Critical point particle number fluctuations from molecular dynamics

Volodymyr Kuznietsov (Taras Shevchenko U., Kyiv & BITP, Kyiv),
o. Savchuk (BITP, Kyiv), M.I. Gorenstein (BITP, Kyiv),
V. Koch (LBNL), V. Vovchenko (INT Seattle)

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Lennard-Jones fluid

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

Reduced variables:
\[ \tilde{r} = r/\sigma \quad \tilde{T} = T/(k_B \varepsilon) \quad \tilde{n} = n\sigma^3 \]

Properties:
- Multiple phase transitions, including critical point
- Tractable with molecular dynamics simulations
- Critical point in 3D-Ising universality class at
  \[ \tilde{T}_c = 1.321 \pm 0.007, \quad \tilde{n}_c = 0.316 \pm 0.005 \]

Toy model to study critical point fluctuations microscopically

Molecular dynamics setup

- Newton’s equations of motion (classical N-body problem)
  \[
  m\ddot{\mathbf{r}}_i = -\sum_j \nabla_i V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)
  \]

- Box simulation
  - Periodic boundary conditions
  - Minimum-image convention

- Microcanonical ($UVN$) and canonical-like ($TVN$) ensembles

- Observables as time averages
  \[
  \langle A \rangle = \frac{1}{\tilde{\tau}} \int_{\tilde{\tau}_{eq}}^{\tilde{\tau}_{eq} + \tilde{\tau}} A(\{\tilde{\mathbf{r}}_i(t), \tilde{\mathbf{v}}_i(t)\})d\tilde{t}
  \]

Implementation:
Velocity Verlet integration scheme implemented on CUDA-GPU (x100-200 speed-up*)
open source: https://github.com/vlvovch/lennard-jones-cuda

*This research used the Lawrencium computational cluster resource provided by the IT Division at the Lawrence Berkeley National Laboratory
Equation of state along a supercritical isotherm $\tilde{T} = 1.06 \tilde{T}_C$

Compressibility factor

$$Z = \frac{\tilde{\rho}}{\tilde{n} \tilde{T}}$$

The low-density limit agrees with the virial expansion.

Grand-canonical scaled variance shows peak near the critical point density $\tilde{n}_c = 0.316$
Fluctuations in molecular dynamics

Variance of conserved particle number distribution inside coordinate space subvolume $|z| < z^{\text{max}}$ as time average

- $\langle N \rangle$, $\langle N^2 \rangle$ as time averages
- Microcanonical ensemble
- $1 - \alpha$ factor to cancel out global conservation
- $\tilde{\omega}^{\text{coord}} \rightarrow \omega^{\text{gce}}$ expected as $\langle N \rangle \rightarrow \infty$

\[ \tilde{\omega}^{\text{coord}} = \frac{1}{1 - \alpha} \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle} \]
Fluctuations in molecular dynamics: momentum space

Experiments measure momenta, not coordinates → consider momentum subvolume instead

\[ |v_z| < v_z^{\text{cut}} \quad (\text{à la } |y| < y^{\text{cut}}) \]

\[ \alpha = \frac{\langle N^{\text{acc}} \rangle}{N} \]

Ideal gas limit: \[ \tilde{\omega}_{\text{id}}^\text{mom,mce} = 1 - \frac{2[\text{erf}^{-1}(\alpha)]^2 e^{-2[\text{erf}^{-1}(\alpha)]^2}}{3\pi \alpha (1 - \alpha)} \]

Large fluctuations near the CP are washed out when momentum cuts imposed instead of coordinates

NB: here no collective flow and expansion

Outlook:

• Collective flow and expansion
• Ensemble averaging instead of time averaging
• High-order cumulants