INTERDIFFUSION IN CRITICAL BINARY MIXTURES BY MOLECULAR DYNAMICS SIMULATION

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Simulation of diffusion phenomena by MOLECULAR DYNAMICS METHODS

POSTERS

MD

- B1 Carbon diffusion in cementite
- B2 —"— —"— —"— austenite
- B5 Diffusion in Pd nanotubes
- B11 Heat & mass transfer in a silicalite membr.
- B17 Transport in the transition region gas/ads.
- B19 Adsorption kinetics of mixtures
- B20 H_2 molecules on graphite surfaces
- .....

alternative simulation methods:

KINETIC MONTE CARLO e.g. B3, B8, B13

CELLULAR AUTOMATA MODELING e.g. B7

Interdiffusion in binary mixtures B4 Formation of a Surface - Sandwich Structure in Pd-Ni Nanoparticles by Interdiffusion

RELATIONS between DYNAMIC PROPERTIES of MATERIALS

(relaxation functions, DIFFUSION and other TRANSPORT coefficients) and the PHASE TRANSITIONS they undergo (e.g. PHASE SEPARATION)

- typical materials CONTAIN SEVERAL COMPONENTS

⇒ INTERDIFFUSION is an issue

e.g. POLYMER MIXTURES or SOLUTIONS (e.g. $C_{16}H_{34} + CO_2$)

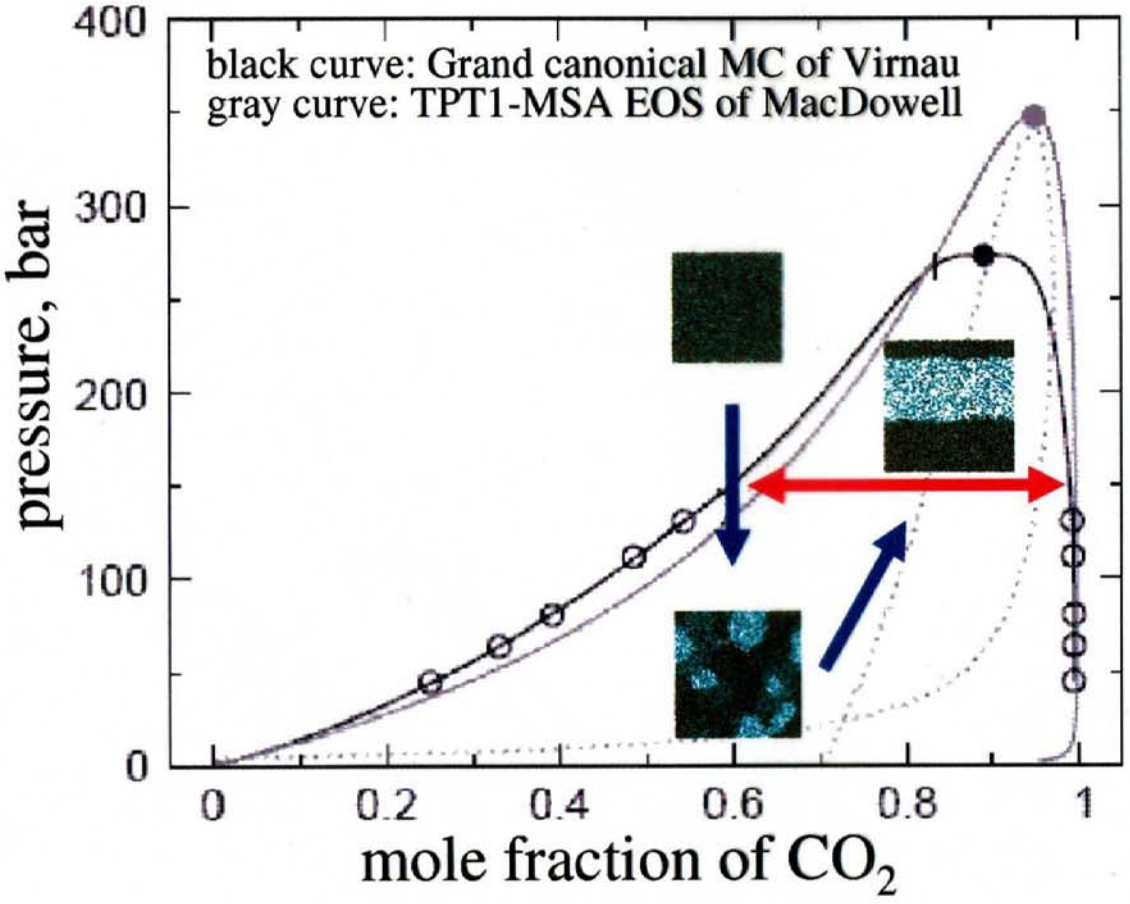
multiscale simulation problem (many decades of length+time!)

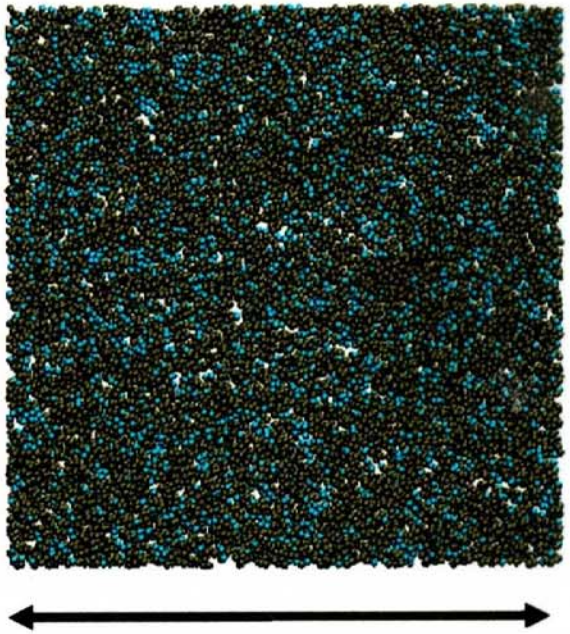
e.g. INORGANIC GLASSFORMERS (e.g. $SiO_2 + Al_2O_3$)

from COVALENT BONDS to MEDIUM RANGE ORDER to LONG RANGE CONCENTRATION FLUCTUATIONS ....

STATUS of MULTISCALE MODELING: solvable for SIMPLE MODEL SYSTEMS combination of MONTE CARLO and MOLECULAR DYNAMICS

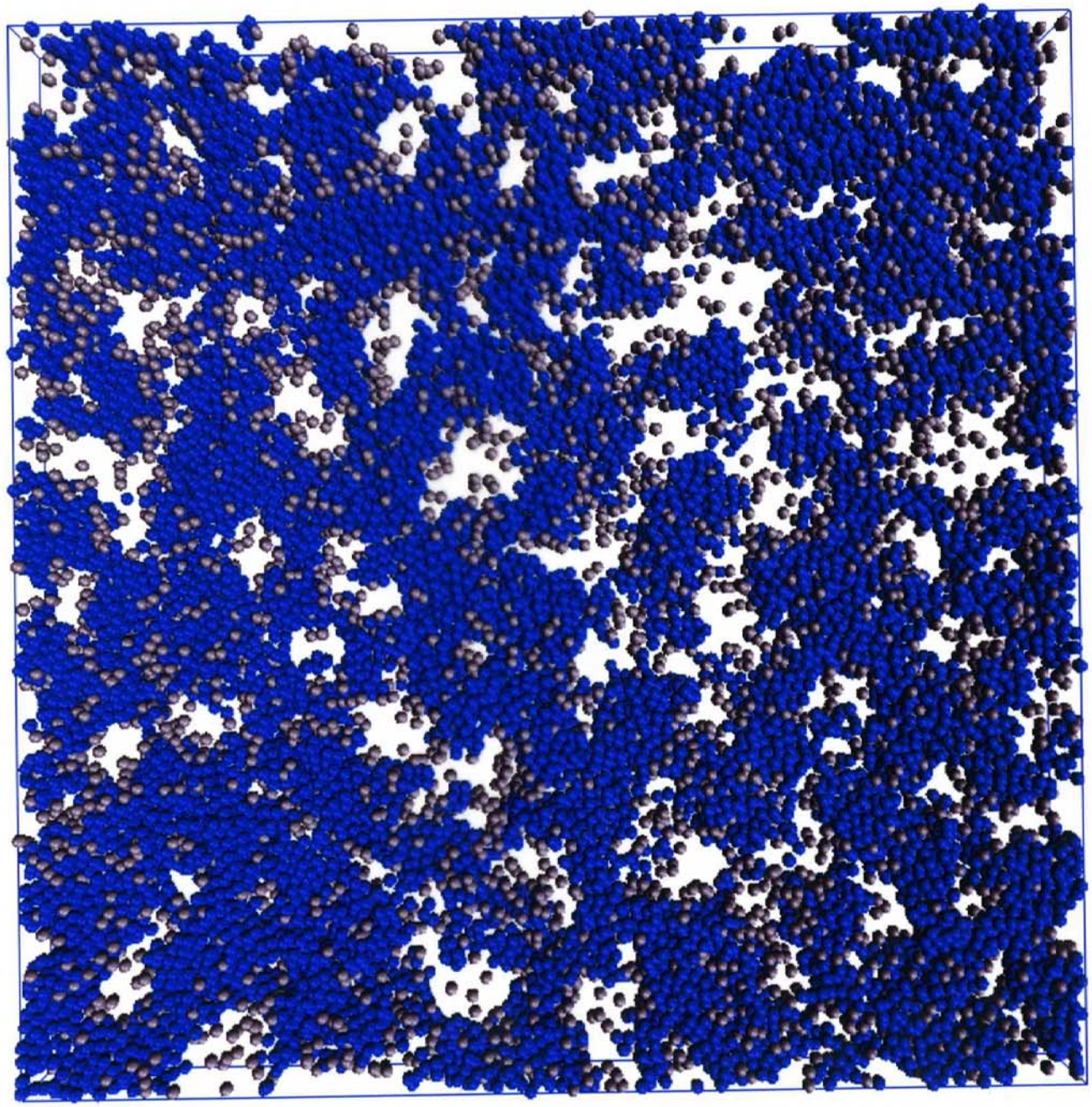
Phase diagram of CO_2+hexadecane at 185°C (T^*=1.16)

