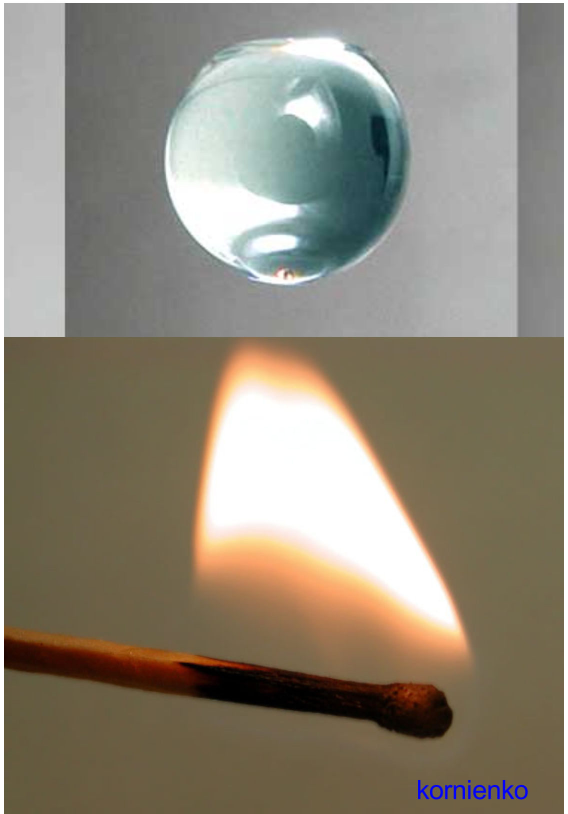
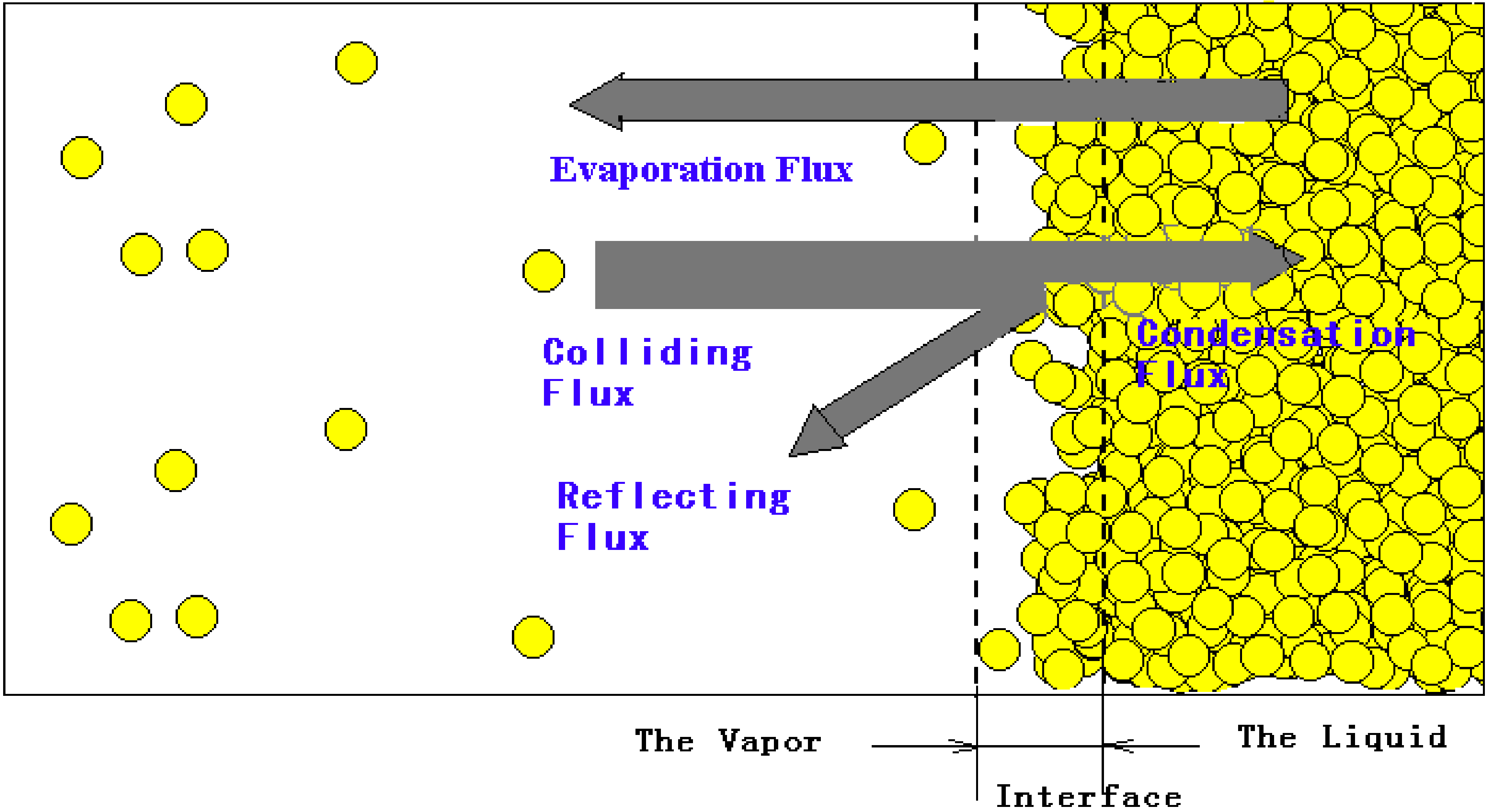
Evaporation/condensation in a microscale

