Computer Simulations of Critical Dynamics in Fluids

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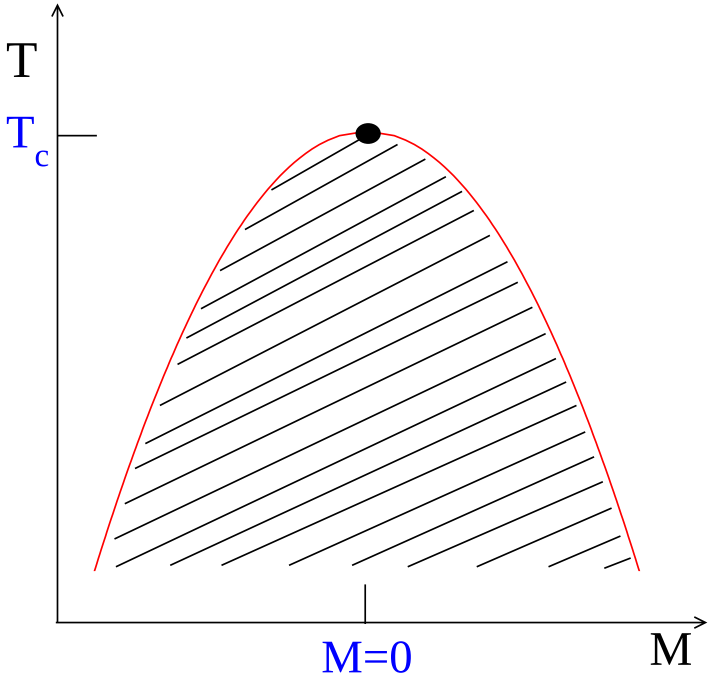
Ref: S.K. Das *et al.*, Phys. Rev. Lett. **97**, 025702 (2006)

J. Chem. Phys. **125**, 024506 (2006)

Critical Phase transitions

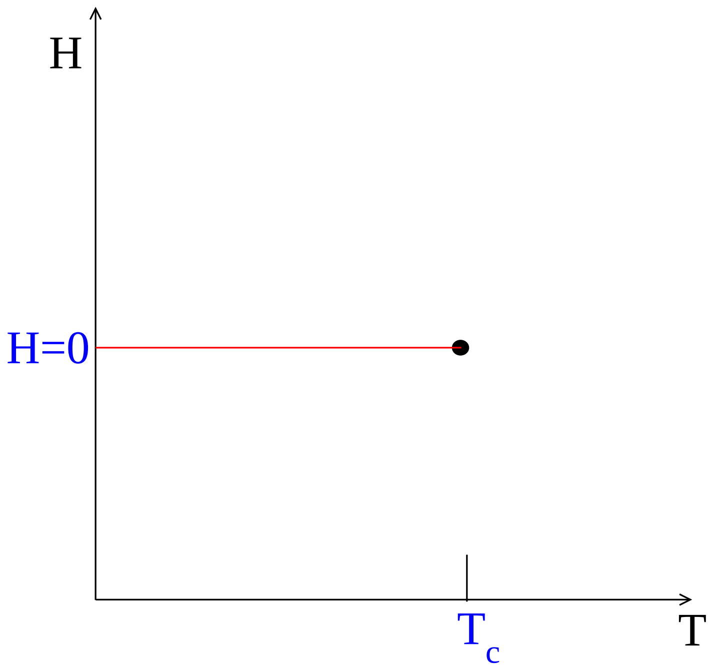


M is order parameter

Fluids: vapor-critical point

$M = \rho - \rho_c$

$H = \mu - \mu_c$



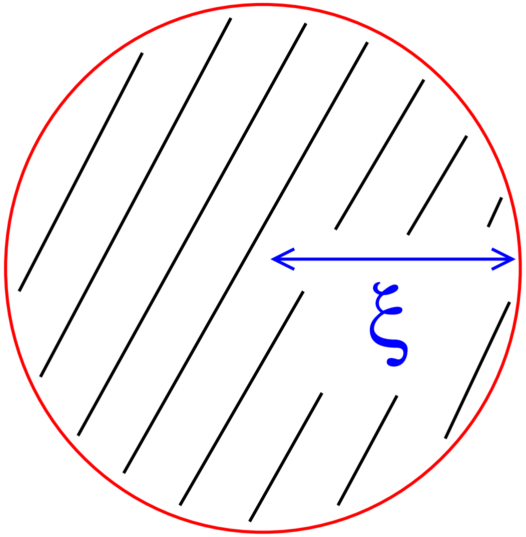
H is ordering field

Fluids: critical point of mixing

$M = x - x_c$

$H = \mu_{12} - \mu_{12,c}$

Critical Power Laws and Universality



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

ξ is correlation length

χ=$(\partial M/\partial H)_T$: susceptibility

$$\xi = \xi_0 \epsilon^{-\nu} \qquad \nu = 0.629$$

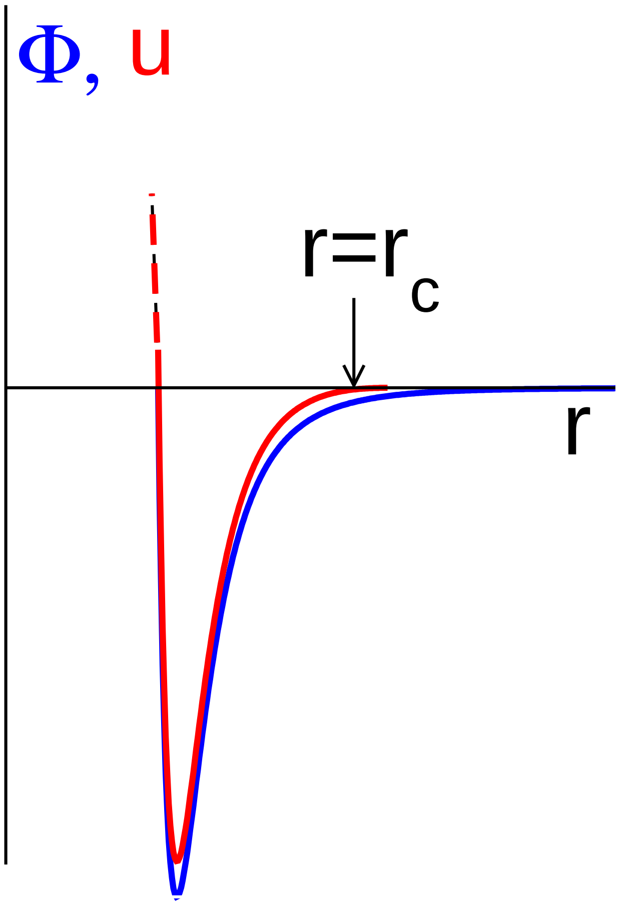
$$\chi = \Gamma_0 \epsilon^{-\gamma} \qquad \gamma = 1.239$$

