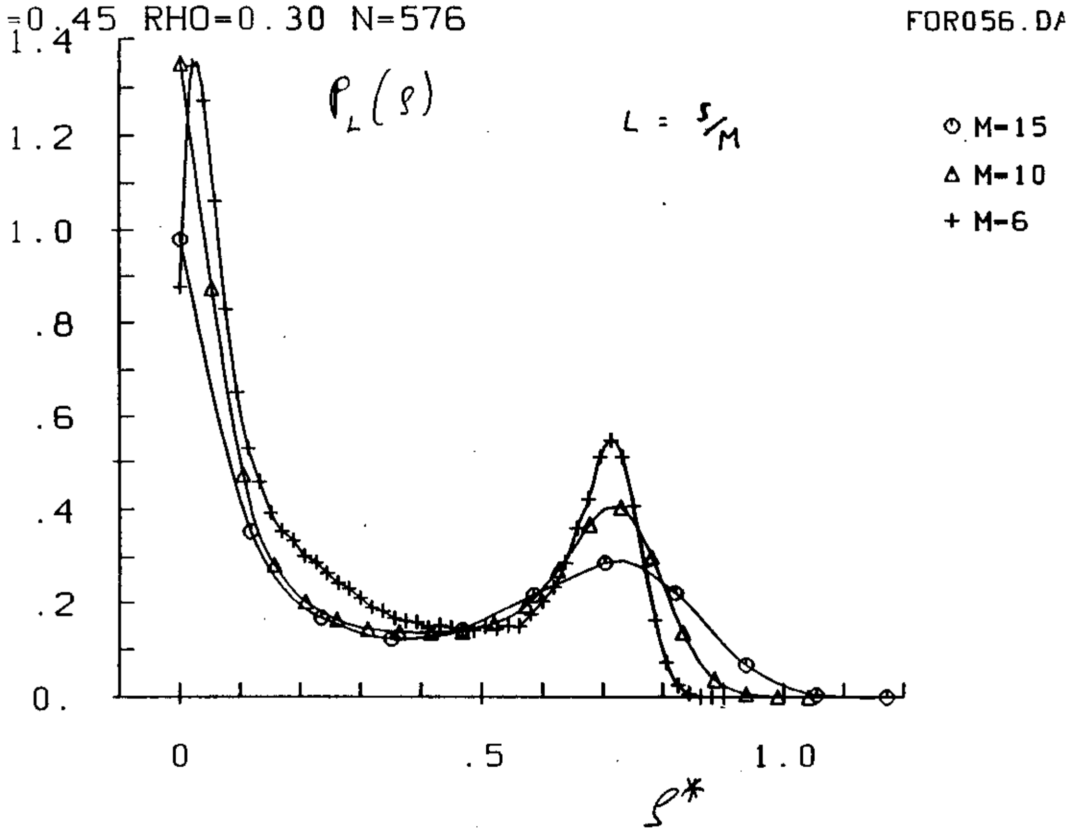
$$P_L(\rho) \;\propto\; A \frac{1}{\rho_{gas}(K_T^{gas})^{1/2}} \exp[-\frac{(\rho-\rho_{gas})^2 L^d}{2\rho_{gas}^2 k_B T K_T^{gas}}] +$$

$$B \frac{1}{\rho_{liq}(K_T^{liq})^{1/2}} \exp[-\frac{(\rho-\rho_{liq})^2 L^d}{2\rho_{liq}^2 k_B T K_T^{liq}}]$$

$A(<\rho>)$ **and** $B(<\rho>)$

determined from $\mu_{gas} = \mu_{liq}$

(43)



(44)

N = 576 T = 0.45 <ρ> = 0.30 COEX.

liquid branch

TABLE I

M_b	ρ_{liq}	$k_B T \rho_{liq} K_T^{liq}$
6	0.711	0.867
7	0.718	0.763
8	0.720	0.730
9	0.718	0.814
10	0.719	0.753
11	0.718	0.875
12	0.698	1.169
13	0.715	0.828
14	0.722	0.830
15	0.715	1.057

SOMETHING ABOUT BLOCKS

RESOLUTION IN DENSITY

$$\delta\rho = 1/L^d \qquad L = S/M$$

LARGE L → GOOD RESOLUTION

BUT

$\frac{\delta n_b}{n_b}$ must be not too small

OPT.

$$L_{min} < L < L_{max} \ll N^{1/d}$$

L_{min} large enough $\frac{\delta\rho}{\rho} \simeq 0.1$

$$L = S/M$$

$d = 2$

take M too LARGE $M^2 \gg N$

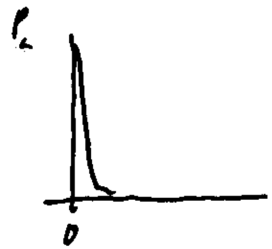
$n_b = 0, 1$

FROM SUM RULES

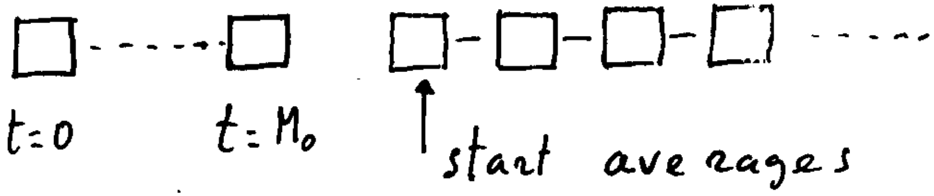
$$\mathcal{N}_b(0)\cdot 0 + \mathcal{N}(1)\cdot 1 \simeq N$$

