NANO BUBBLE – SIZE DEPENDENCE OF SURFACE TENSION AND INSIDE PRESSURE

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SUMMARY

1. ARTICLE'S PROPOSAL
2. METHOD
3. RESULTS
4. CONCLUSION

ARTICLE'S PROPOSAL

- Answer the question: how far is the Young-Laplace Equation applicable for nano bubbles?

$$P_{vap} = P_{liq} + \frac{2\gamma}{R} \quad or \quad \Delta P = P_{vap} - P_{liq} = \frac{2\gamma}{R};$$

"A bubble of $R = 10$ nm in water at room temperature ($\gamma \cong 0{,}073$) will show $\Delta P = 150$ atm. How can this tiny bubble be mechanically stable under atmospheric pressure?"

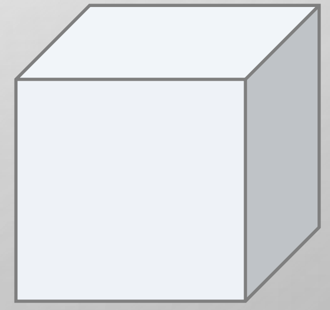
1. Abandon the Y-L equation, assuming that it works only in macroscopy or continuum level;
2. Y-L equation still applicable for nano bubbles, but the surface tension of them differs from the usual value, i.e., flat surface;

METHOD

- MD simulation of two systems of monoatomic simple liquid with 25,000 and 125,000 particles using the Lennard-Jones potential:

$$\emptyset_{LJ} = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad \sigma = 0.34nm$$

- Canonical ensemble comparing a system with $\frac{k_B T}{\varepsilon} = 0{,}7$ (close to the triple point temperature) and $\frac{k_B T}{\varepsilon} = 1{,}0$.

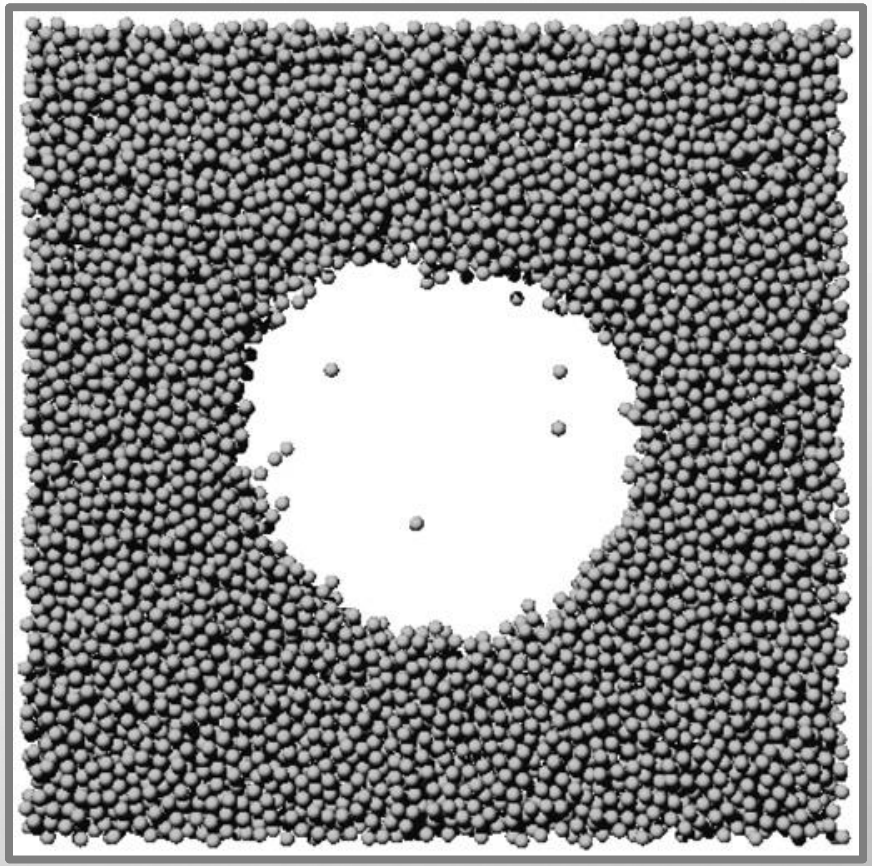


METHOD

- A repulsive external force field is applied at the central part of the cell to generate a space, or a “bubble”;