$$\gamma \simeq 2\nu$$

Simulations: binary L-J liquid

all parameters have been made dimensionless with the aid of the Lennard-Jones parameters

$$\sigma_{AA} = \sigma_{BB} = \sigma_{AB} = \sigma$$
$$\varepsilon_{AA} = \varepsilon_{BB} = 2\varepsilon_{AB}$$
$$r_c = 2.5\sigma$$



Simulation Procedure: Monte Carlo

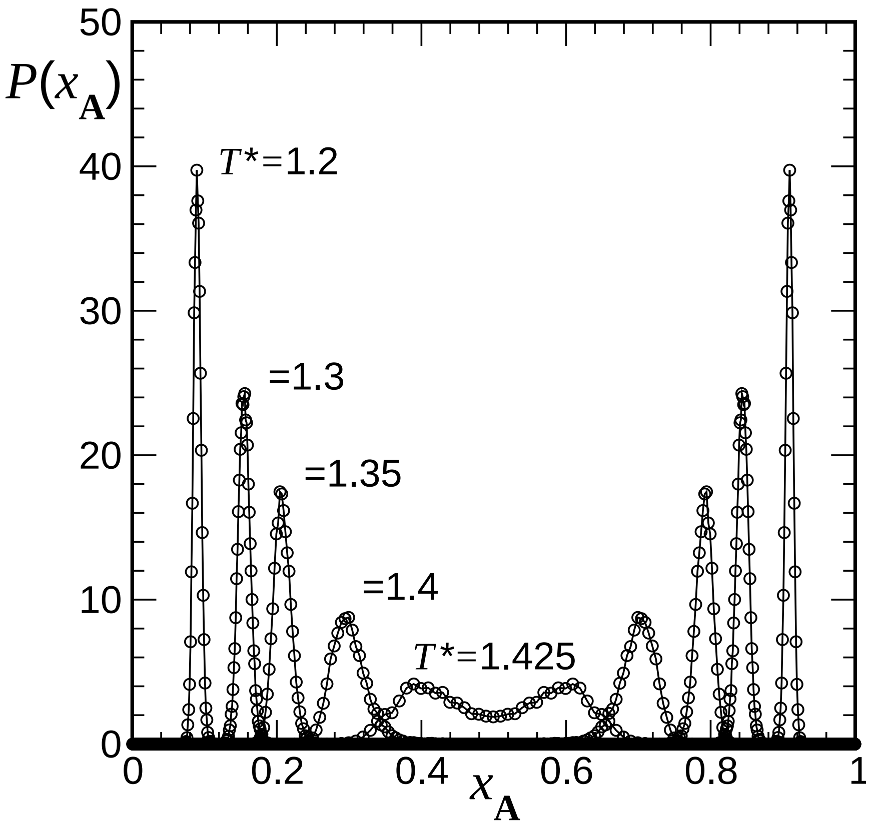
From atoms at random positions in a box of length L

- Equilibration in the canonical ensemble $N_A = N_B, V, T$ via MC
- Continue equilibration in the semi-grand-canonical ensemble via MC (SGMC)
  – $N_A + N_B$ fixed, N_A fluctuates

• In a finite system at criticality, the slowest relaxation time $\tau_{max} \propto L^z$

for SGMC $z \simeq 2$

In SGMC $x_A = N_A/N$ is a fluctuating quantity



Moments:

$$\langle x_A^k \rangle = 2\int_{1/2}^{1} x_A^k P(x_A)dx_A$$

Susceptibility:

$$k_B T\chi = N(\langle x_A^2\rangle - \langle x_A\rangle^2)$$

Binder Parameter:

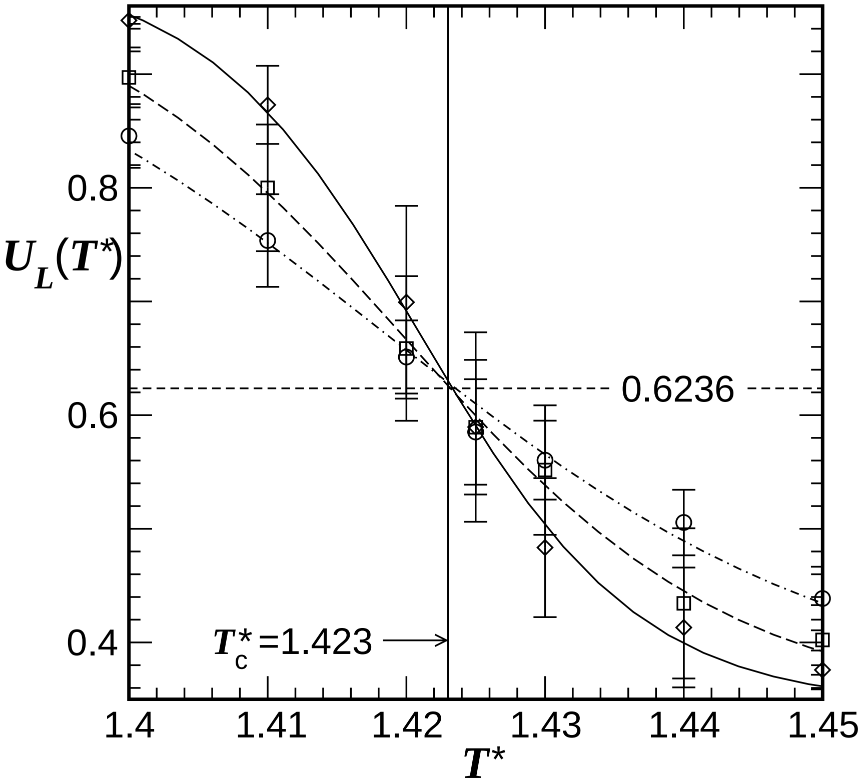
$$U_L(T) = \frac{(\langle (x_A - \frac{1}{2})^4\rangle}{[\langle (x_A - \frac{1}{2})^2\rangle^2]}$$