$$\mathcal{N}_b(0) + \mathcal{N}_b(1) \simeq M^2$$

$$\mathcal{N}_b(0) \simeq M^2$$



Relaxation time to equilibrium



$$\tau_A^{rel} << M_0/N$$

→ metastable states

$$\tau_A^{rel} \simeq \tau_0 \exp\left[\frac{\Delta U}{k_B T}\right]$$

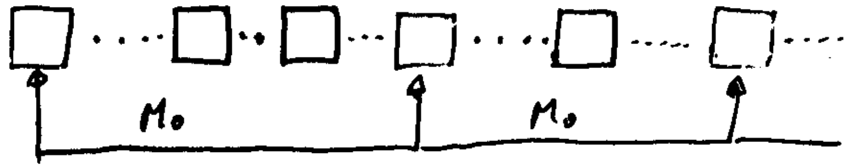
→ close to T_c

$$\delta T = T - T_c$$

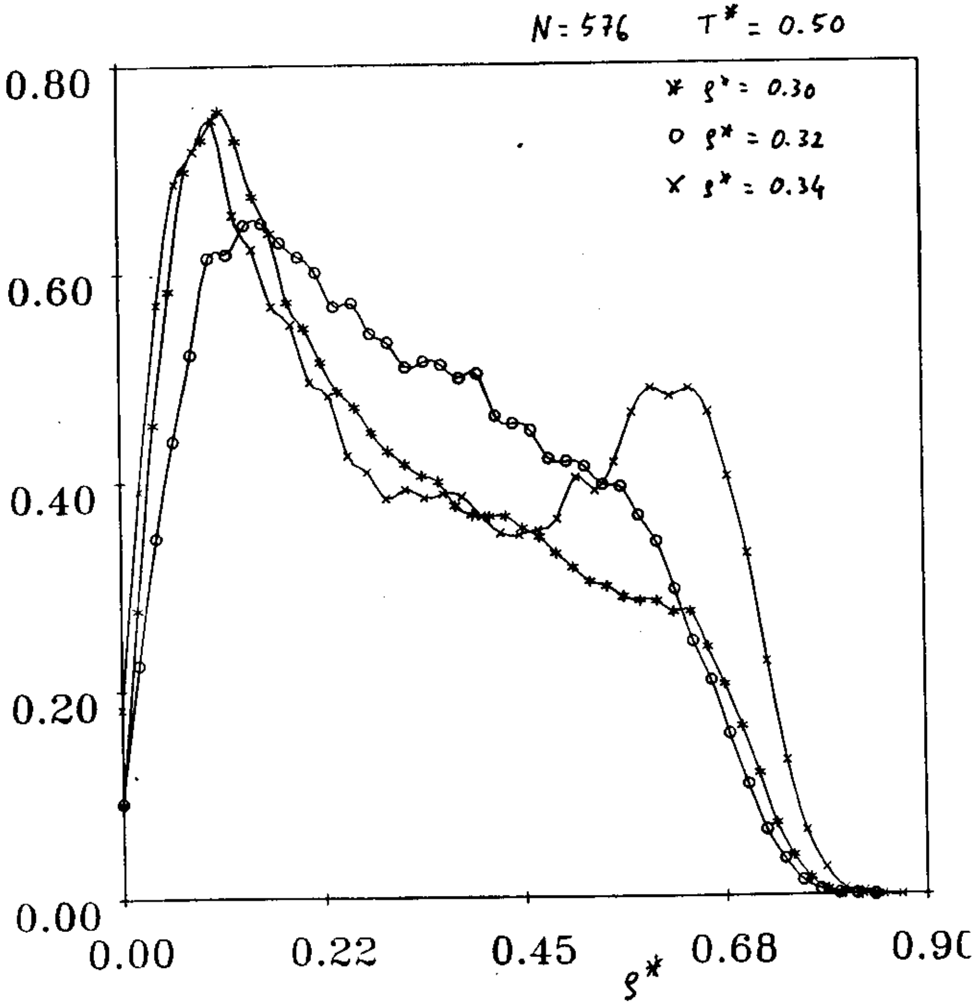
$$\tau_A^{rel} \sim |\delta T|^{-\Delta_A(\delta T)}$$

$$\chi_{AA} \sim \langle A^2 \rangle - \langle A \rangle^2 \rightarrow \tau_A^{rel} \sim \chi_{AA}$$

Average on indipendent configurations:



$$\tau_{AA} << (M - M_0)/N$$



4-th order reduced cumulant

$$\Delta \rho = \rho - \langle \rho \rangle$$

$$U_L(T,\rho) = 1 - \frac{\langle \Delta\rho^4 \rangle_L}{3 \langle \Delta\rho^2 \rangle_L^2}$$