- When the system reaches equilibrium the force field is removed;

- We can see particles inside the bubble, they evaporated spontaneously;



RESULTS

- There is three quantities to consider:
  - Density profile: - average number of density at distance r from r_0 (bubble's "center of mass");
  - Pressures: - Liquid pressure with Virial expression;
    - Vapor pressure empirical equation of state;
  - Surface tension: - Y-L equation.

RESULTS

<u>Density Profile</u>

$$n(r) = \frac{n_{liq}+n_{vap}}{2} + \frac{n_{liq}-n_{vap}}{2} tanh\left(\frac{r-R}{w}\right)$$

n_{liq}: liquid density

n_{vap}: vapor density

R: bubble radius

w: width of interface

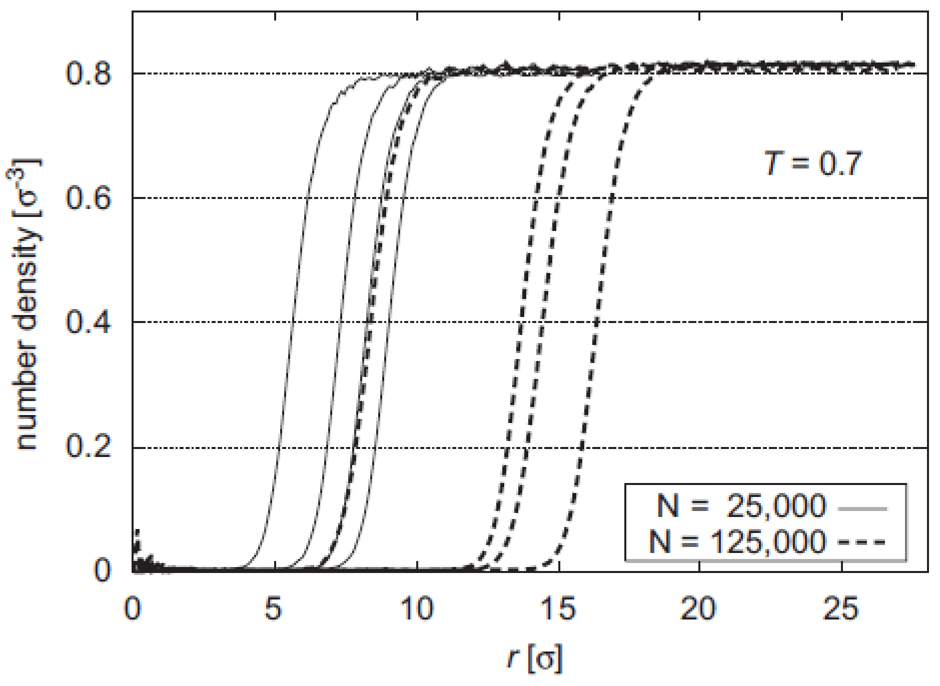


Fig. 2. Density profile from the bubble center: at low temperature.