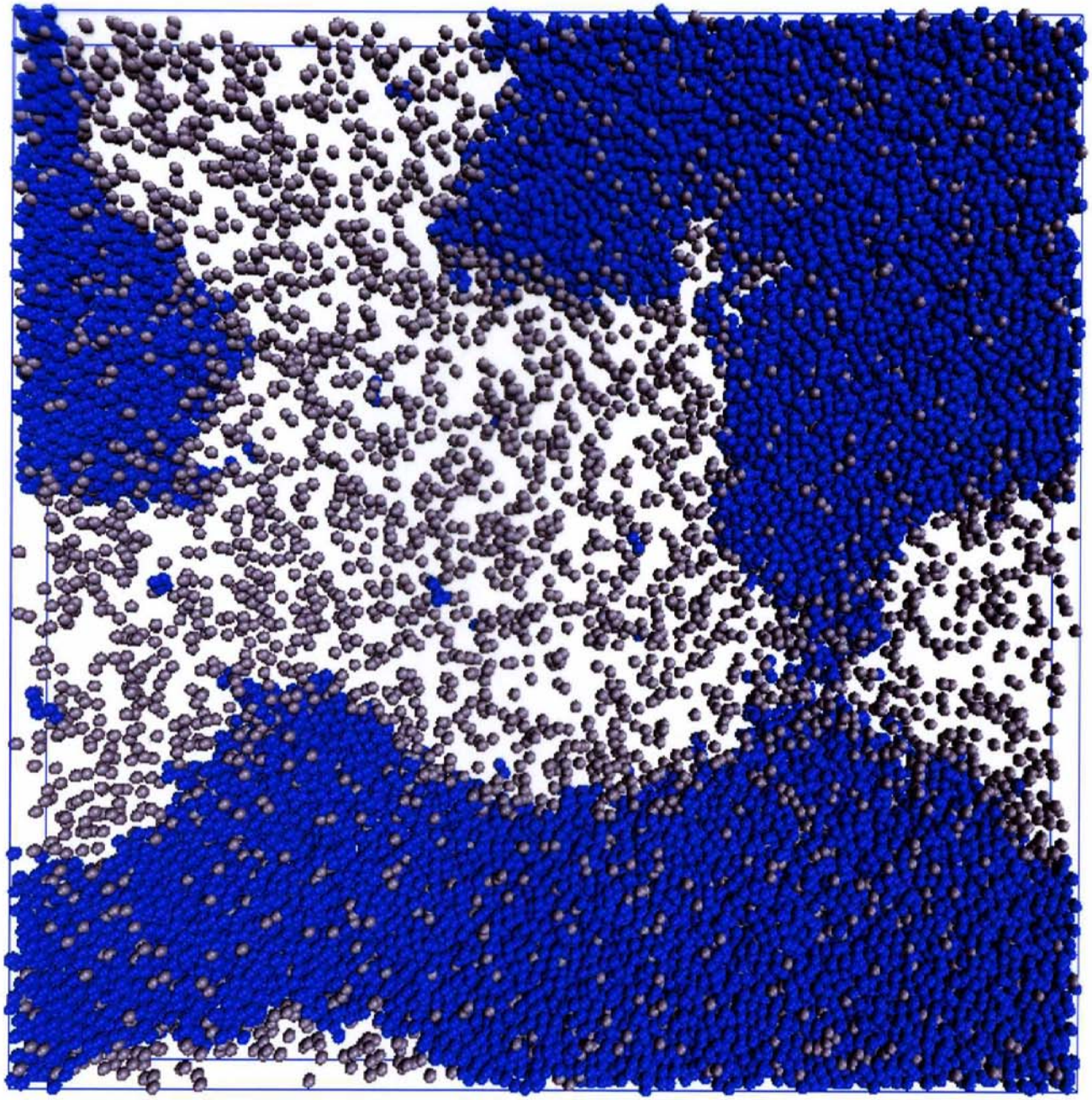


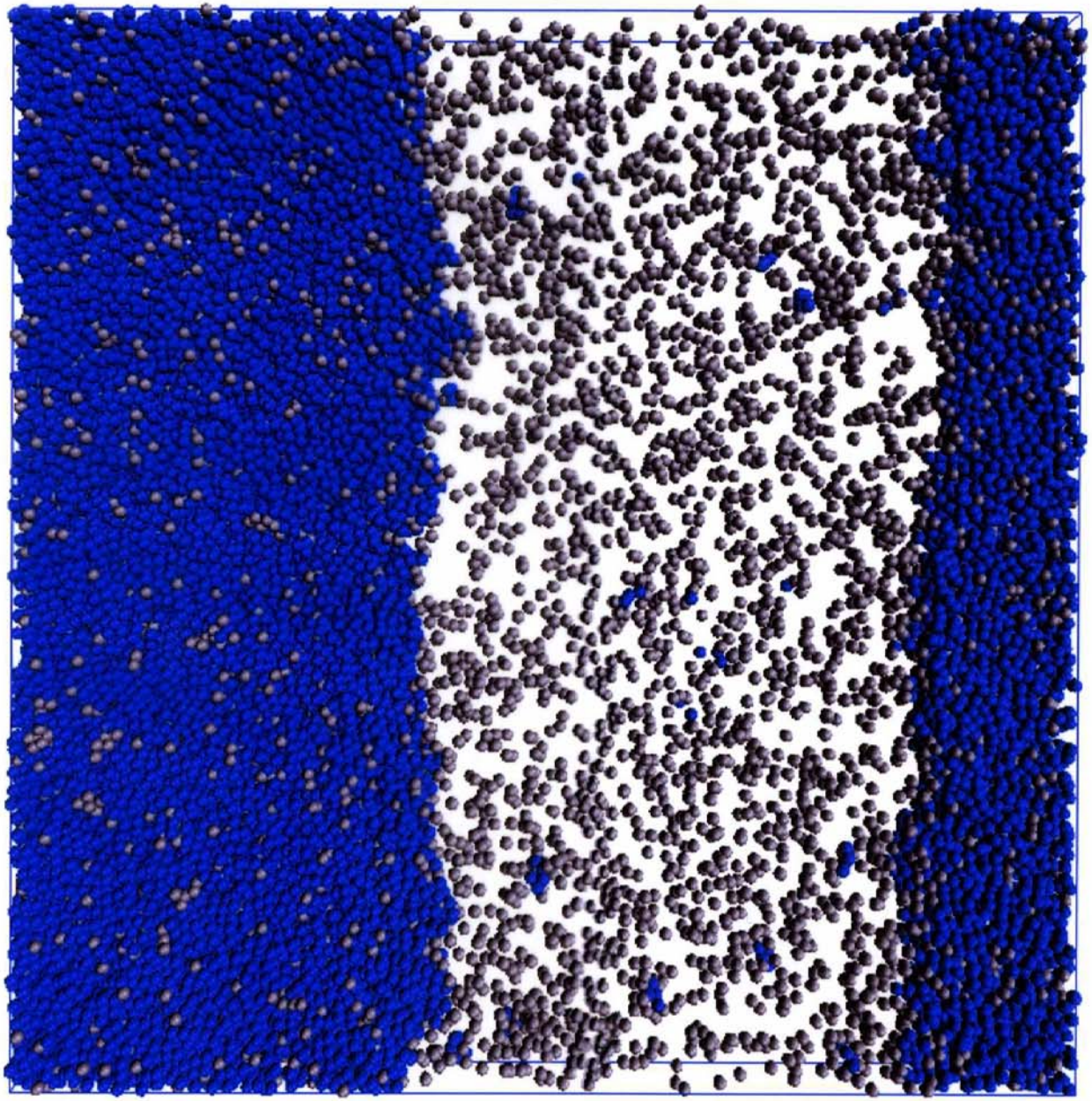


≈100σ
(435136 particles)

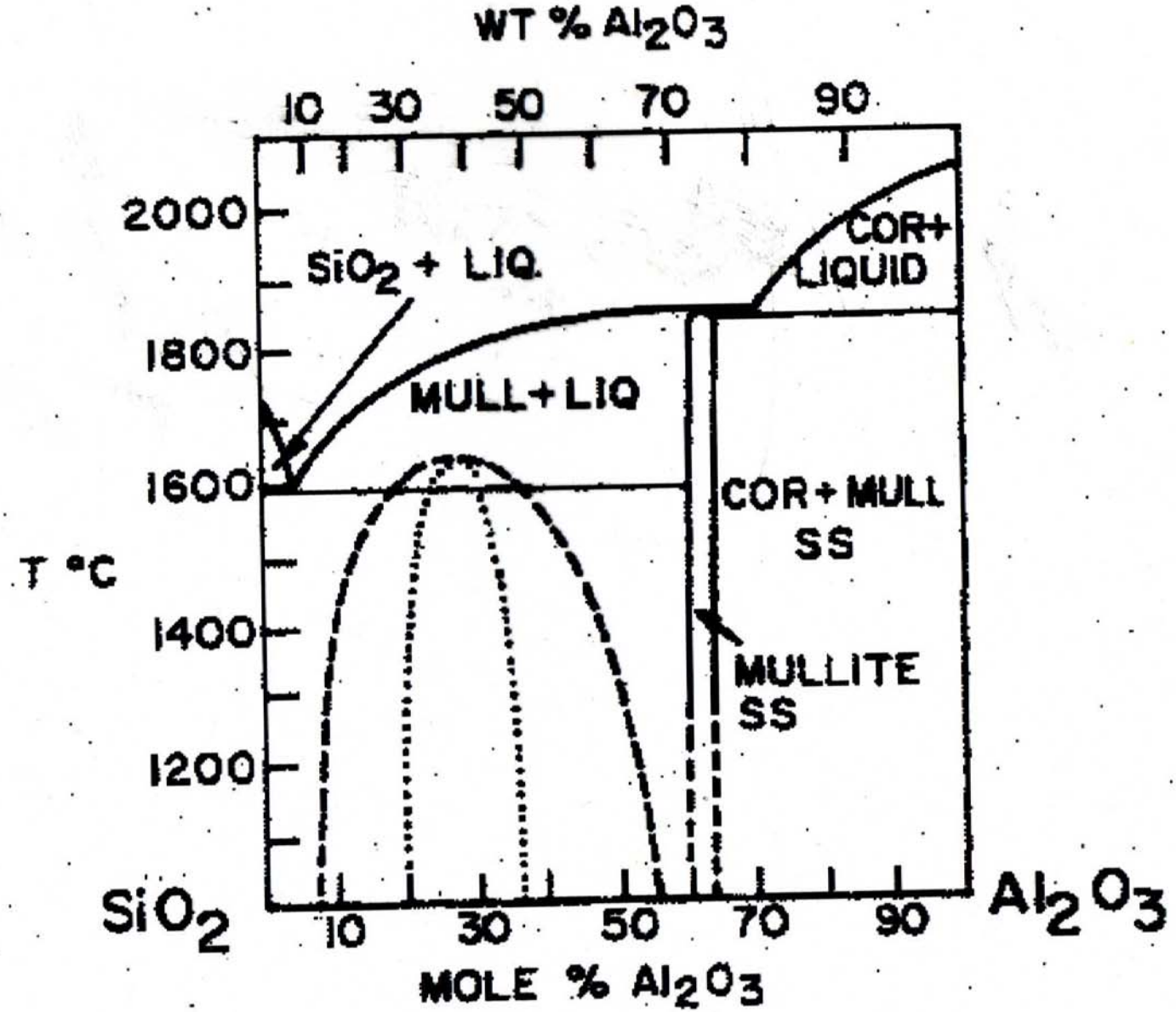
Simulations on a long length scale!