Ising:

$$U_L(T) = 1 - \frac{\langle s^4 \rangle}{3 \langle s^2 \rangle^2}$$

$T \gg T_c \qquad U_L(T) \sim L^{-d} \to 0$

$T \ll T_c \qquad U_L(T) \to 2/3 = 0.6666..$

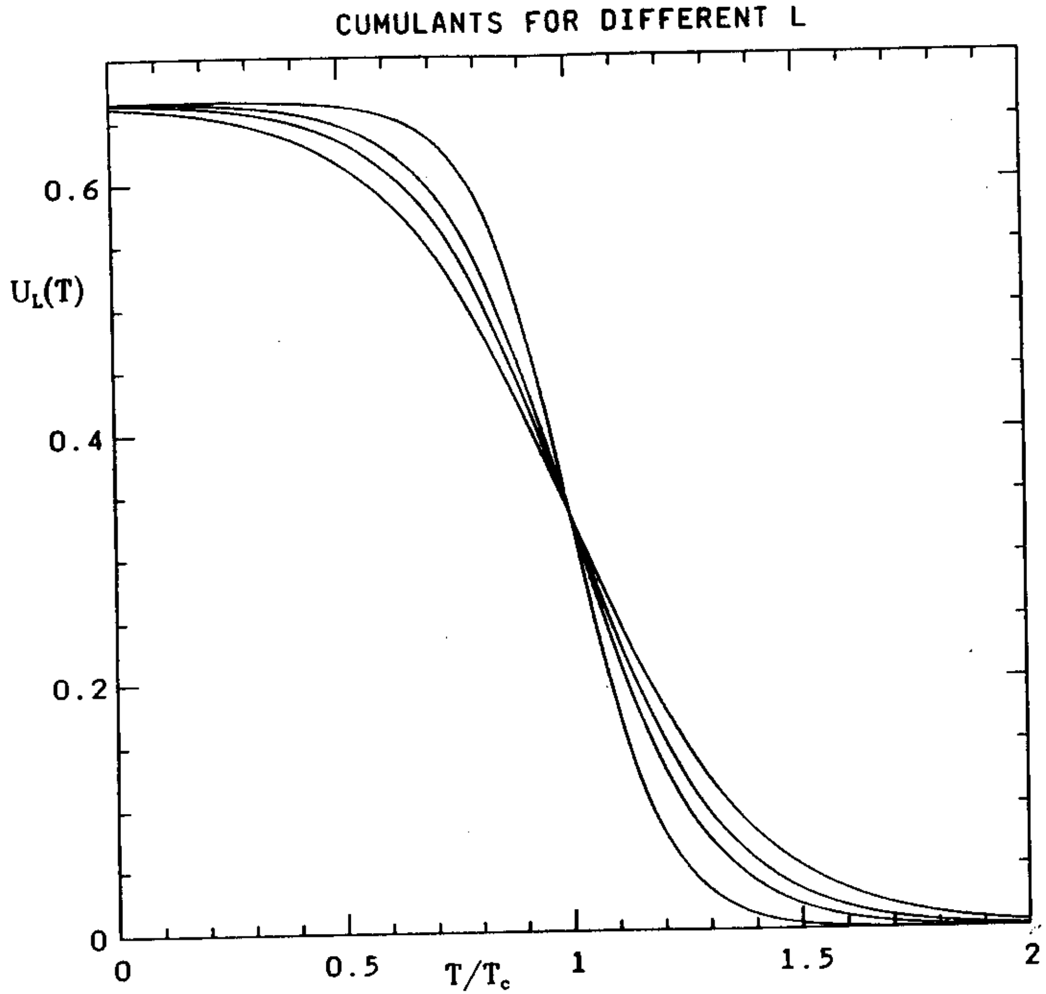
$T \to T_c \qquad U_L(T) \to U^*$

(40)

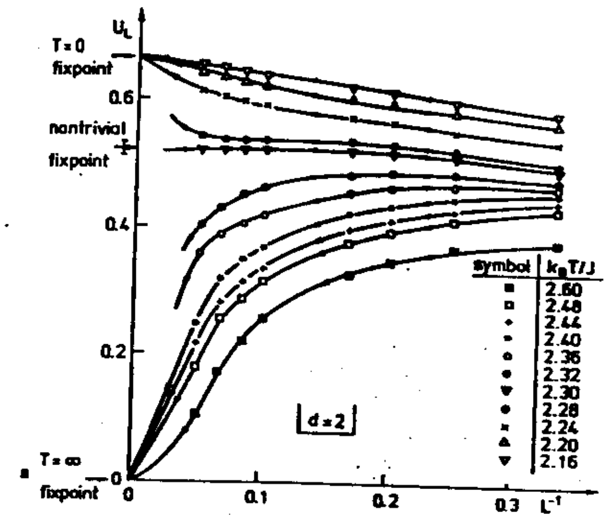
$$U(L,T) = 1 - \frac{\langle S^4 \rangle_L}{3 \langle S^2 \rangle_L^2}$$