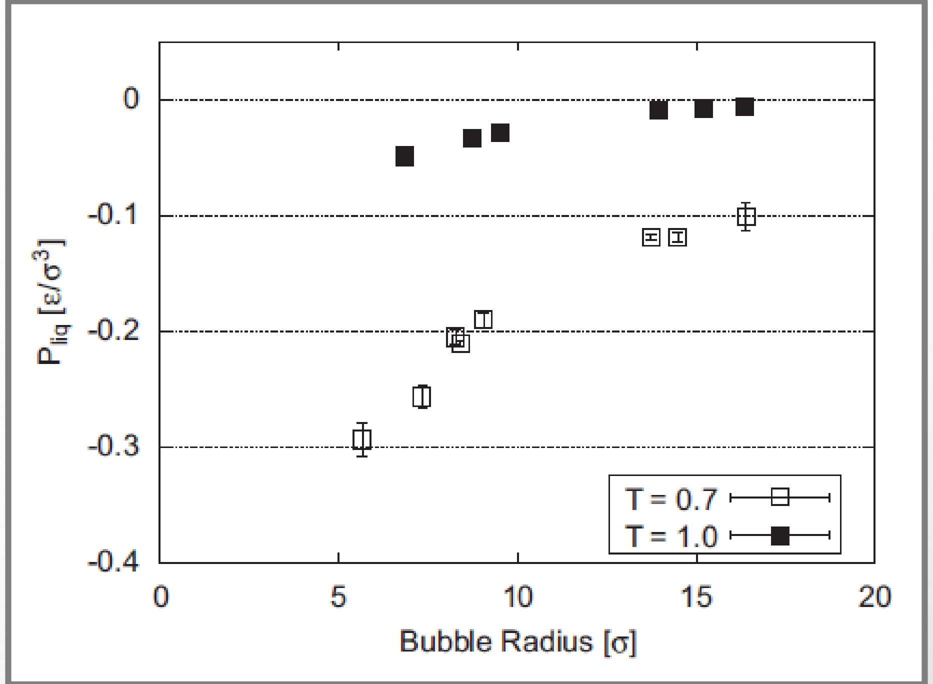
$w(T = 0.7) \cong 0.8 - 1.0\sigma\,; w(T = 1.0) \cong 1.8 - 2.0\sigma$ [almost independente of R]

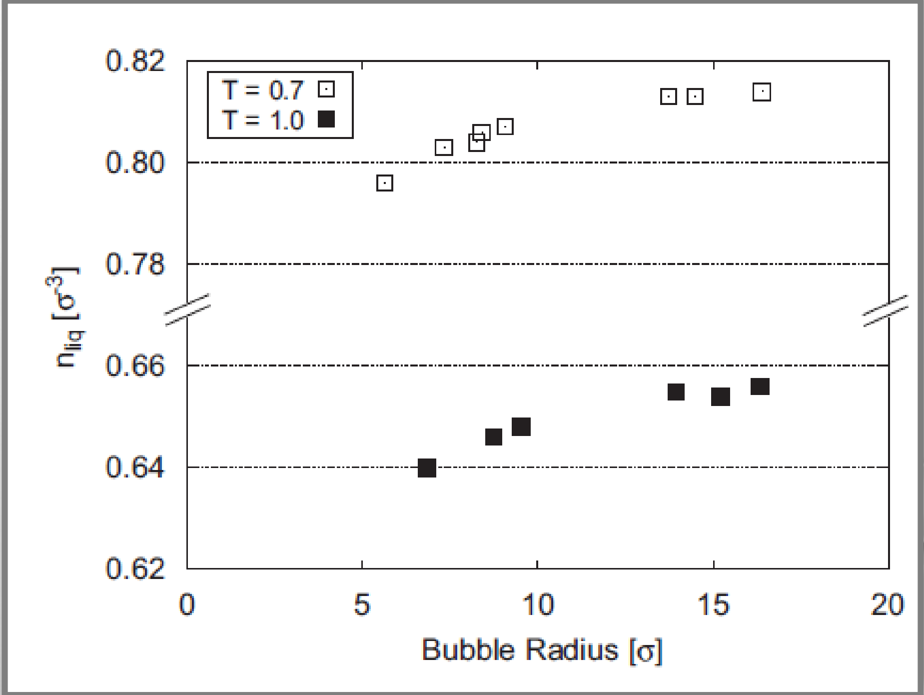
RESULTS

<u>Liquid pressure</u>

$$P = \frac{N}{V} k_B T - \frac{1}{6V} \left\langle \sum_{ij} r_{ij} \cdot \frac{\partial \emptyset_{LJ}(r_{ij})}{\partial r_{ij}} \right\rangle$$

- P_{liq}: applying virial to the "bulk" liquid region;
- $P \approx P_{liq}$ since the contribution of the bubble region is much smaller than the liquid region;
- Negative vaules of P_{liq} means that the surrounding liquid is in a stretched state (surface tension is the reason).