Estimation of T_c

From

Binder Parameter $U_L(T)$

$L \simeq 11.7, 14.7, 18.61$

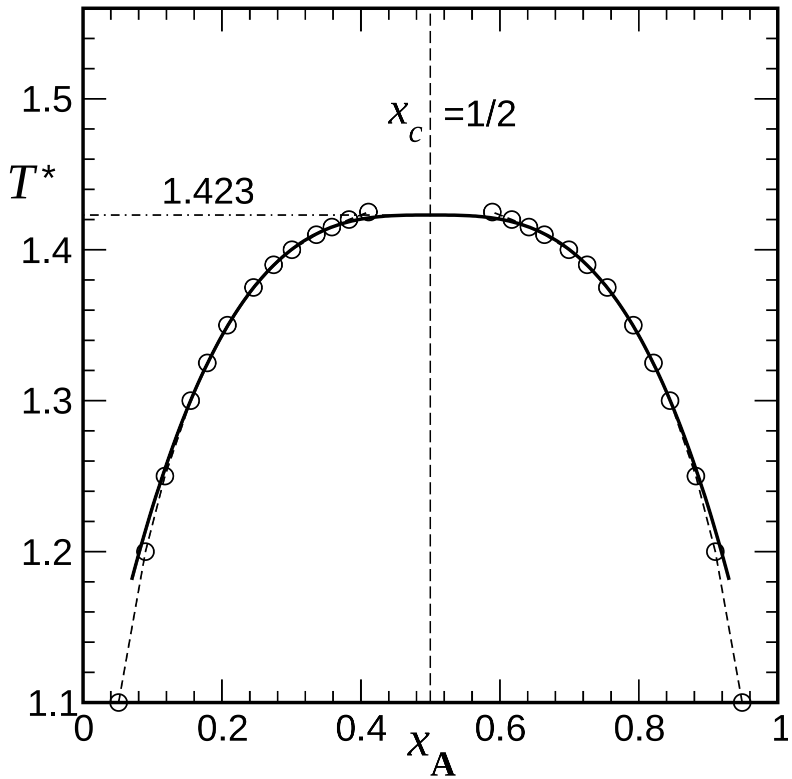


$T_c = 1.4230 \pm 0.0005$

and

Coexistence curve

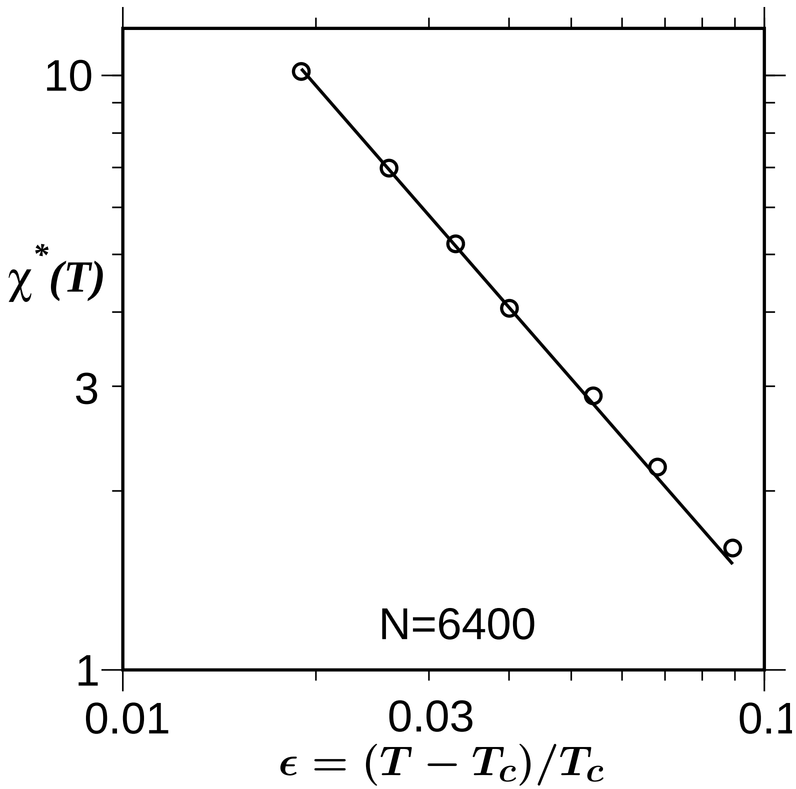
$x_A^{(2)} - x_A^{(1)} = B(1 - T/T_c)^{\beta}$