$T \to \infty \quad U \to 0$

$T \to 0 \quad U = 2/3$

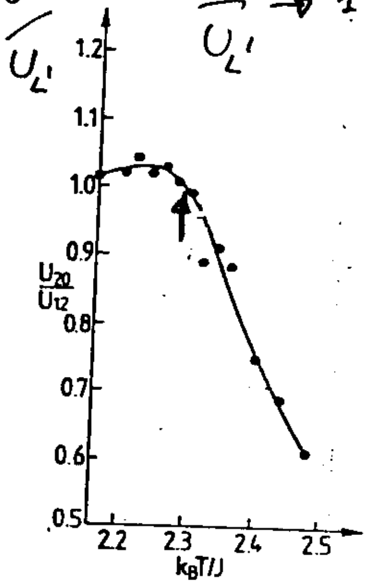


Binder 81



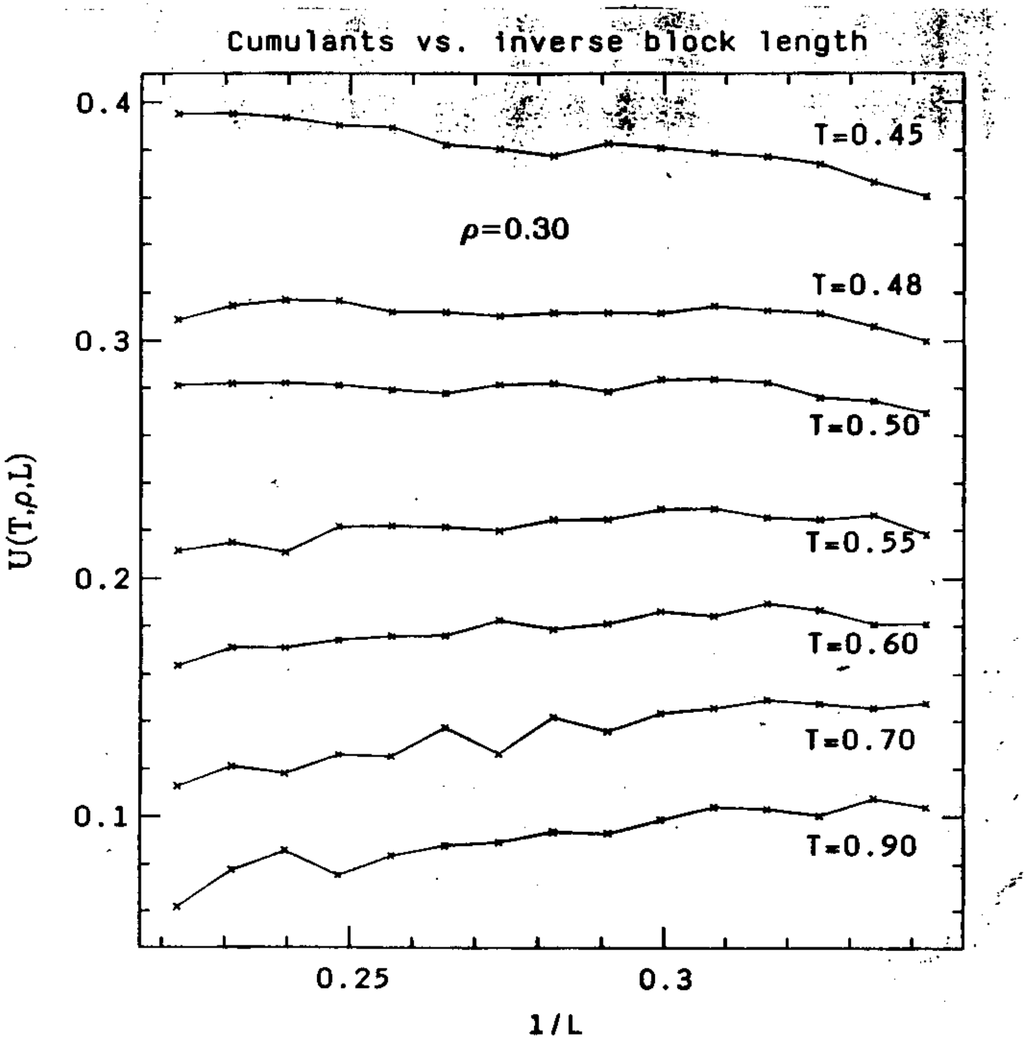
L^{-1}

$\frac{U_L}{U_{L'}}$ $\quad \frac{U_L}{U_{L'}} \to 1$



$$\frac{k_B T_c}{J} = 2.269$$

(51)



(52)

$$P_L(\rho) = L^y \tilde{P}\{(\rho-\rho_c)L^y, (p-p_c)L^x, L/\xi\}$$

$$\longrightarrow L^{\beta/\nu}\tilde{P}\{(\rho-\rho_c)L^{\beta/\nu}, (p-p_c)|\epsilon|^{-\beta}, L|\epsilon|^{\nu}\}$$

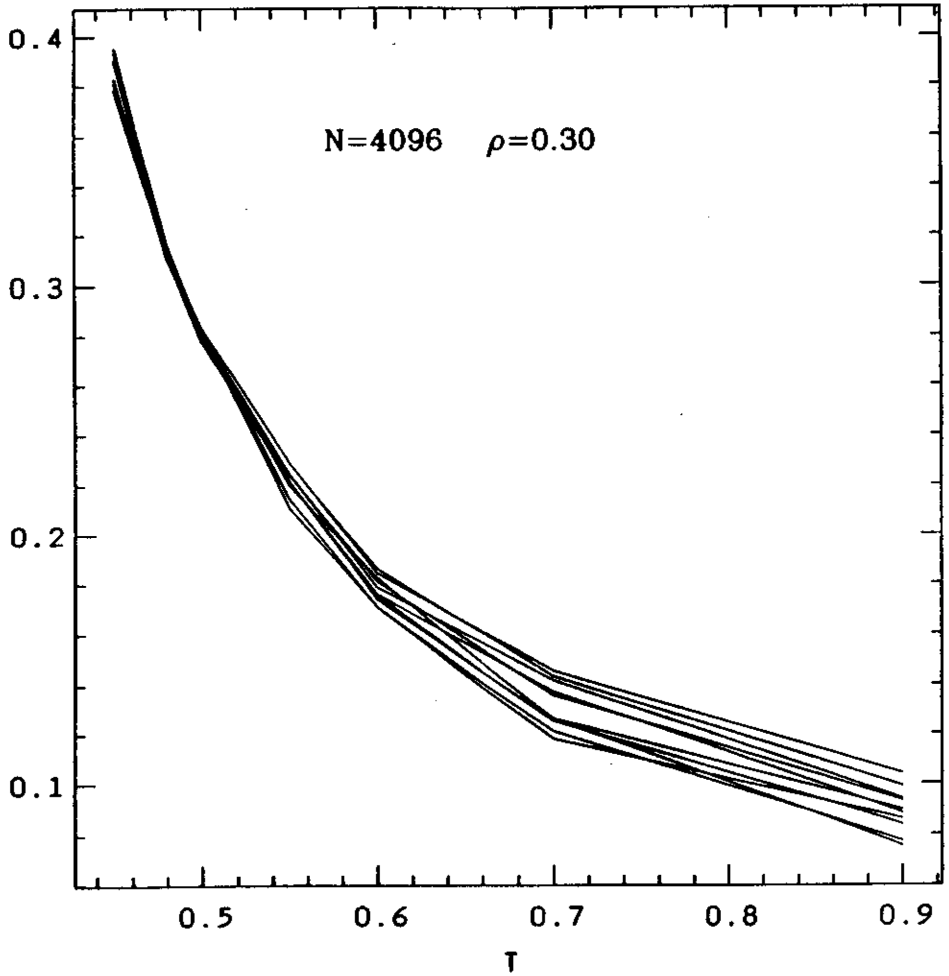
$$U_L \approx f_u\{(<\rho> - \rho_c)\epsilon|^{-\beta}, L|\epsilon|^{\nu}\}$$

