Capturing the divergence of length and time scales at the critical point by molecular dynamics simulation

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Corresponding states and molecular modeling


**Simple molecular models**

Lennard-Jones 2CLJD / 2CLJQ

σ, ε

noble gases
methane

78 real fluids
97.4% of their mixtures

**Parametrization**

Fit to large number of VLE data

or

\( T_c \) and \( \rho_c \)

\( T_c, \rho_c, \rho_c, \) and \( p_s(0.7 \ T_c) \)
Determination of the critical point

In the critical limit,

- the correlation length $\xi$,
- the relaxation time $\tau$,
- local density fluctuations (e.g. $\beta_T$),
- local energy fluctuations (e.g. $c_v$),

... diverge while for VLE data, the precision decreases.

Experiment: Critical opalescence.
Innovative HPC Methods for Molecular Simulation

future challenges!

adsorption
ionic liquids
critical behaviour
toxic/explosive fluids
Direct approach: Isochoric heat capacity

relaxation of initially homogeneous systems

N = 2^{22}

u in units of $\varepsilon$

simulation time in LJ units

(0.00 0.02 0.04 0.06)

$T^* = 1.06$

$T^* = 1.08$

$T^* = 1.1$

relaxed state

(truncated-shifted LJ potential; the time unit roughly corresponds to 2 ps)
Indirect approach: Phase coexistence below $T_c$
Interfacial relaxation time

$T^* = 1.06$ (below $T_c$) \hspace{1cm} t^* = 900

$T^* = 1.1$ (above $T_c$) \hspace{1cm} t^* = 900
Interfacial relaxation time

\[ T^* = 1.06 \text{ (below } T_c \text{)} \quad t^* = 4500 \]

\[ T^* = 1.1 \text{ (above } T_c \text{)} \quad t^* = 4500 \]
Critical temperature by extrapolation

Binodal line for the truncated-shifted LJ fluid

\[ T_c \approx 1.078 \varepsilon/k \]


Guggenheim approach
Assumption: critical exponent \( \beta = 1/3 \)
Scaling of the \textit{ls1 mardyn} program

homogeneous truncated-shifted LJ system

- HLRS nehalem cluster Baku/Laki

methane + graphite

- 2 000, 4 000, 8 000, and 16 000 particles per process

- uniform subdomains
- static load balancing

- simulation loop
- input/output
Communication and load balance

OpenMPI, gcc-4.1.2, HLRS nehalem cluster Baku/Laki.
Conclusion

Approaches to analyzing critical behaviour by molecular simulation:

- Divergence of fluctuation related quantities
- Disappearance of the vapour-liquid coexistence

... require relatively large systems and a long simulation time.

- Extrapolation of VLE properties

... data become less reliable near $T_c$.

- Extrapolation of interface properties

... in the vicinity of $T_c$, relatively large $V$ and $\Delta t$ are required as well.

competence in high performance computing $\rightarrow$ capturing critical behaviour