$T_c = 1.423 \pm 0.002$

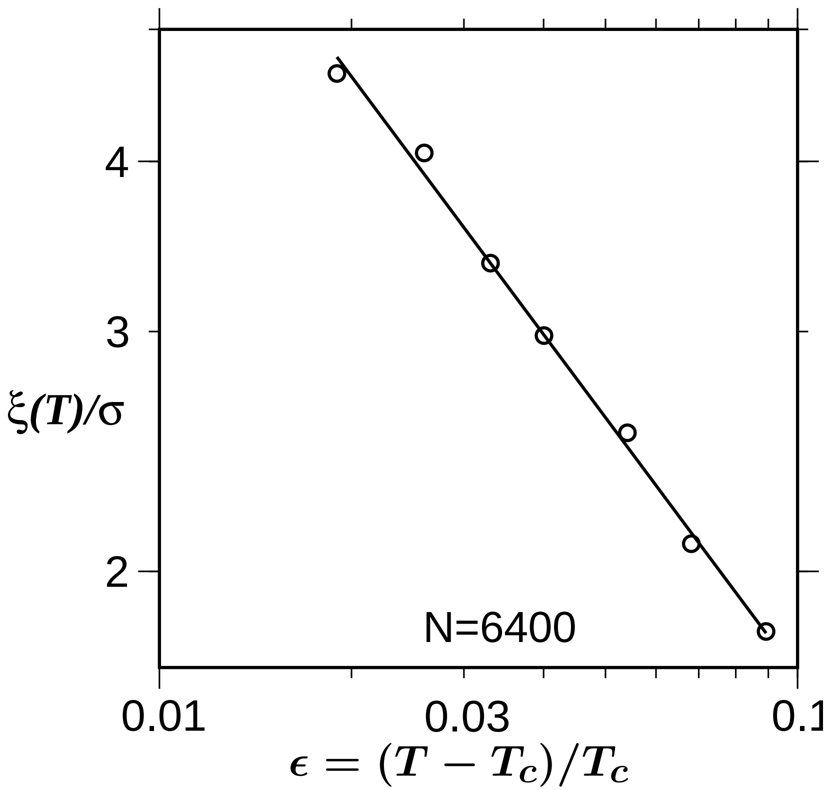
Static critical behavior

$\gamma = 1.239$ (fixed)



$\Gamma_0 = 0.076 \pm 0.006$

$\nu = 0.629$ (fixed)



$\xi_0 = (0.395 \pm 0.025)\sigma$

Critical slowing down of fluctuations

Classical Van Hove theory

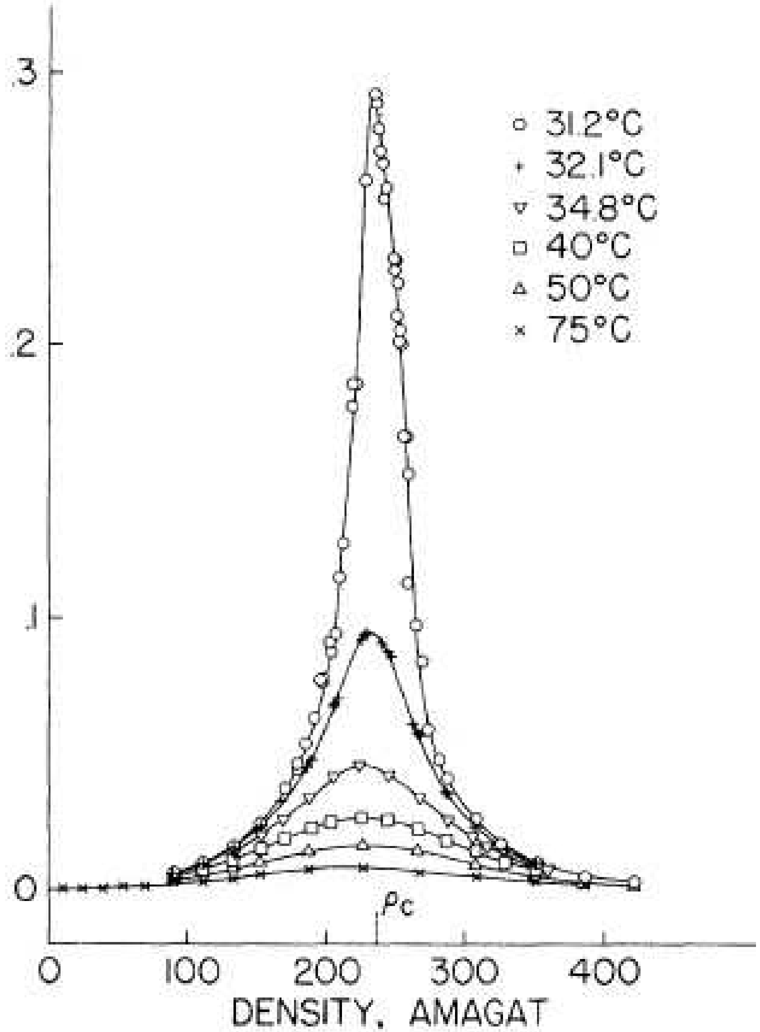
$$s(q,t) = s(q,0)e^{-D_T q^2 t}$$

$$D_T = \frac{\lambda}{\rho C_p}$$

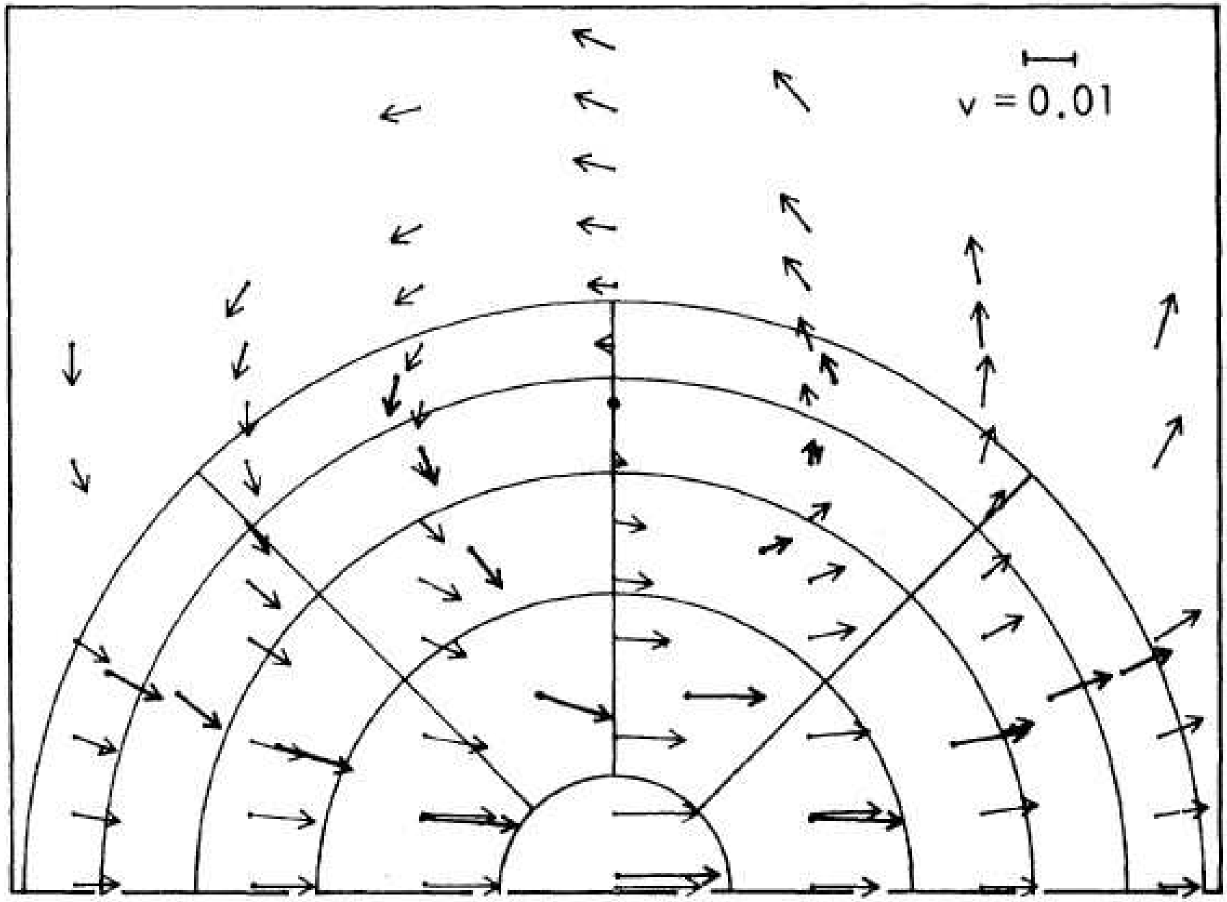
$C_p \to \infty$, λ finite
$\Rightarrow D_T \to 0$ as C_p^{-1}