$$<\rho> = \rho_c \qquad T \longrightarrow T_c$$

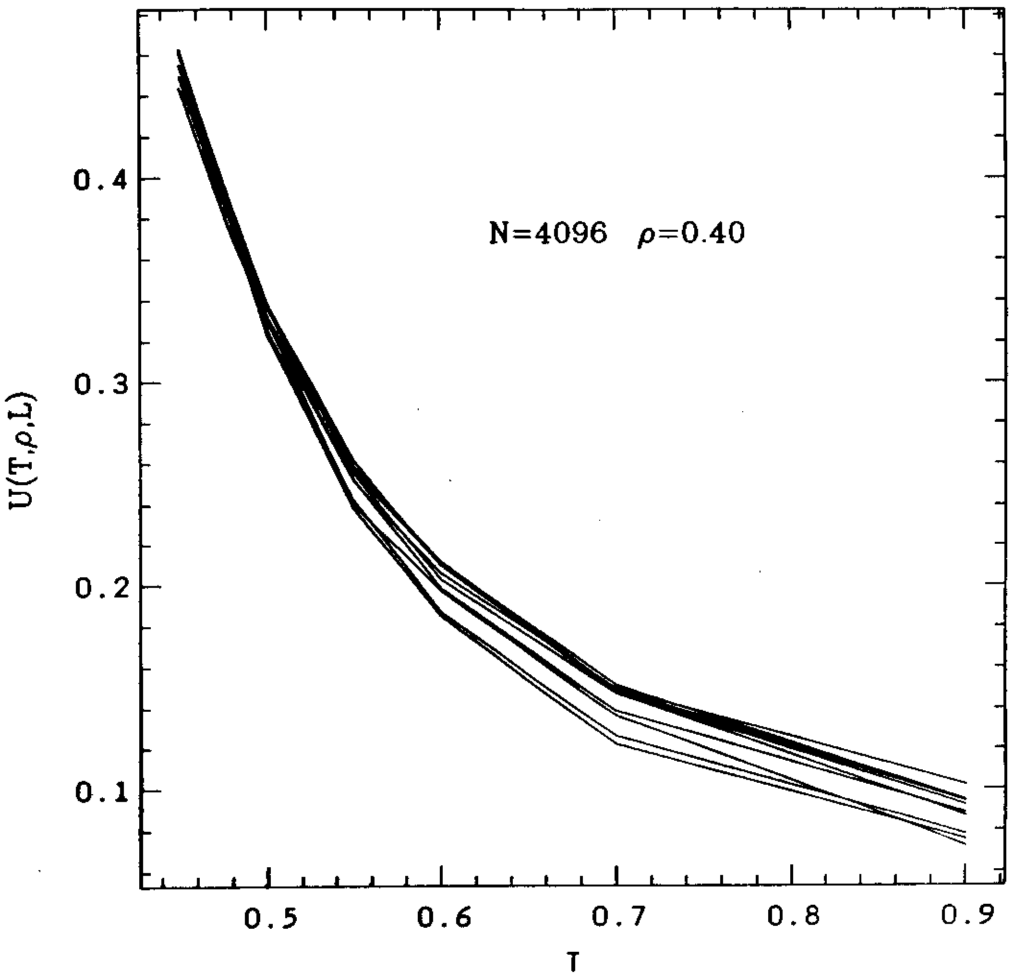
$$U_L \longrightarrow U^* = f_u(0,0)$$

(53)