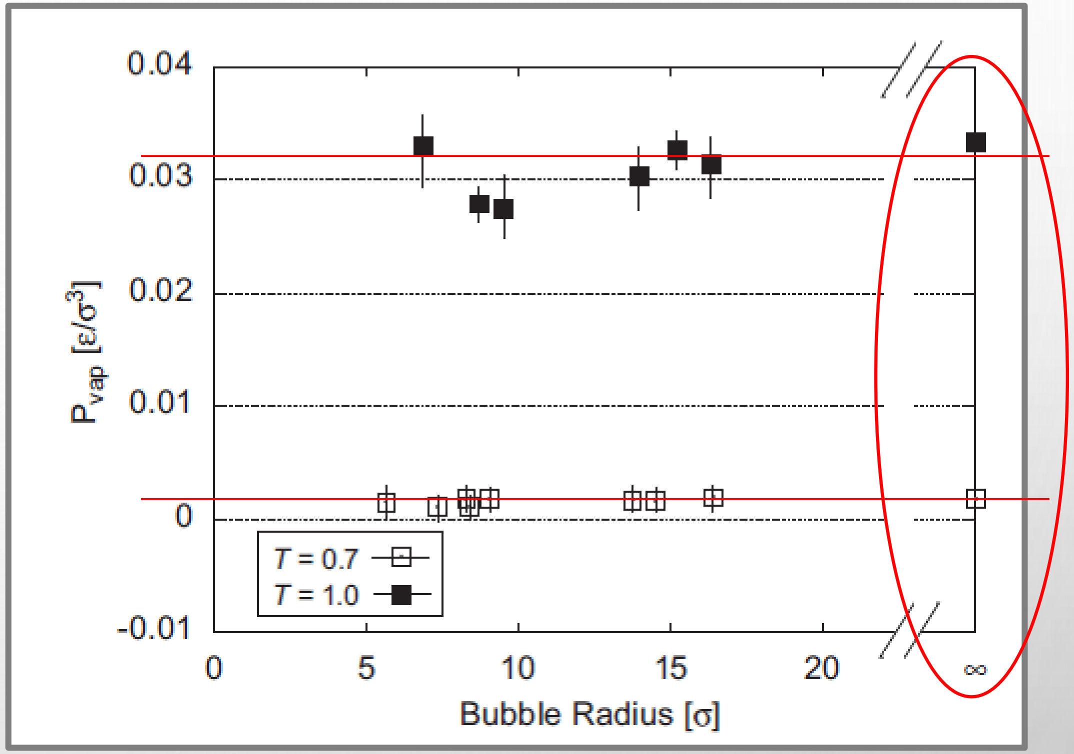




RESULTS

<u>Vapor pressure</u>

$$P = \frac{N}{V} k_B T - \frac{1}{6V} \left\langle \sum_{ij} r_{ij} \cdot \frac{\partial \phi_{LJ}(r_{ij})}{\partial r_{ij}} \right\rangle$$