Thermal conductivity λ

$\Delta\lambda(W/m^oC)$



$T_c = 31^oC$



B.J. Alder and T.E. Wainwright, PRL **18**, 988 (1967).

CRITICAL DYNAMICS

Vapor-Liquid critical point

$$D_T = \lambda/\rho C_p = (\lambda_b + \Delta\lambda)/\rho C_p$$

Liquid-Liquid critical point

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

Stokes-Einstein relation:

$$\Delta D = \frac{\Delta\mathcal{L}}{\chi} = \frac{R_D k_B T}{6\pi\eta(T)\xi(T)}$$

$$R_D = 1.05 \pm 0.03$$

Viscosity η diverges as $\xi^{0.068}$

ΔD vanishes as $\xi^{-1.068}$

These theoretical predictions have been confirmed experimentally quite accurately. For references see:

J.V. Sengers and M.R. Moldover, PRL **94**, 069601 (2006).

Molecular Dynamics Simulations of a Fluid near Its Critical Point

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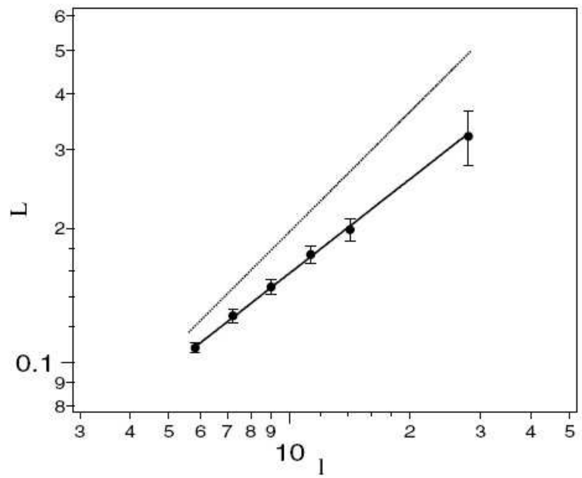
We present computer simulations for the static and dynamic behavior of a fluid near its consolute critical point. We study the Widom-Rowlinson mixture, which is a two component fluid where like species do not interact and unlike species interact via a hard core repulsion. At high enough densities this fluid exhibits a second order demixing transition that is in the Ising universality class. We find that the mutual diffusion coefficient D_{AB} vanishes as $D_{AB} \sim \xi^{-1.26\pm0.08}$, where ξ is the correlation length. This is different from renormalization-group and mode coupling theory predictions for model H, which are $D_{AB} \sim \xi^{-1.065}$ and $D_{AB} \sim \xi^{-1}$, respectively.