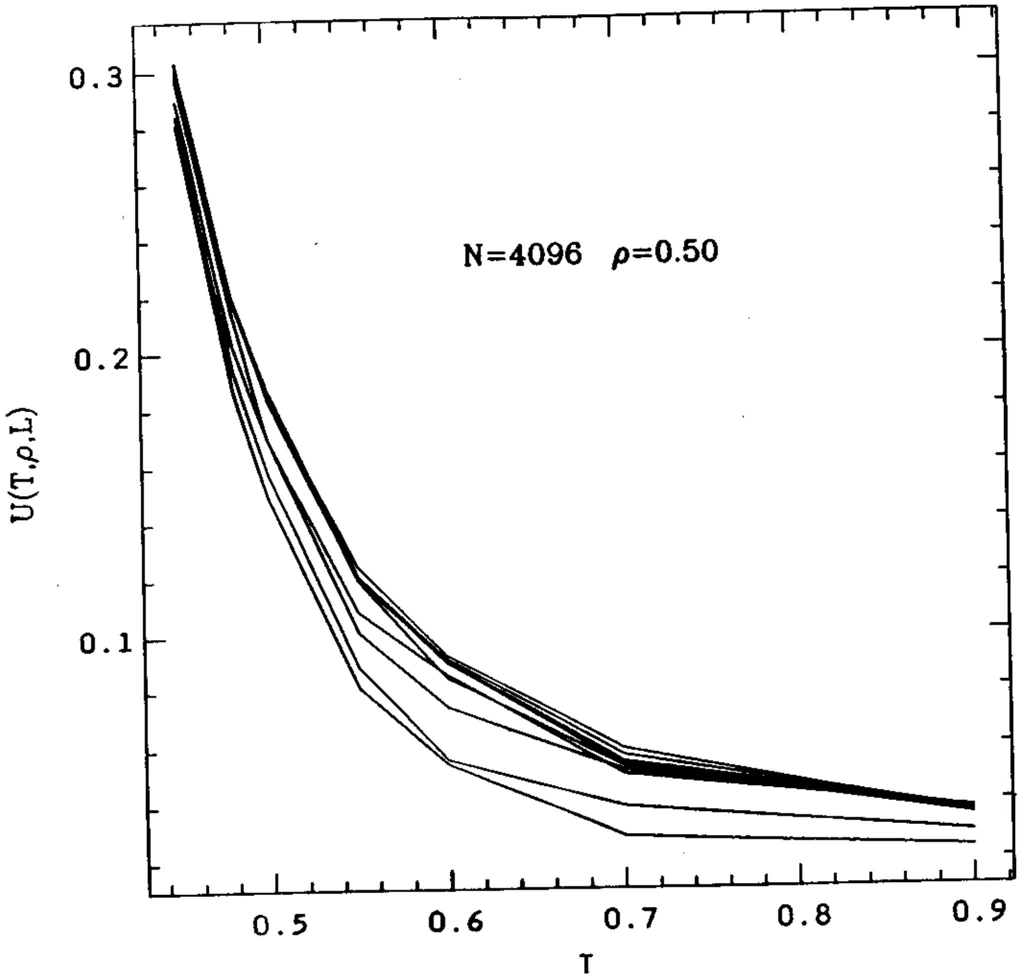
Cumulants for different block sizes



(54)