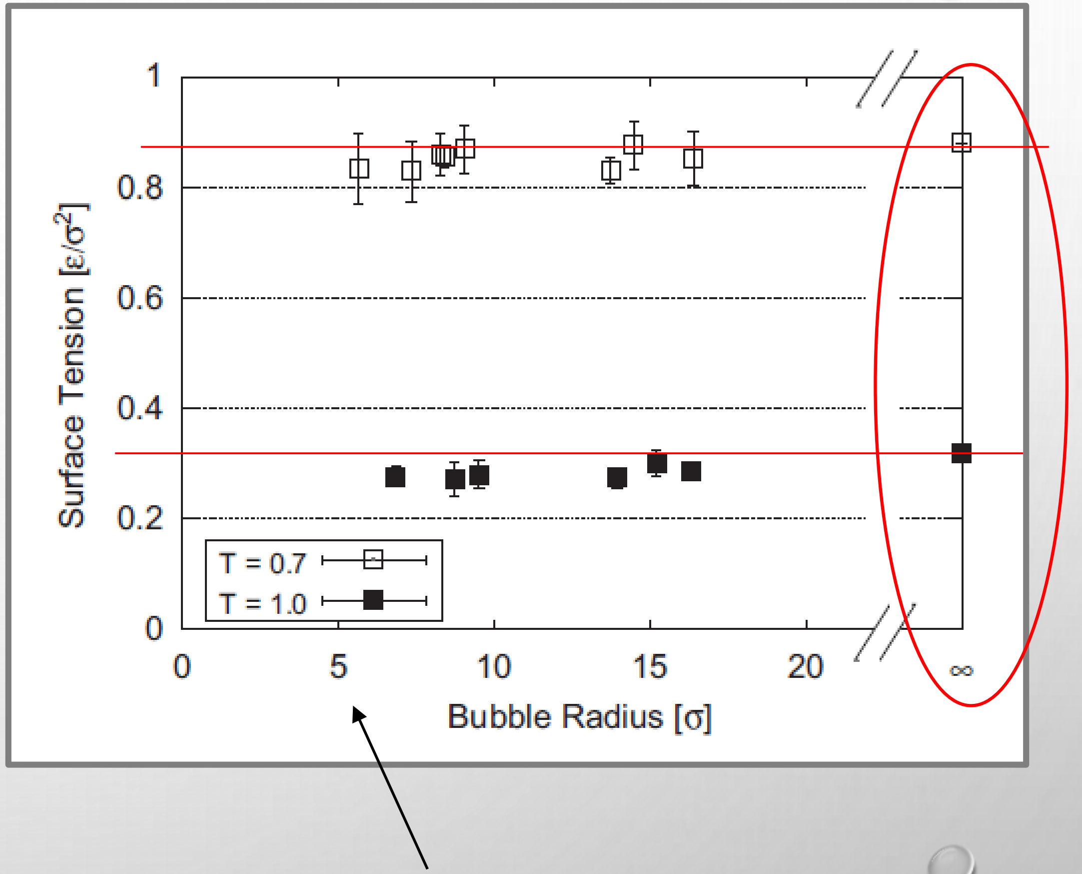
- P_{vap}: can't apply virial due to low vapor density;
- MD simulation of vapor phase to make an empirical equation of state $[n_{vap}(P_{vap})]_T$
- n_{vap} is found by counting particles inside the bubble and P_{vap} by comparing with the empirical equation.

RESULTS

<u>Surface tension</u>

$$P_{vap} = P_{liq} + \frac{2\gamma}{R}$$

- γ is independent of R;
- This result differs from other works:
  - 1st reason: difference of Method to evaluate γ;
  - 2nd reason: difference of system size.



5σ = 1.7 nm

CONCLUSION

- The vapor density and the vapor pressure inside the bubble is independent of the bubble radius, equal to those of the saturated vapor in bulk equilibrium;
- The liquid surrounding the bubble is at a strongly stretched state. As the bubble size decreases, the liquid is exposed to more tensile stress;
- The surface tension evaluated with assumption of the Y–L equation is also little dependent on the bubble radius, and agrees with the surface tension of a planer interface;
- If Y-L equation is valid, stable nano bubbles can exist only in liquid under highly tensile stress, or large negative pressure – under atmospheric pressure they exist only at some non-equilibrium state or because of some impurity.