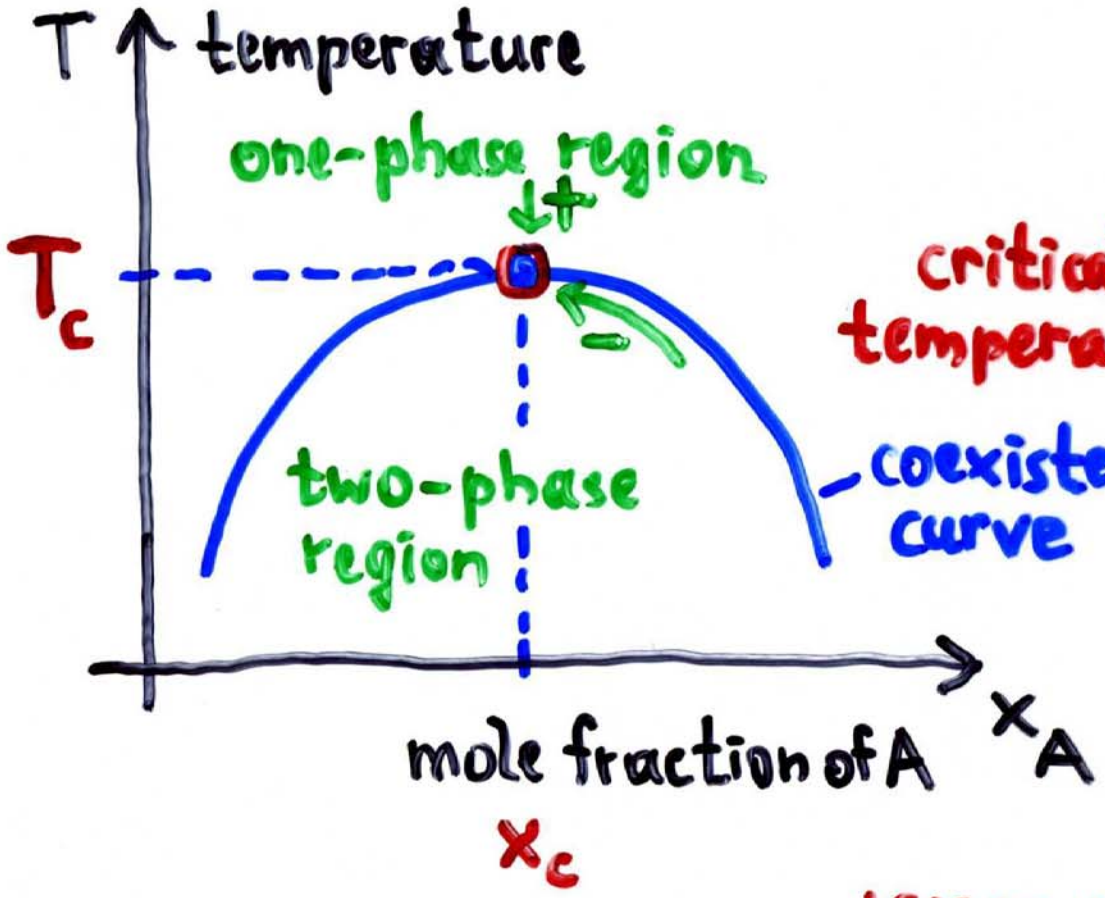




Experimental Phase Diagram



CRITICAL BEHAVIOR OF BINARY MIXTURES (AB)



$$x_A^{coex} - x_c = \hat{B}(1 - T/T_c)^{\beta}$$

concentration "susceptibility"

$$\chi = \hat{\chi}_{\pm} |1 - T/T_c|^{-\gamma}$$

correlation length of concentration fluctuations

$$\xi = \hat{\xi}_{\pm} |1 - T/T_c|^{-\nu}$$

β, γ, ν : critical exponents

ISING MODEL universality class:

$\beta \approx 0.325$ $\gamma \approx 1.24$ $\nu \approx 0.63$

CRITICAL SLOWING DOWN OF FLUCTUATIONS

"Conventional" [VAN HOVE] theory:

INTERDIFFUSION COEFFICIENT $D_{AB} = \Lambda(T)/\chi$

VAN HOVE: $\Lambda(T_c)$ finite $\Rightarrow D_{AB} \propto (T/T_c - 1)^{\gamma}$

selfdiffusion constants D_A^*, D_B^* } not singular

viscosity η

FLUID MIXTURES: Van Hove theory is WRONG!

Mode coupling theory (Kawasaki et al. 1970-1995)
Renormalization group (Siggia, Halperin, Hohenberg 1976)
Experiments (Burstyn & Sengers 1982)
} $\Rightarrow$

$\Lambda(T \to T_c) \to \infty$, $\eta(T \to T_c) \to \infty$

consequence: NO SIMPLE RELATION between D_{AB} and D_A, D_B

CRITICAL DYNAMICS FROM SIMULATIONS ?

Difficulty: CRITICAL SLOWING DOWN makes EQUILIBRATION SLOW and causes LARGE "STATISTICAL" ERRORS due to strong correlations between subsequently generated system configurations

SYSTEM of size L^3 at T_c: relaxation time $\tau \propto L^z$

z = "DYNAMIC CRITICAL EXPONENT"

only states separated by times of order τ along a trajectory are statistically independent !

LIQUID BINARY MIXTURE:

MD (strictly microcanonical ensemble needed!) $z \approx 3$

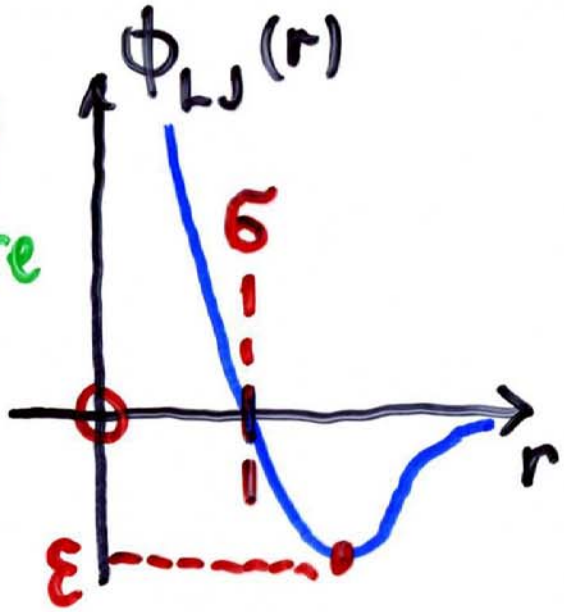
MC (canonic $N_A N_B VT$ ensemble) $z \approx 4$ (also for vanHove theory)

SGMC (semi-grandcanonical $\Delta\mu NVT$ ensemble) $z \approx 2$

⇒ equilibrate system by SGMC: ensemble of initial states for MD

Model system and simulation techniques

Binary symmetric Lennard-Jones mixture



$$\phi_{LJ}(r_{ij}) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r_{ij}}\right)^{6}\right]$$

$$r_{ij} = |\vec{r}_i - \vec{r}_j| \qquad \alpha, \beta \in A, B$$

potential is truncated at $r_{ij} = r_c$ and modified so that both potential and forces are continuous:

$$u(r_{ij}) = \phi_{LJ}(r_{ij}) - \phi_{LJ}(r_c) - (r_{ij} - r_c)\left(d\phi_{LJ}/dr_{ij}\right)\Big|_{r_{ij}=r_c} \qquad (r_{ij} \leq r_c)$$

$$u(r_{ij}) \equiv 0 \quad \text{for} \quad r_{ij} > r_c$$

parameters: $\sigma_{AA} = \sigma_{AB} = \sigma_{BB} = \sigma \equiv 1$; $r_c = 2.5\sigma$

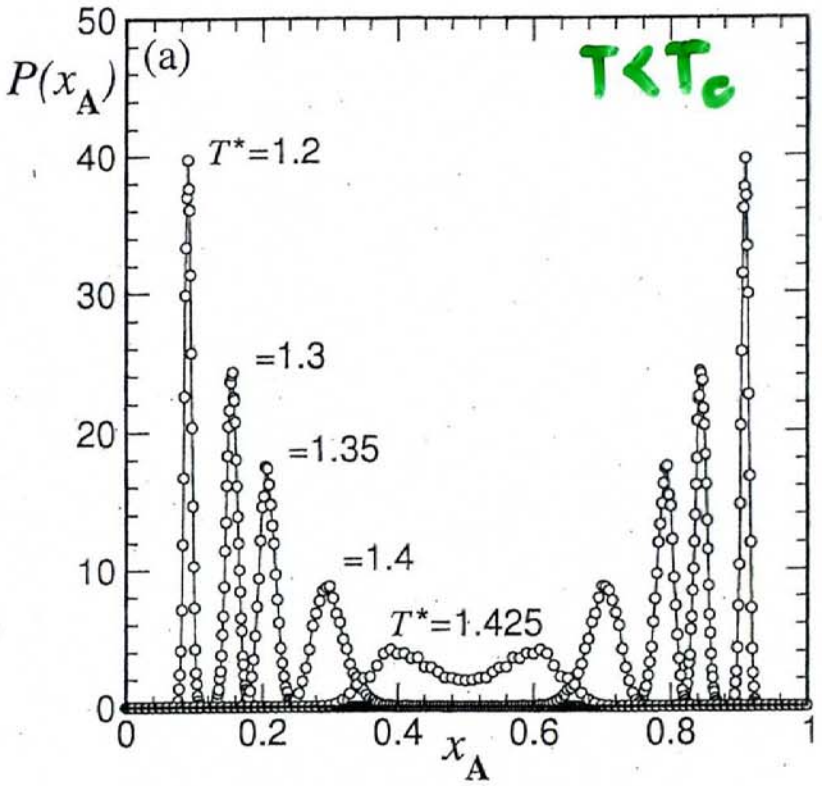
particle number $N = N_A + N_B$ and volume $V = L^3$ chosen such that reduced density $\rho^* = \rho\sigma^3 = (N/V)\sigma^3 = 1 \Rightarrow$ { crystallization avoided / gas-liquid trans.