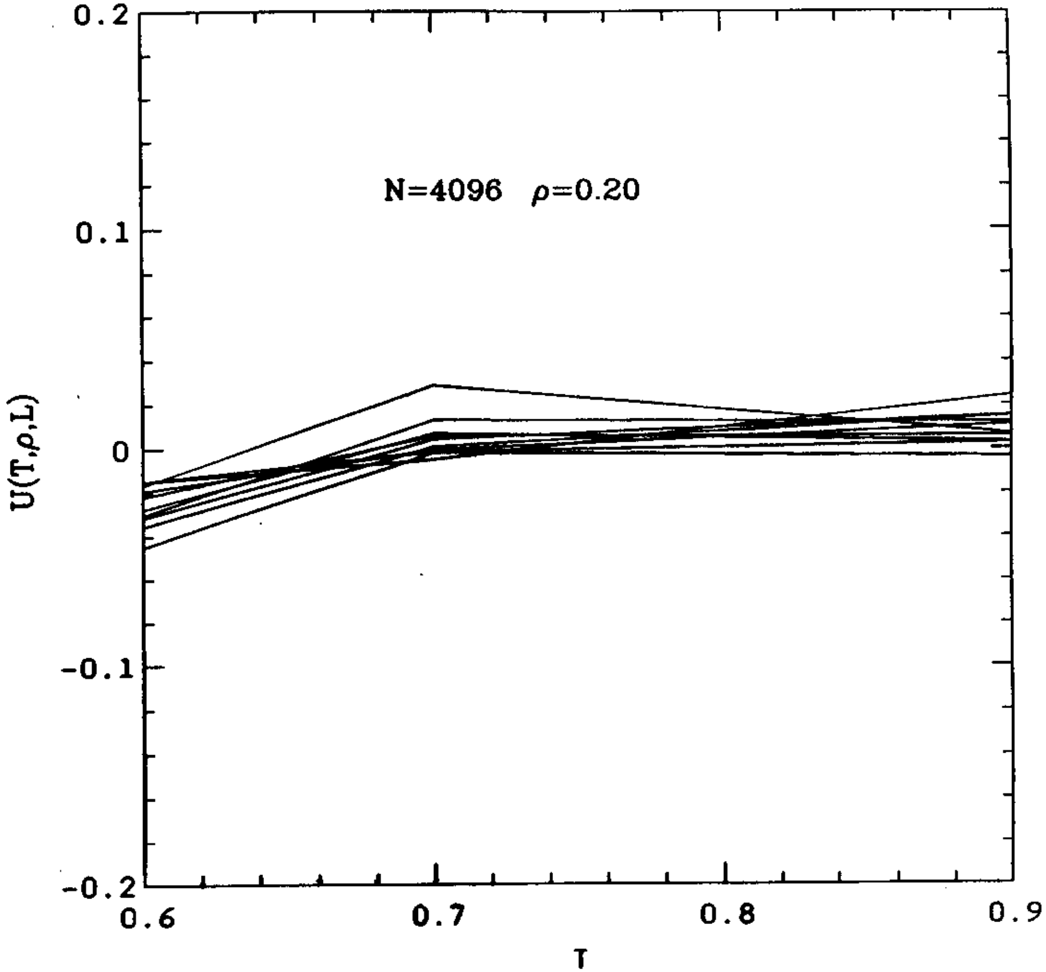


55



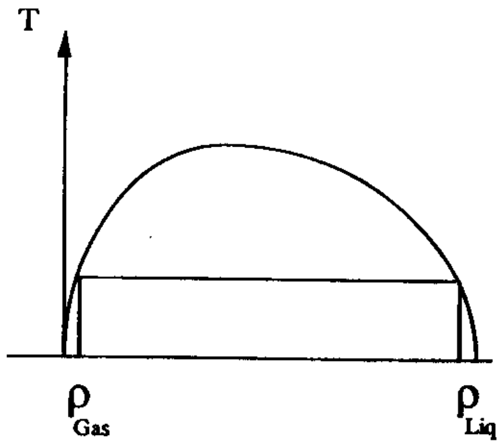
N=4096 ρ=0.50
U(T,ρ,L)
0.3
0.2
0.1
0.5
0.6
0.7
0.8
0.9
T

56

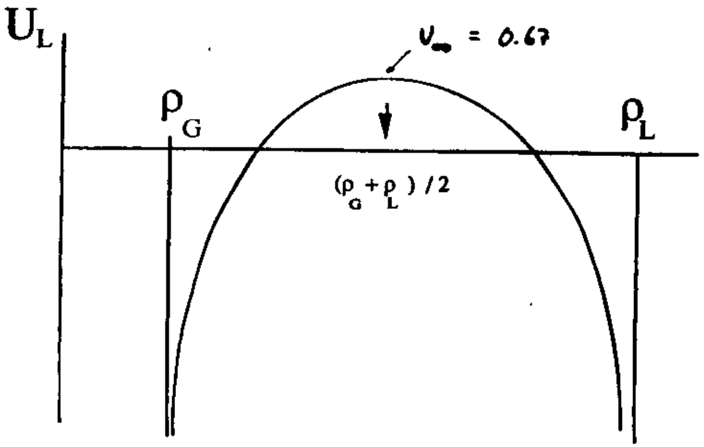


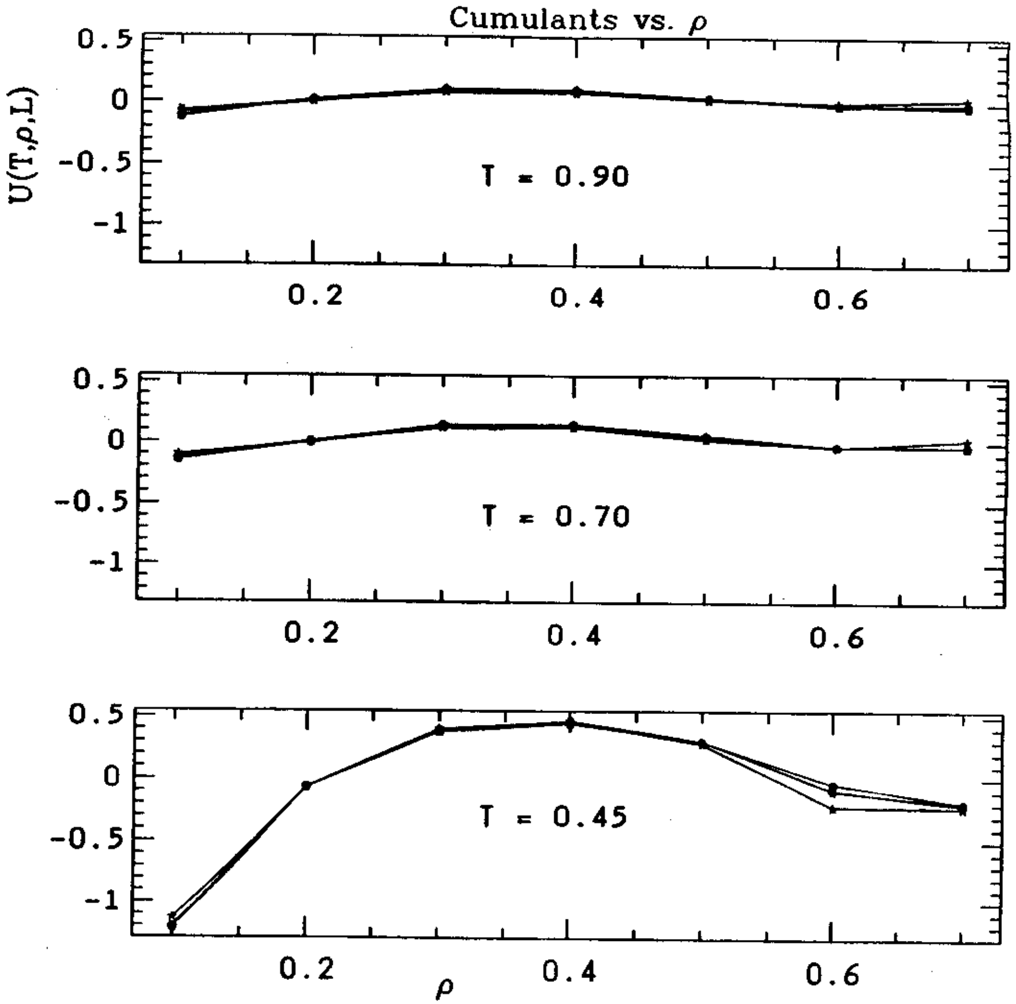
N=4096 ρ=0.20
U(T,ρ,L)
0.2
0.1
0
-0.1
-0.2
0.6
0.7
0.8
0.9
T