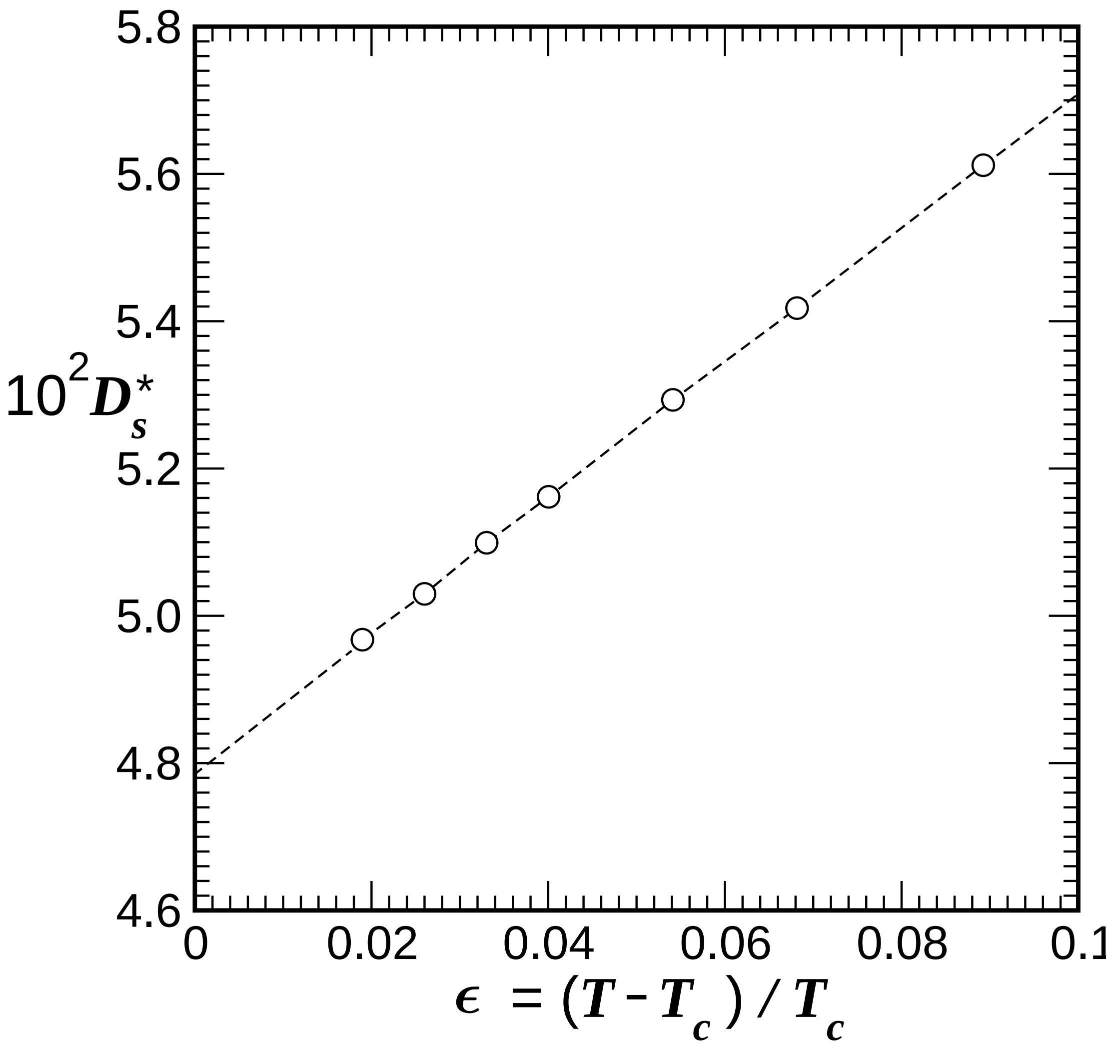


Simulation Method: Molecular dynamics

Solution of equations of motion with $m_A = m_B = m$

- Take equilibrated configurations from semi-grand-canonical Monte Carlo runs with $N_A = N_B$
- Thermalize in the NVT ensemble
- Production runs at NVE ensemble
- Molecular Dynamics: Relaxation exponent $z \simeq 3$