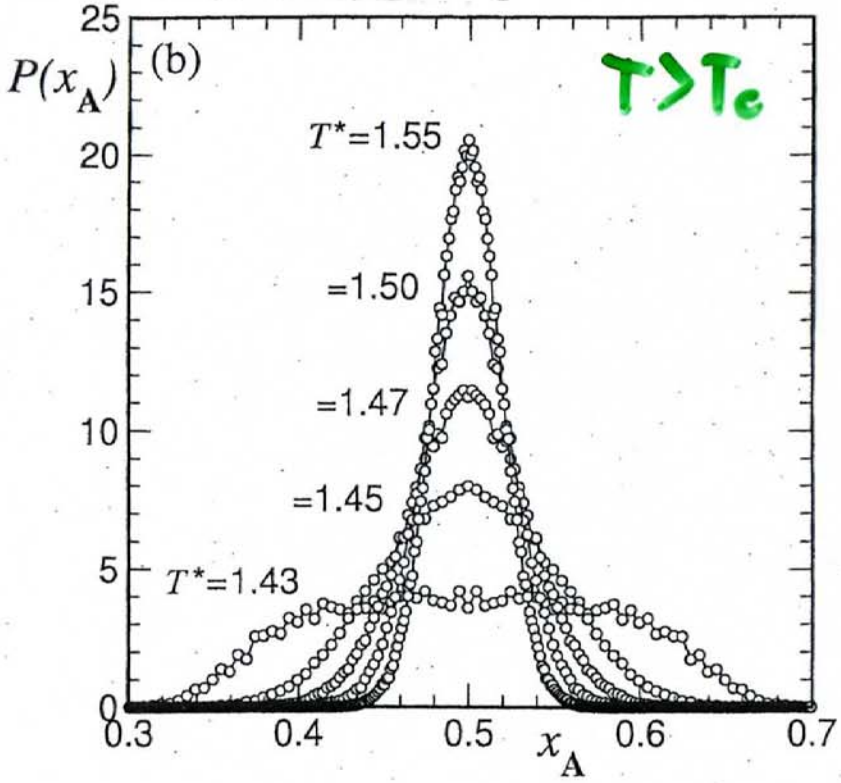
$\varepsilon_{AA} = \varepsilon_{BB} = 2\varepsilon_{AB}$ $\quad T^* = k_B T/\varepsilon_{AA}$

Equilibration first MONTE CARLO in canonical ensemble

$N_A N_B V T^*$ chosen; trial displacements of coordinates $[-\frac{\delta}{20}, \frac{\delta}{20}]$

after 10^4 MCS/particle the SEMI-GRANDCANONICAL MONTE CARLO RUN STARTS : A ↔ B identity switches (chemical potential difference $\Delta\mu = 0$) $\Rightarrow \langle x_A \rangle = \langle x_B \rangle = x_c = 1/2$ $(T > T_c)$





$\Rightarrow$ sample the probability distribution $P(x_A)$

$x_A = \frac{N_A}{N}$

$T < T_c$: $x_A^{coex} = \langle x_A \rangle$ if $\langle x_A^k \rangle = 2 \int_{1/2}^{1} x_A^k P(x_A)\, dx_A$

PHASE DIAGRAM OF THE SYMMETRIC BINARY L.J-MIXTURE

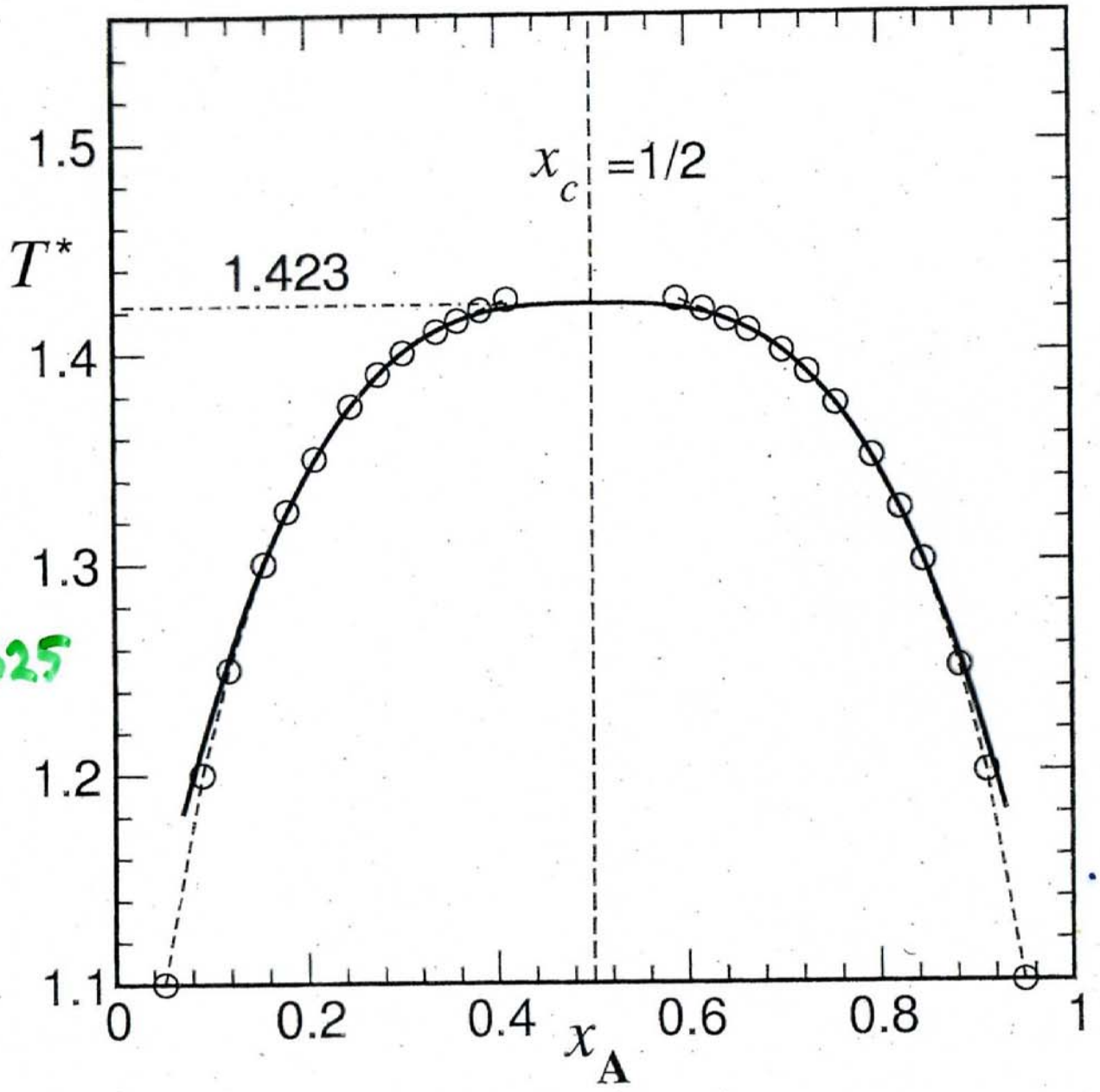
peak positions of $P(x_A)$ yield (preliminary) estimates of the two branches of the coexistence curve

$x_A^{coex(1)}$, $x_A^{coex(2)}$

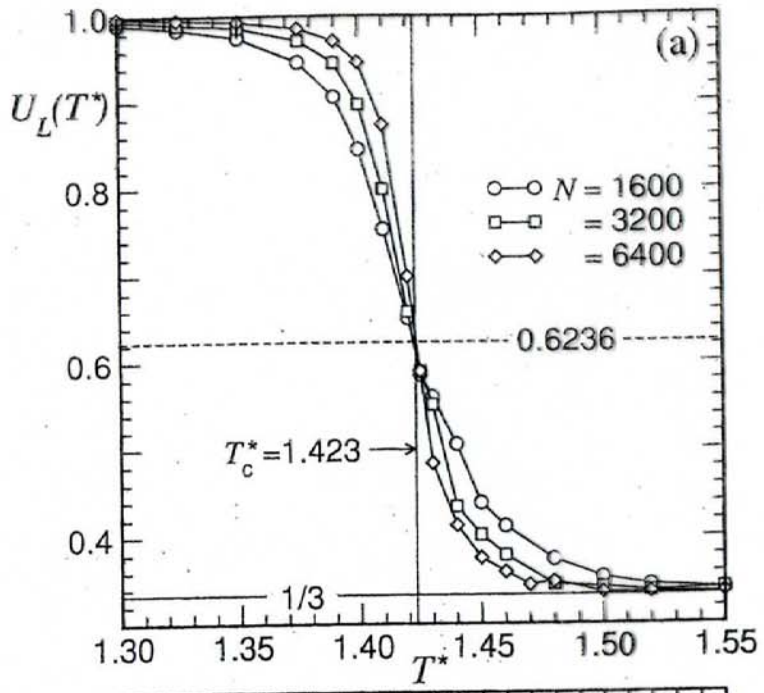
full curve: power law fit with $x_c = 1/2$, $\beta = 0.325$

$$x_A^{coex(1,2)} - x_c = \pm \hat{B} (1 - T^*/T_c^*)^{\beta}$$

$$\Rightarrow T_c^* = 1.423 \pm .002$$



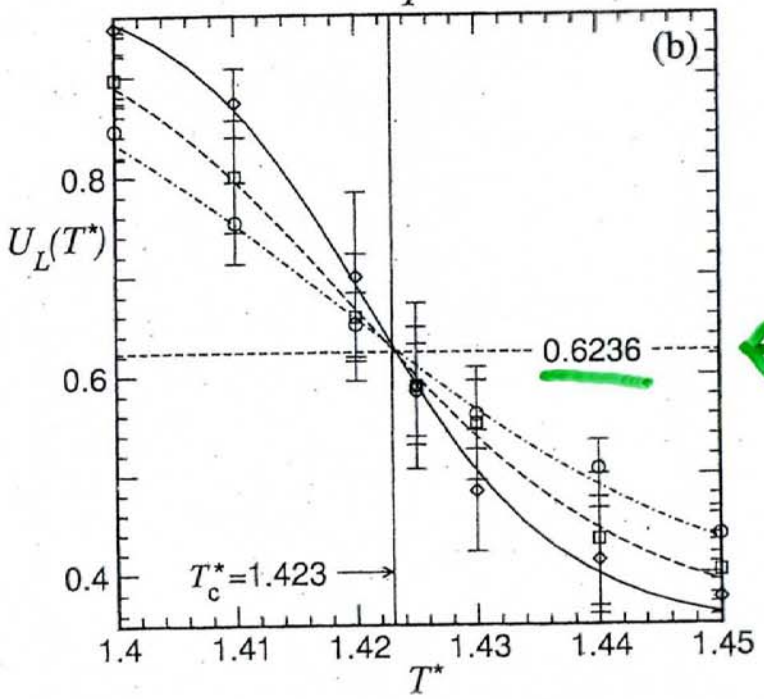
FINITE SIZE SCALING ANALYSIS: T_c^* found from cumulant intersections



$$U_L(T^*) = \frac{\langle (x_A - x_c)^4 \rangle}{\langle (x_A - x_c)^2 \rangle^2}$$