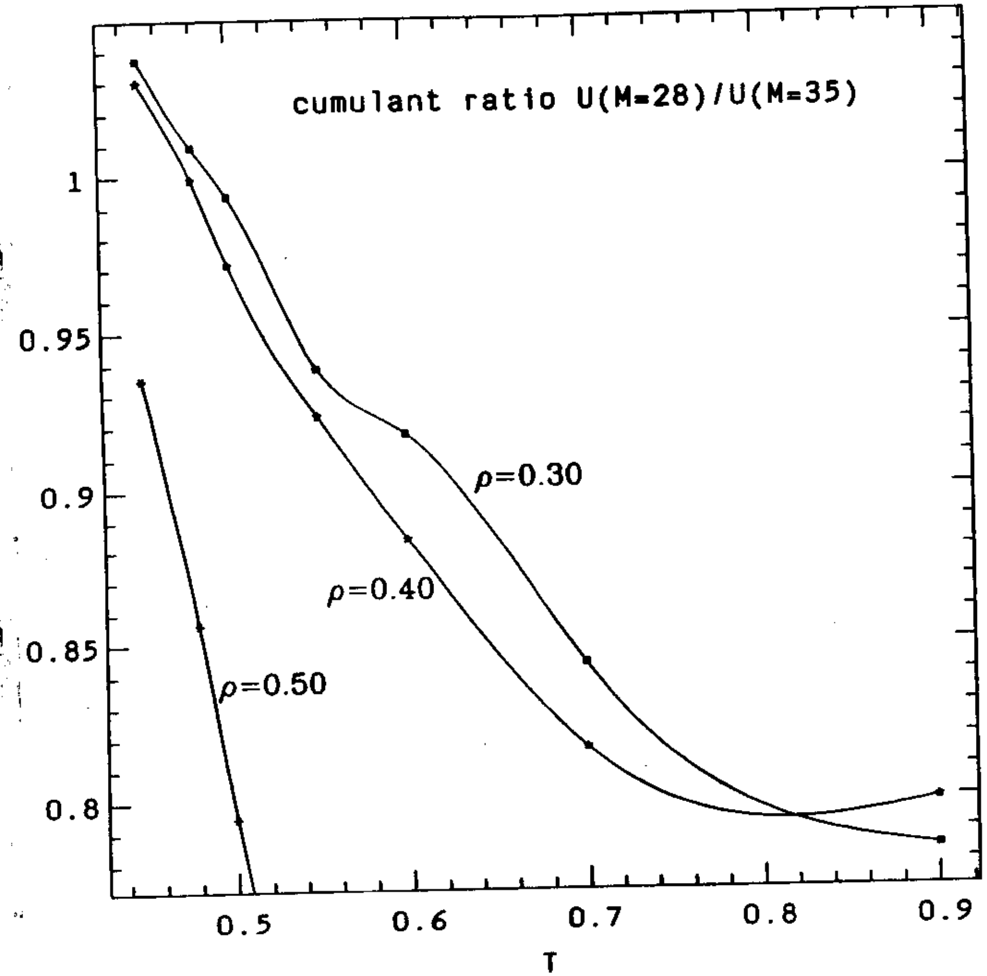
$T \ll T_c$ below the coexistence curve



$$P_L \sim a\,\delta(\rho - \rho_{Gas}) + b\,\delta(\rho - \rho_{Liq})$$







REDUCED CUMULANT

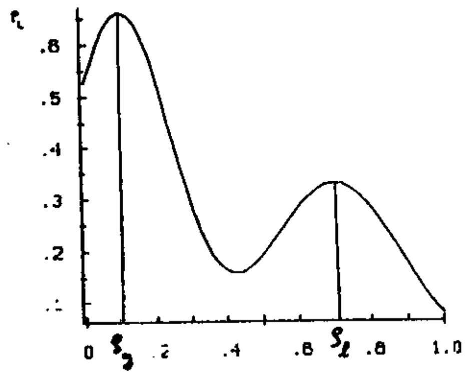
$$\boxed{U_L = 1 - \frac{\langle (\rho - \langle\rho\rangle)^4 \rangle_L}{3\langle (\rho - \langle\rho\rangle)^2 \rangle_L^2}}$$

$T \gg T_c$ $\quad\quad \xi \ll L$

$$U_L \sim L^{-d}$$

$T \ll T_c$

P_L



$\xi \ll L$ $\quad\quad U_L \to 0.67 . \quad\quad \rho = \frac{1}{2}\left(\rho_l + \rho_g\right)$

Conclusions

1- more detailed analysis of the results near T_c (scaling etc.)

2- Comparison with Gibbs ensemble

3 - dynamics !

4 - critical slowing down

Future

- combine with other methods
Gibbs ensemble, G.C. MC

- different systems
phase separation in fluid mixtures