Self Diffusion D_s



No anomaly at critical point

$\eta \approx \eta_b (Q_0 \xi)^{\ x_\eta}$

$\Rightarrow \eta \approx \eta_0 \ \epsilon^{-\nu x_\eta}$

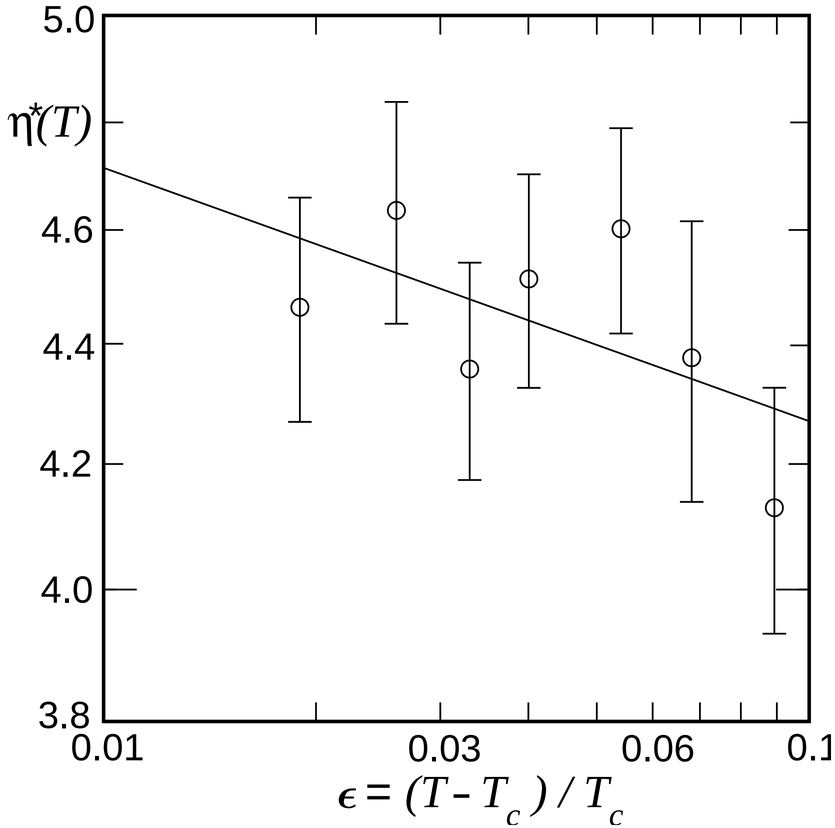
with

$\eta_0 = \eta_b (Q_0 \xi_0)^{x_\eta}$; $x_\eta = 0.068$

Experimental: $\eta_0 \simeq 0.9 \eta_b$

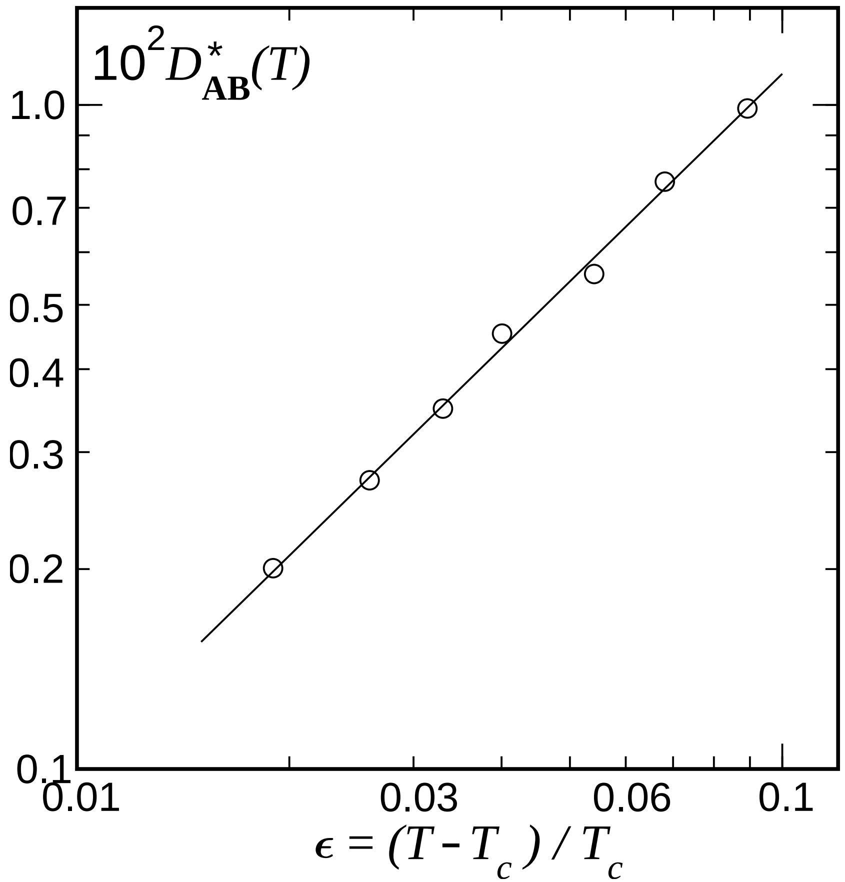
Burstyn *et al.*

PRA **28**, 1567 (1983).



Viscosity exponent fixed at 0.068

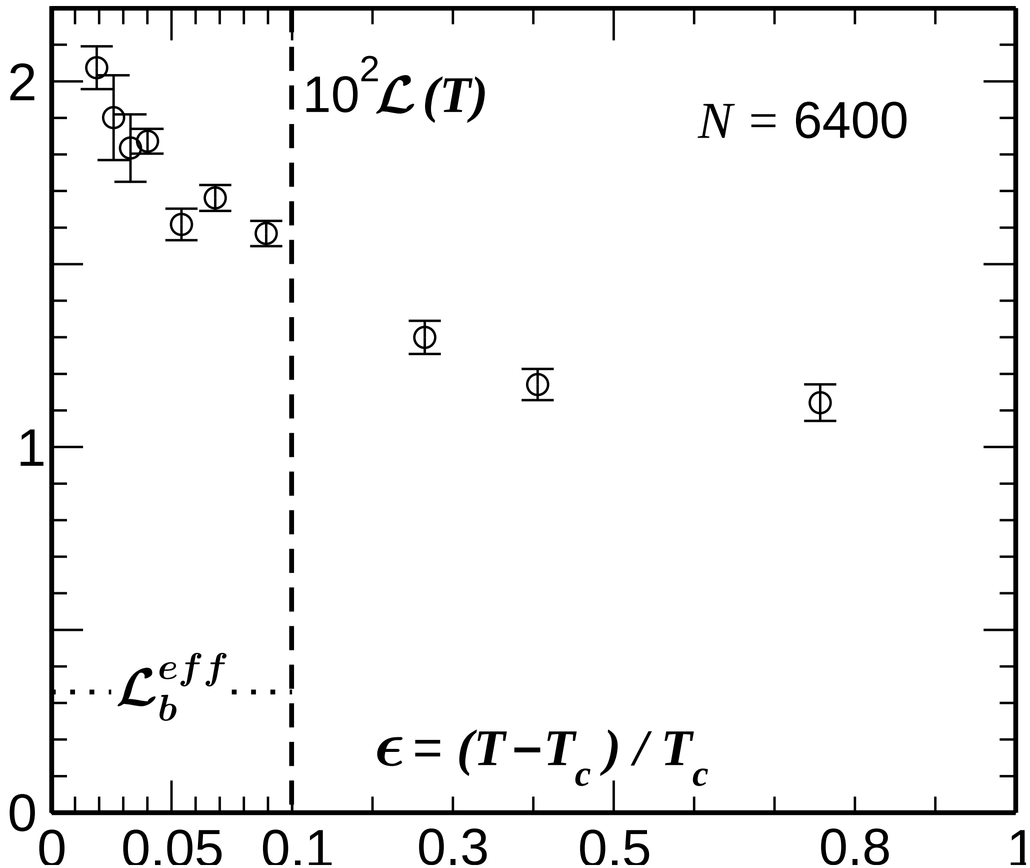
Viscosity amplitude $\eta_0 = 3.87 \pm 0.30$



D_{AB} seems to vanish as $\xi^{-1.6}$

which is even worse than the result $\xi^{-1.26}$ found by J & Y

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



$$\Delta D_{AB} = \Delta\mathcal{L}/\chi$$

Since ΔD_{AB} vanishes in accordance with the Stokes-Einstein relation, it follows that in dimensionless units

$$\Delta\mathcal{L} = \frac{R_D T^* \chi^* \sigma}{6\pi\eta^*\xi} = Q T^* \epsilon^{-0.567}$$

With Q=$\frac{R_D\Gamma_0}{6\pi\eta_0\xi_0}$

Finite-size scaling of $\Delta\mathcal{L}$

(Fisher'1971)

In the thermodynamic limit $(L \to \infty)$

$$\Delta\mathcal{L}(T) \approx Q T^* \epsilon^{-\nu_\lambda}; \; \nu_\lambda = 0.567$$

For finite box $(L < \infty)$: basic ansatz $(y = L/\xi)$

$$\Delta\mathcal{L}_L(T) \approx Q T^* W(y) \epsilon^{-\nu_\lambda}$$

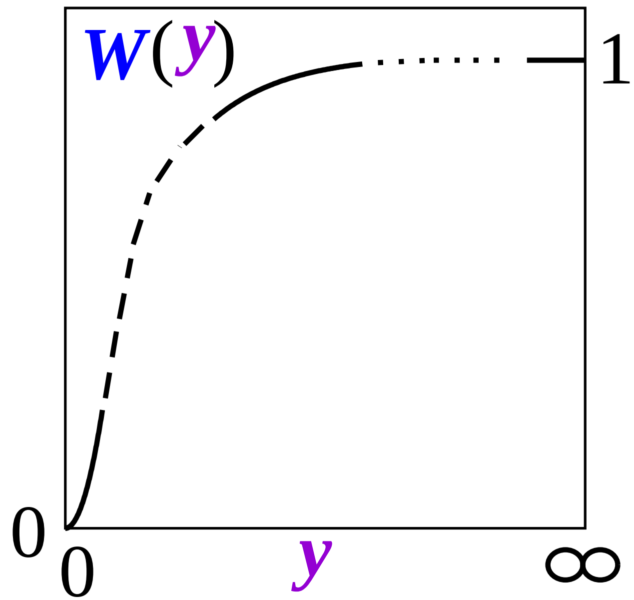
SCALING FUNCTION:

as $y \to 0$

$W(y) = y^{\nu_\lambda/\nu}[W_0 + W_1 y^{1/\nu} + ...]$

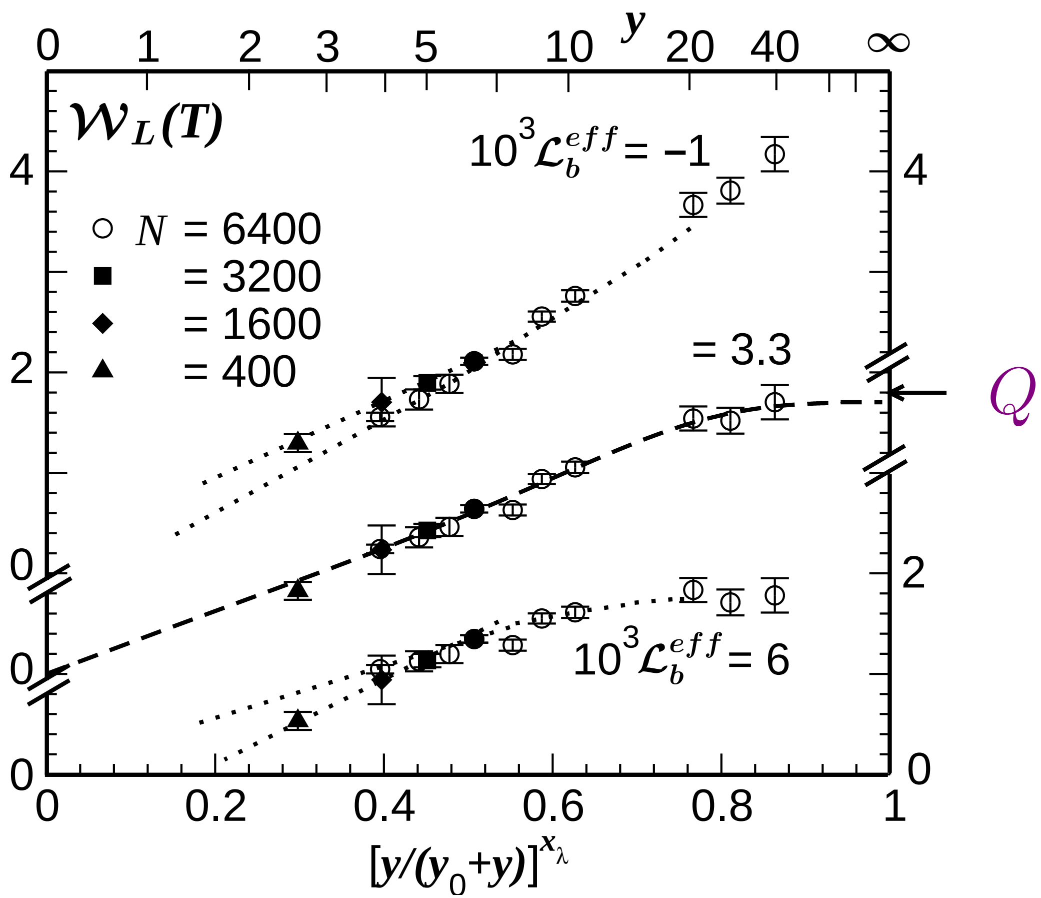
as $y \to \infty$

$W(y) \to 1$



Finite-size scaling ansatz: $\Delta\mathcal{L}_L \approx QT^* W(y)/\epsilon^{\nu_\lambda}$; $y = L/\xi$

Define $\mathcal{W}_L(T) \equiv (\Delta\mathcal{L}_L/T^*)\epsilon^{\nu_\lambda}$



Amplitude of Stokes-Einstein relation

$$Q = \frac{R_D \Gamma_0}{6\pi\eta_0\xi_0}$$

$$\Gamma_0 = 0.076 \pm 0.006,\ \xi_0 = 0.395 \pm 0.025,\ \eta_0 = 3.87 \pm 0.30,$$
$$R_D = 1.05 \pm 0.03$$

$$\Rightarrow Q_0 = 0.0028 \pm 0.0004$$

From Molecular Dynamics simulation

$$Q_0 = 0.0027 \pm 0.0004$$

with $\mathcal{L}_b^{eff} = 0.0033 \pm 0.0008$

Non-critical background

$$D_{AB} = D_b + \Delta D_{AB} = \frac{\mathcal{L}}{\chi} = \frac{\mathcal{L}_b + \Delta\mathcal{L}}{\chi}$$

$$\Delta D_{AB} = \frac{\Delta\mathcal{L}}{\chi} = \frac{R_D k_B T}{6\pi\eta\xi}$$

$$D_b = \frac{\mathcal{L}_b}{\chi} = \frac{k_B T}{16\eta_b \xi^2 q_c}$$

Wave number q_c

$$q_c^{-1} = \frac{16\eta_b \xi_0^2 \mathcal{L}_b}{T^* \Gamma_0}$$

$$\eta_b = 1.1\eta_0$$
$$\xi_0 \simeq 0.395$$
$$\Gamma_0 \simeq 0.076$$
$$\mathcal{L}_b^{eff} \simeq 0.0033$$

$$\Rightarrow q_c^{-1} \simeq 0.8\xi_0$$

to be compared with

$$q_c^{-1} \simeq 0.8\xi_0$$

as determined from experiments by Burstyn *et al.* PRA **28**, 1567 (1983).

CONCLUSION

Our computer simulations of critical dynamics are consistent with theory and with experiment (including the Stokes-Einstein relation for the critical diffusivity) provided that one accounts for a noncritical short-range contribution and for finite-size effects on the appropriate Onsager coefficient.

Note: Finite-size effects for dynamical long-range critical behavior are much larger than for static long-range critical behavior.