$\Rightarrow T_c^* = 1.4230 \pm .0005$

$L \approx 11.7, 14.7, 18.6$



← known value for Ising model universality class

partial structure factor

$$S_{\alpha\beta}(q) = \frac{1}{N}\sum_{k=1}^{N_\alpha}\sum_{l=1}^{N_\beta}\left\langle e^{i\vec{q}\cdot(\vec{r}_k - \vec{r}_l)}\right\rangle$$

number density structure factor $S_{nn}(q)$

$$S_{nn}(q) = S_{AA}(q) + 2S_{AB}(q) + S_{BB}(q)$$

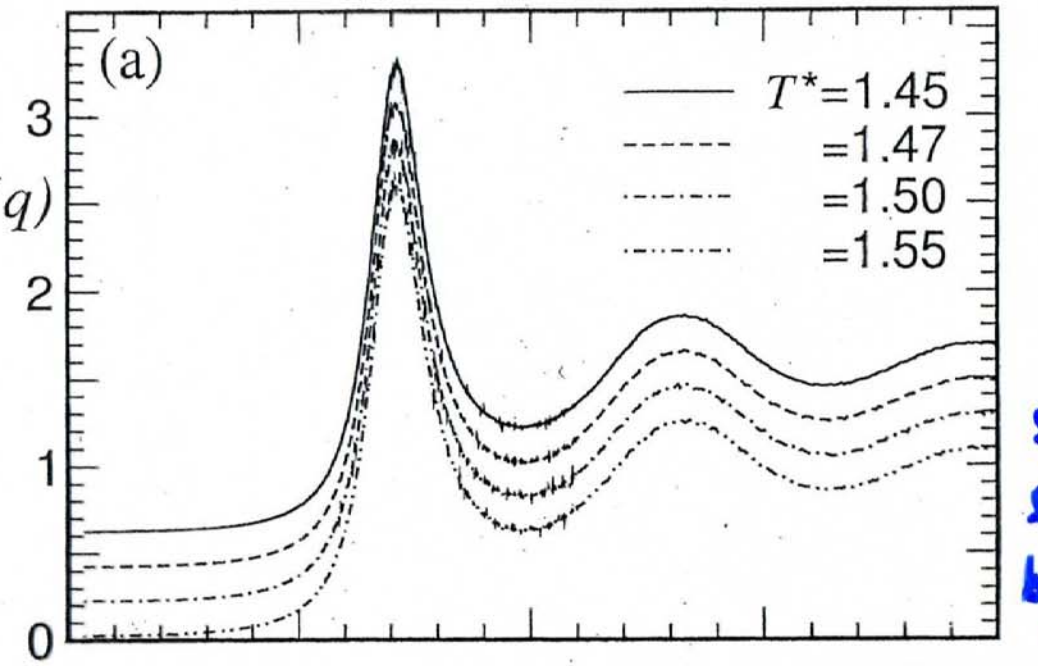
→ no effect of the approach to T_c^*

concentration fluctuation-structure factor $S_{cc}(q)$

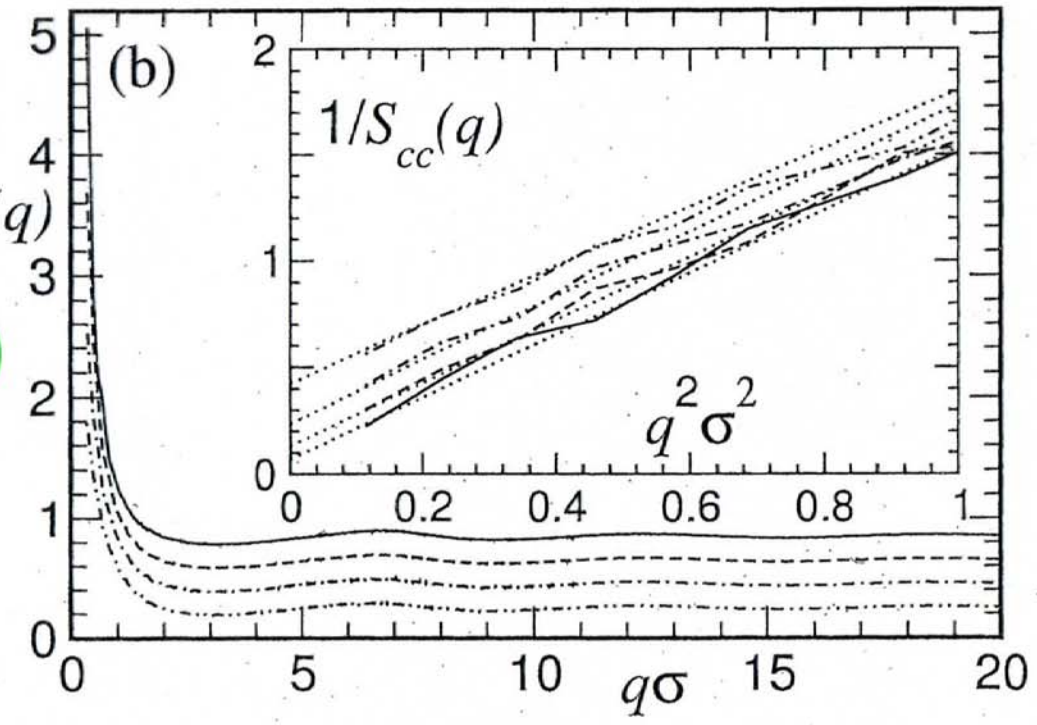
$$S_{cc}(q) = (1-x_A)^2 S_{AA}(q) + x_A^2 S_{BB}(q) - 2x_A(1-x_A)S_{AB}(q)$$

$$S_{cc}(q) = k_B T \chi / [1 + q^2\xi^2 + \dots]$$

Ornstein-Zernike



scales shifted by 0.2

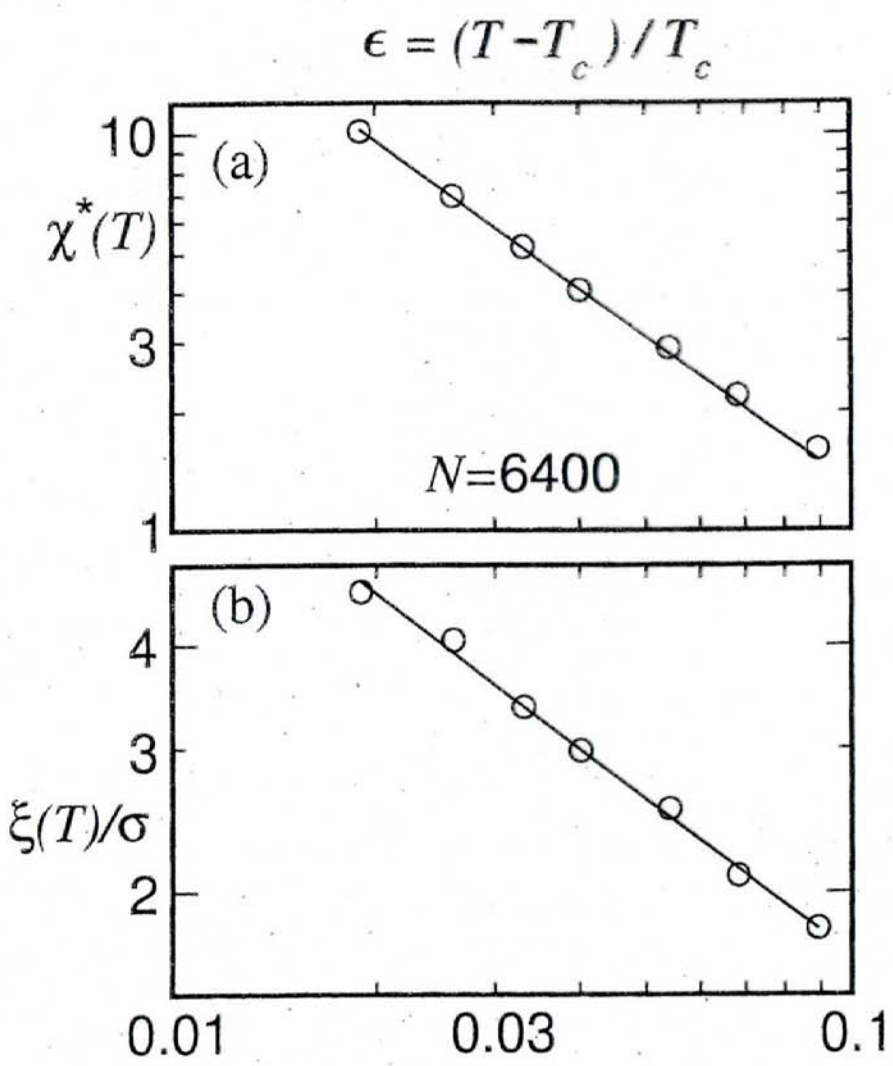


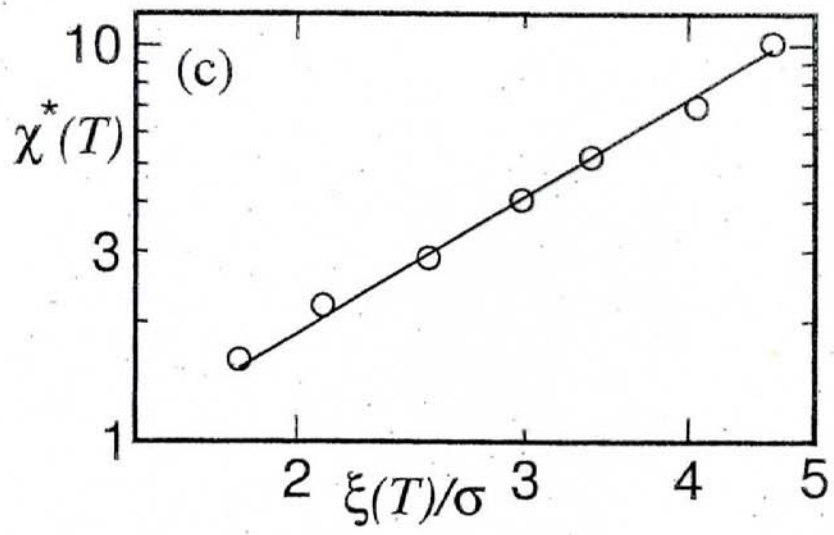
Test for Ising critical behavior by log-log plots

slopes = theoretical exponents! ⇒ "critical amplitudes"

$\hat{\chi}_+ \approx 0.076 \pm 0.006$

$\hat{\xi}_+ \approx (0.395 \pm 0.025)\sigma$

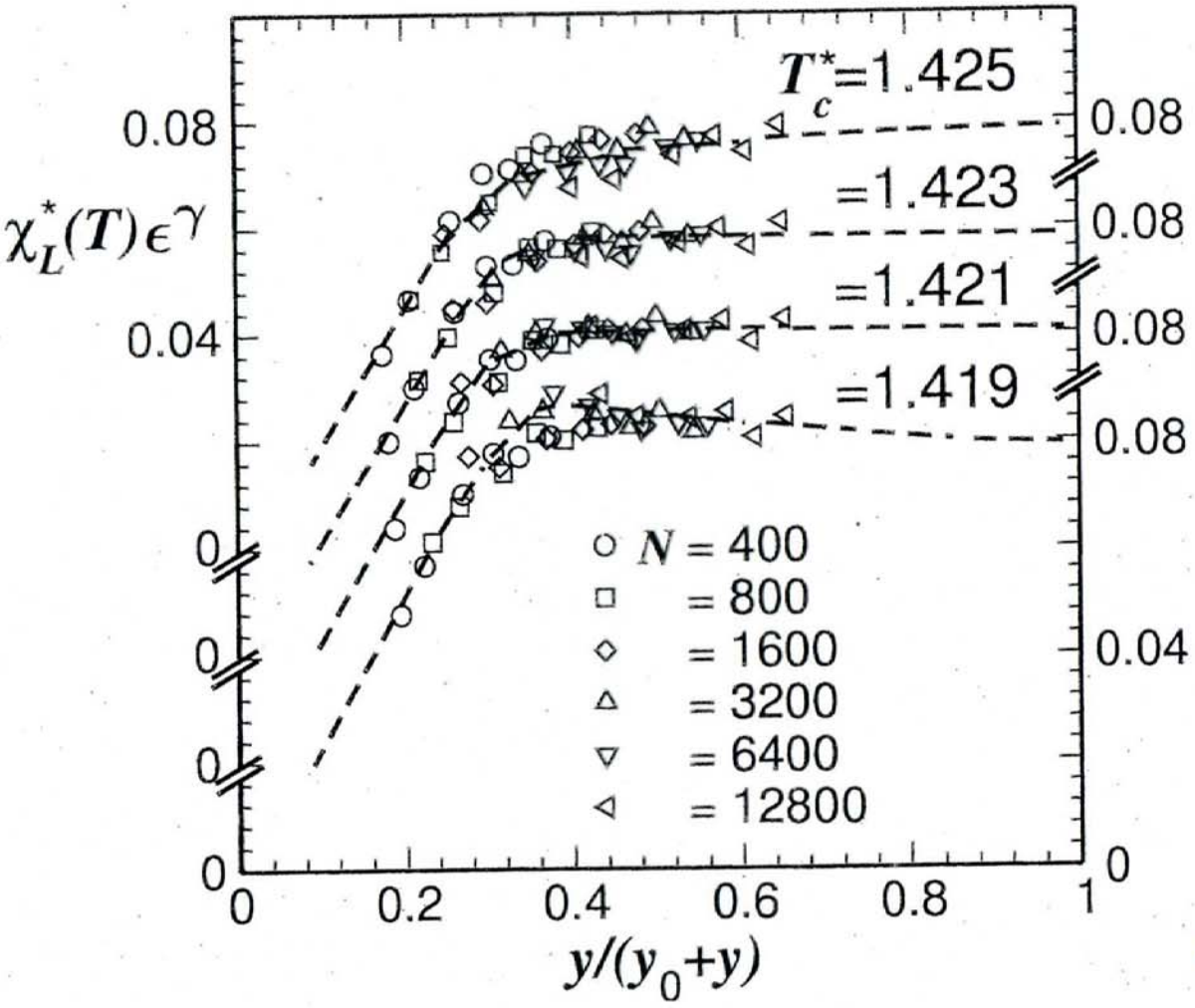




⇒ static critical behavior verified, as expected

Finite size scaling plot of "susceptibility" χ_L

$$k_B T \chi_L = L^3 (\langle x_A^2 \rangle - x_c^2) \quad , \quad T > T_c$$



$$\varepsilon = \frac{T - T_c}{T_c}$$

$y = L/\xi(T)$

choice of variable convenient to display data for both $y \ll 1$ and $y \gg 1$

$y_0 = 7$

mean square displacements of tagged particles from MOLECULAR DYNAMICS runs

$$g_A(t) = \left\langle \left[\vec{r}_{iA}(0) - \vec{r}_{iA}(t) \right]^2 \right\rangle$$

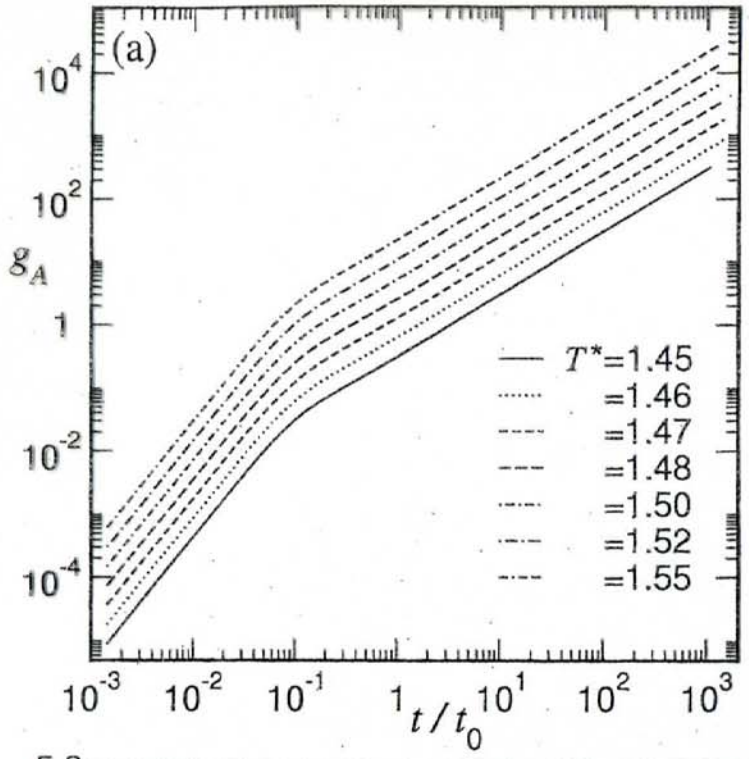
EINSTEIN RELATION

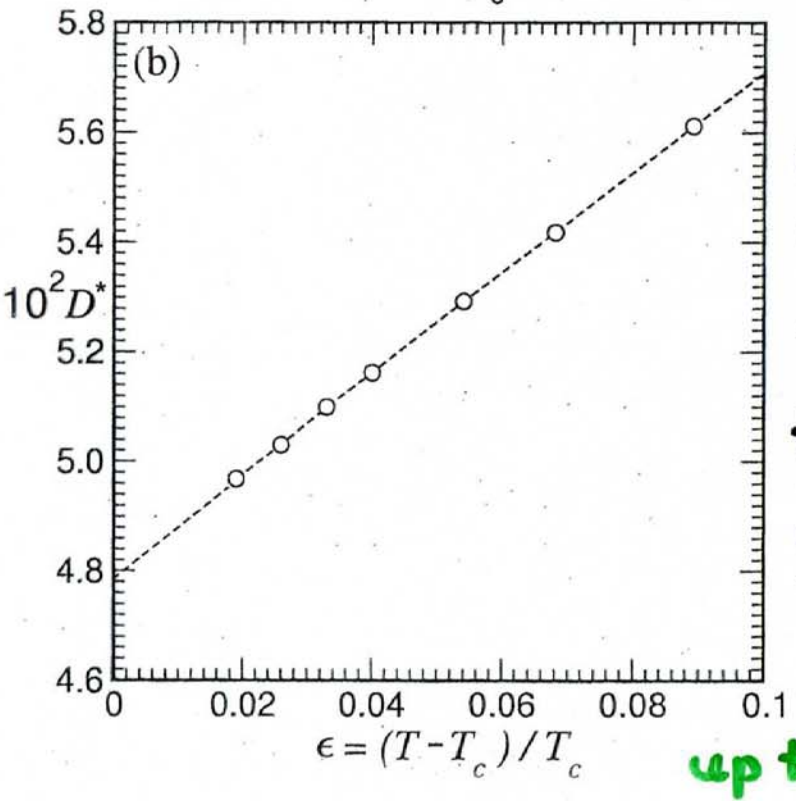
$\Rightarrow$ self-diffusion constant

$$D_A^* = \frac{t_0}{\sigma^2} \lim_{t \to \infty} \left[g_A(t)/6t \right]$$

$$\langle x_A \rangle = \langle x_B \rangle = \frac{1}{2} : D_A^* = D_B^* = D^*$$

NO CRITICAL ANOMALY OF THE SELF-DIFFUSION COEFFICIENT !





MD: velocity Verlet algorithm

$$t_0 = \left(\frac{m\sigma^2}{\varepsilon_{AA}} \right)^{\frac{1}{2}}$$

MD time unit

$m_A = m_B = m$ masses of particles

integration time step

$$\delta t^* = \frac{0.01}{\sqrt{48}}$$

$t^* = t/t_0$

up to 2.8×10^6 steps

SHEAR VISCOSITY FROM GREEN-KUBO RELATION

$$\eta(T) = \frac{1}{V k_B T} \int_0^\infty dt \langle \sigma_{xy}(0)\, \sigma_{xy}(t) \rangle$$

pressure tensor

$$\sigma_{xy}(t) = \sum_i m_i v_{ix} v_{iy}$$

$$+ \frac{1}{2} \sum_{j(\neq i)} |x_i - x_j| F_y(|\vec{r}_i - \vec{r}_j|)$$

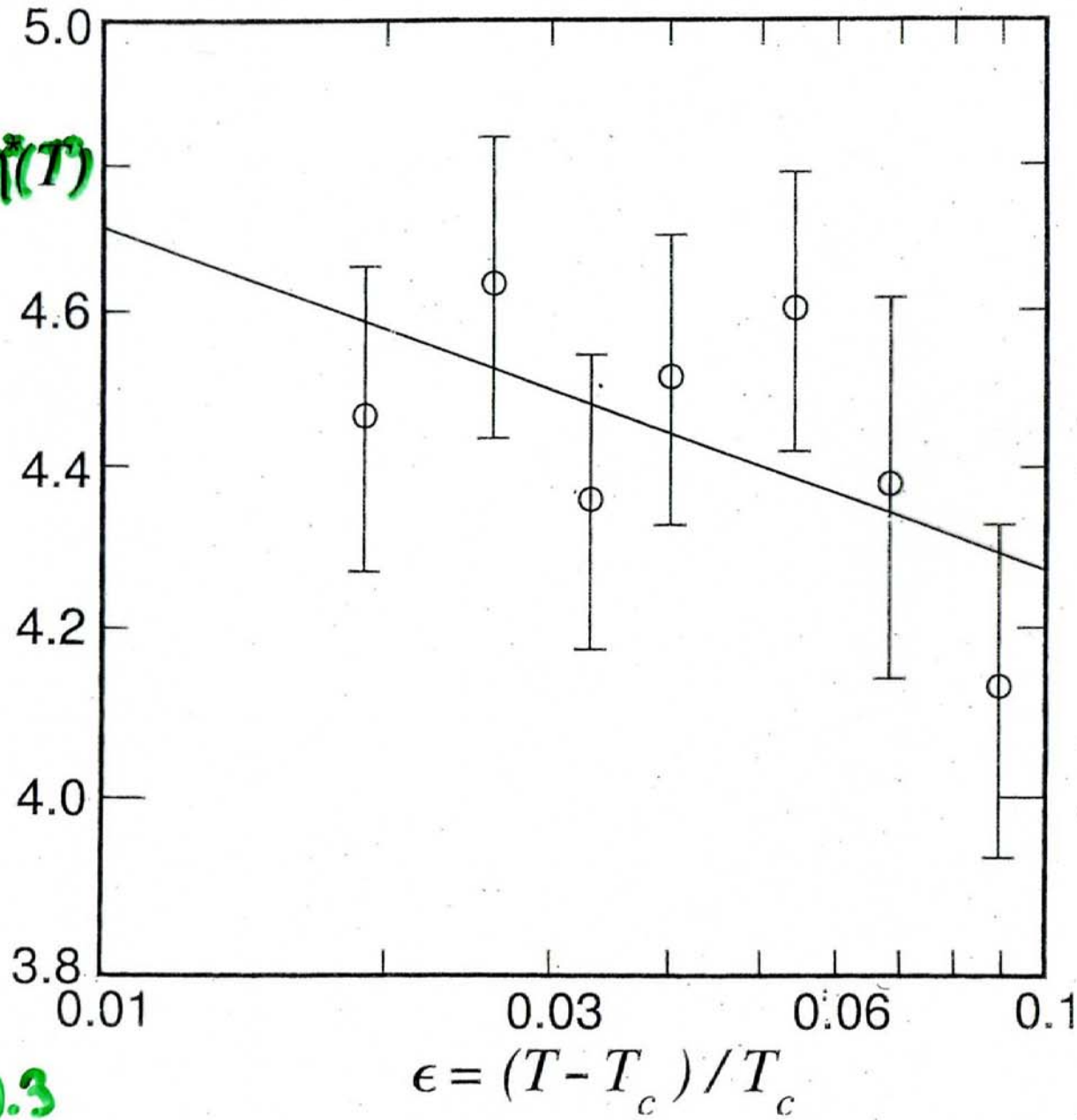
↑ force

$$\eta^* = \frac{t_0^3 \varepsilon_{AA}}{\sigma m^2} \eta$$

straight line: theoretical prediction

$$\eta^* = \eta_0 \epsilon^{-\nu x_\eta}$$

$x_\eta = 0.068 \Rightarrow \eta_0 = 3.8 \pm 0.3$



INTERDIFFUSION COEFFICIENT FROM GREEN-KUBO RELATION

Onsager coefficient

$$\mathcal{L}(T,t) = \frac{t_0}{N\sigma^2 T^*}\int_0^t dt' \langle J_x^{AB}(0) J_x^{AB}(t')\rangle$$

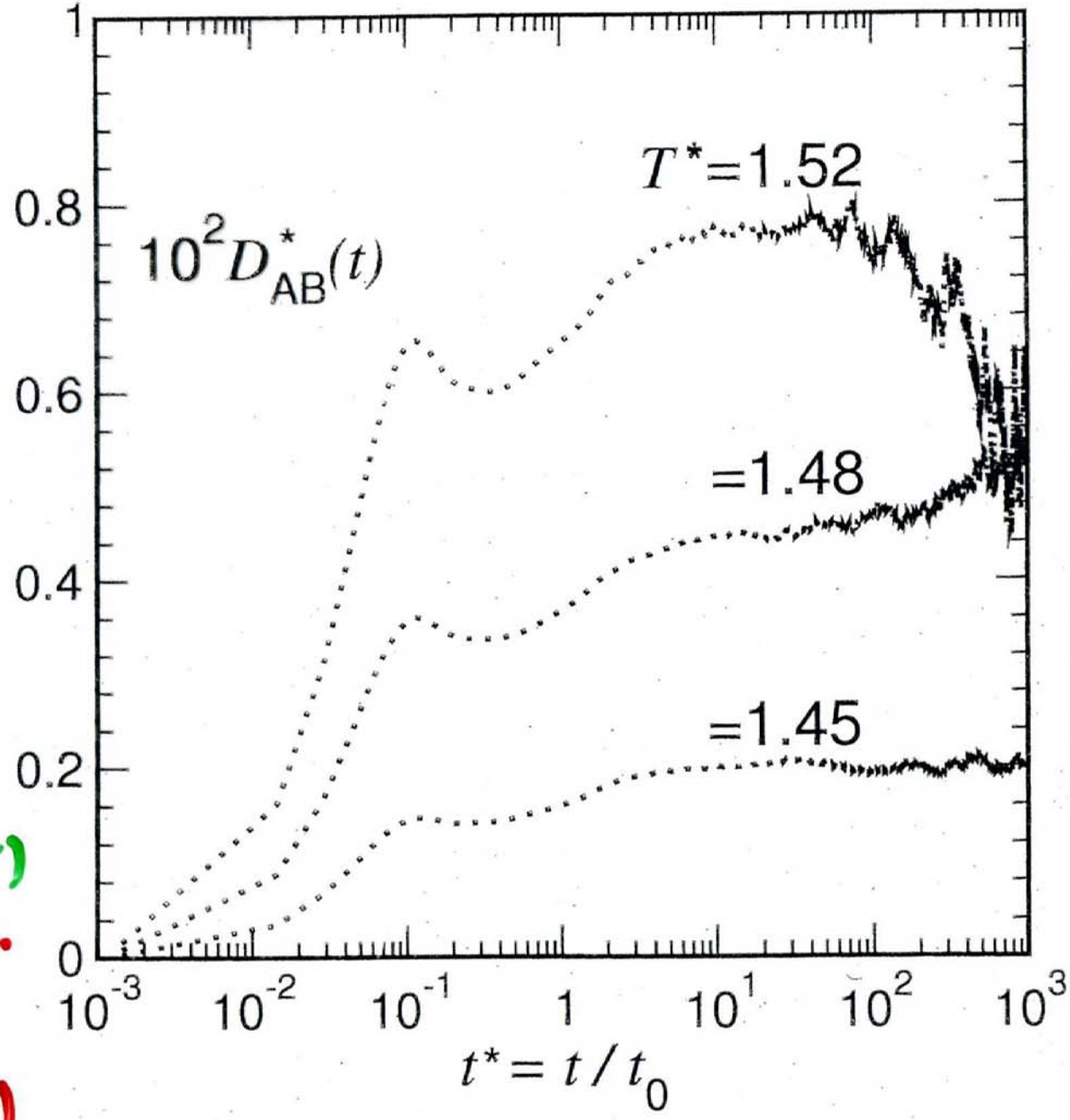
$$\vec{J}^{AB}(t) = x_B \sum_{i=1}^{N_A} \vec{v}_{i,A}(t) - x_A \sum_{i=1}^{N_B} \vec{v}_{i,B}(t)$$

↑ velocity of i^{th} B-particle

$$D_{AB}^*(t) = \mathcal{L}(T,t)/\chi^*(T)$$

$$\mathcal{L}(T) \equiv \mathcal{L}(T, t\to\infty)$$

$$D_{AB}^*(T) \equiv D_{AB}^*(t\to\infty)$$



NAIVE ANALYSIS: Log-log plot of "raw data" for $D^*_{AB}(T)$ versus ε

theoretical prediction:

$$D^*_{AB} \propto \varepsilon^{(2-\eta-x_\lambda)\nu}$$

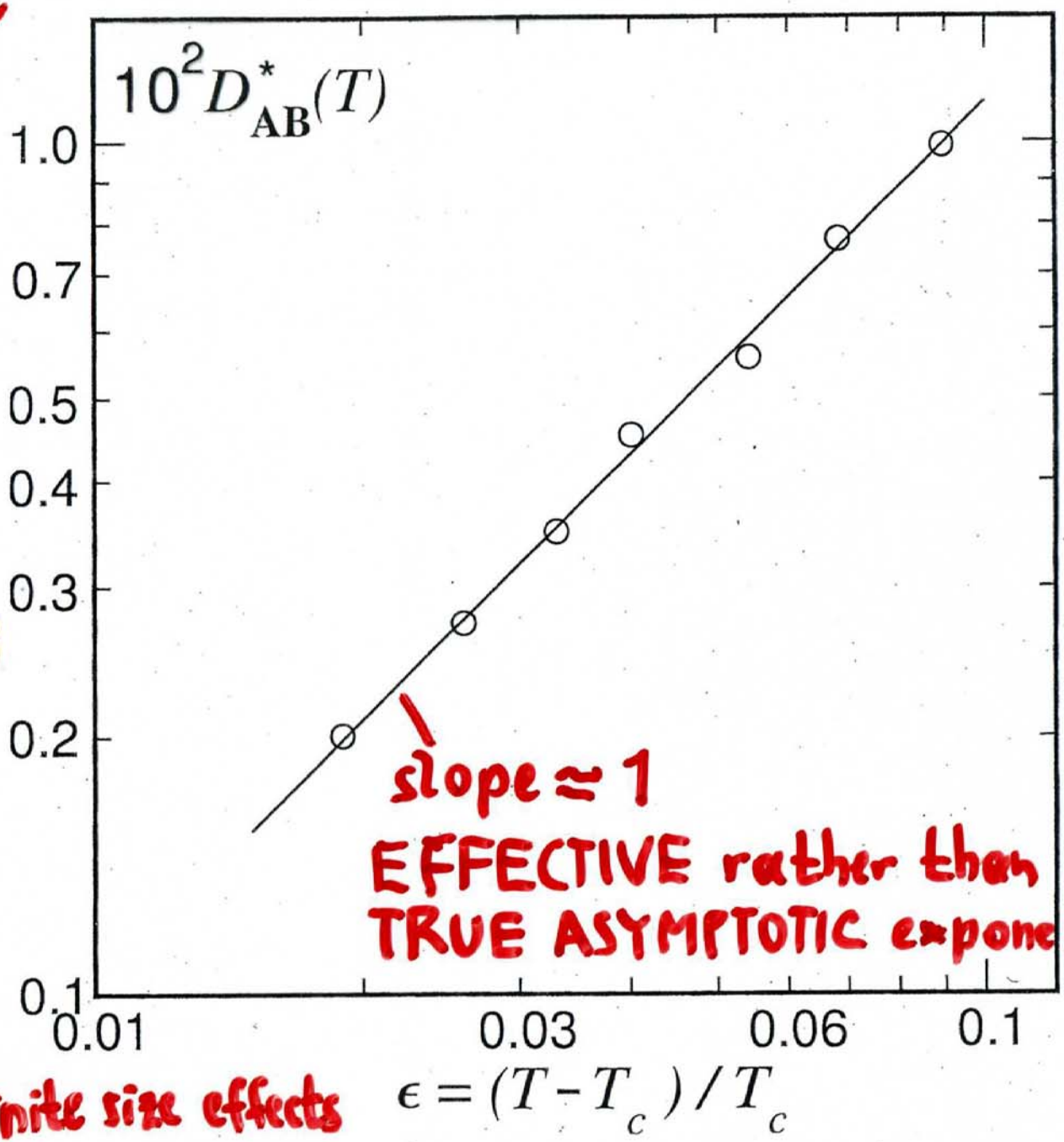
$\eta = 0.03$

$x_\lambda = 1 - \eta - x_\eta \approx 0.902$

(van Hove: $x_\lambda = 0$!)

$(2-\eta-x_\lambda)\nu \approx$

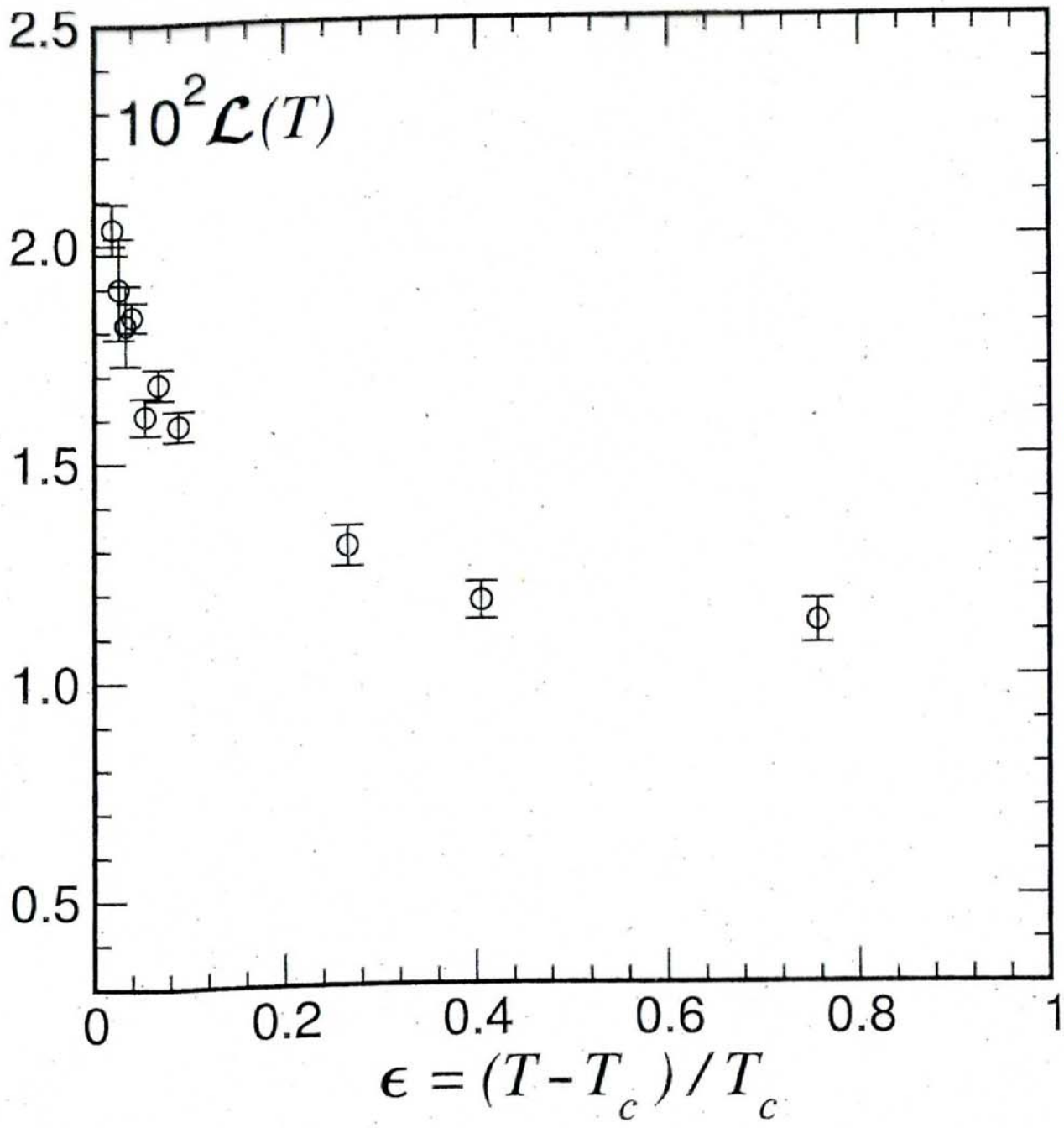
$\approx 1.068\nu \approx \underline{0.673}$



naive analysis NEGLECTS

(i) background (ii) finite size effects

ONSAGER COEFFICIENT from the Green-Kubo analysis



theoretical prediction:

$\mathcal{L}(T) = \mathcal{L}_b(T) + \Delta\mathcal{L}(T)$

↑ background term: noncritical at T_c (van Hove-theory contribution!)

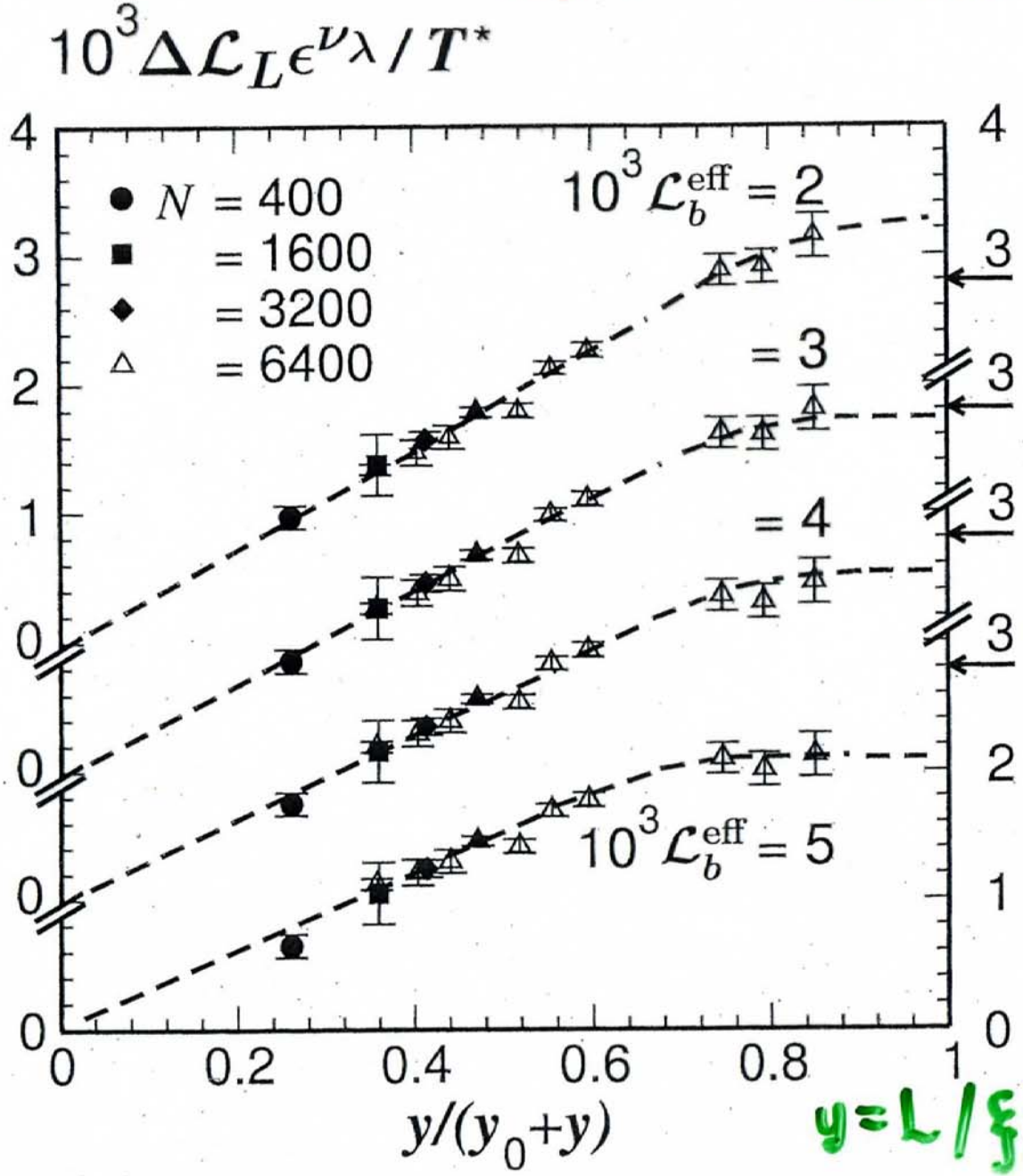
only $\Delta\mathcal{L}(T)$ diverges:

$\Delta\mathcal{L}(T) \propto \varepsilon^{-\nu x_\lambda}$

$$D_{AB}(T) = \frac{\mathcal{L}_b(T) + \Delta\mathcal{L}(T)}{\chi(T)}$$

↗ $\chi(T)$ has no such background term!

FINITE SIZE SCALING ANALYSIS OF THE CRITICAL PART OF THE ONSAGER COEFFICIENT



$\mathcal{L}_b^{\rm eff} (= \mathcal{L}_b(T_c))$ taken as a parameter

$\Rightarrow \mathcal{L}_b^{\rm eff} = (3.3 \pm 0.8) \times 10^{-2}$

consistent with theoretical estimation by Burstyn et al. (1983)

$\Rightarrow \Delta\mathcal{L} \approx Q T^* \varepsilon^{-\nu\lambda}$

implied by straight lines for small y

$\Rightarrow Q = (2.7 \pm 0.4) \times 10^{-3}$

consistent with theoretical prediction Burstyn et al. (1980)

$y = L/\xi(T)$

CONCLUSIONS

- Combining SGMC (for equilibrating an ensemble of initial states, and accurate data on static properties) and microcanonical MD (no artifacts from thermostats!) it is possible to study the dynamics of binary mixtures INCLUDING THE CRITICAL REGION
(approach is similar in spirit to SPIN DYNAMICS simulations of critical dynamics of magnetic systems: D.P. LANDAU et al.)

- For UNDERSTANDING THE RESULTS one must consider FINITE SIZE EFFECTS and NONCRITICAL BACKGROUND terms (it pays off to pay attention to corresponding analytical theory)

- The generalization to CHEMICALLY REALISTIC MODELS OF ACTUAL MATERIALS remains a challenge for the future