Robert Hołyst
Institute of Physical Chemistry PAS, Poland



kornienko

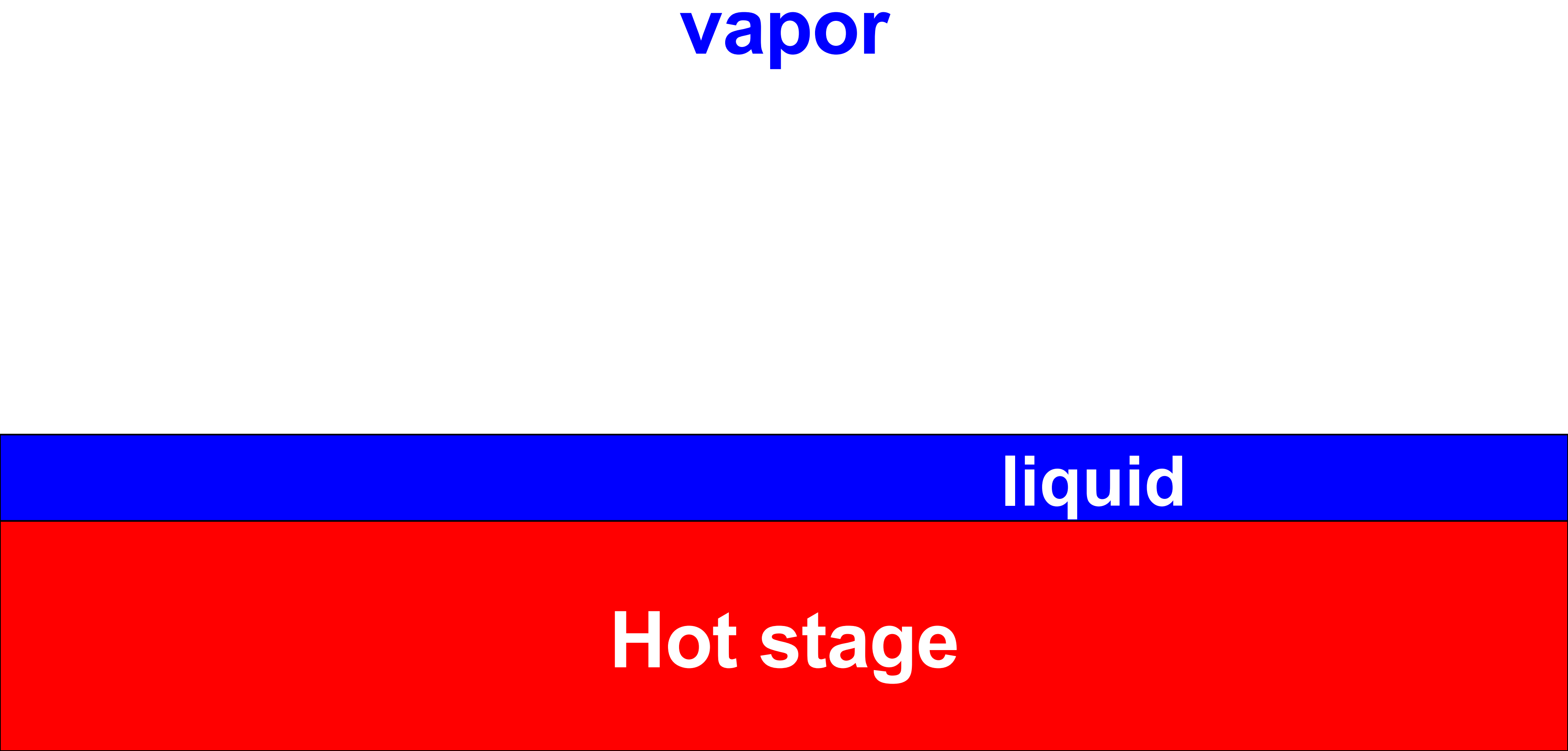
Vova Babin



Maxwell (1877) – microscopically evaporation is driven by particles diffusion in the isothermal process

IS IT?

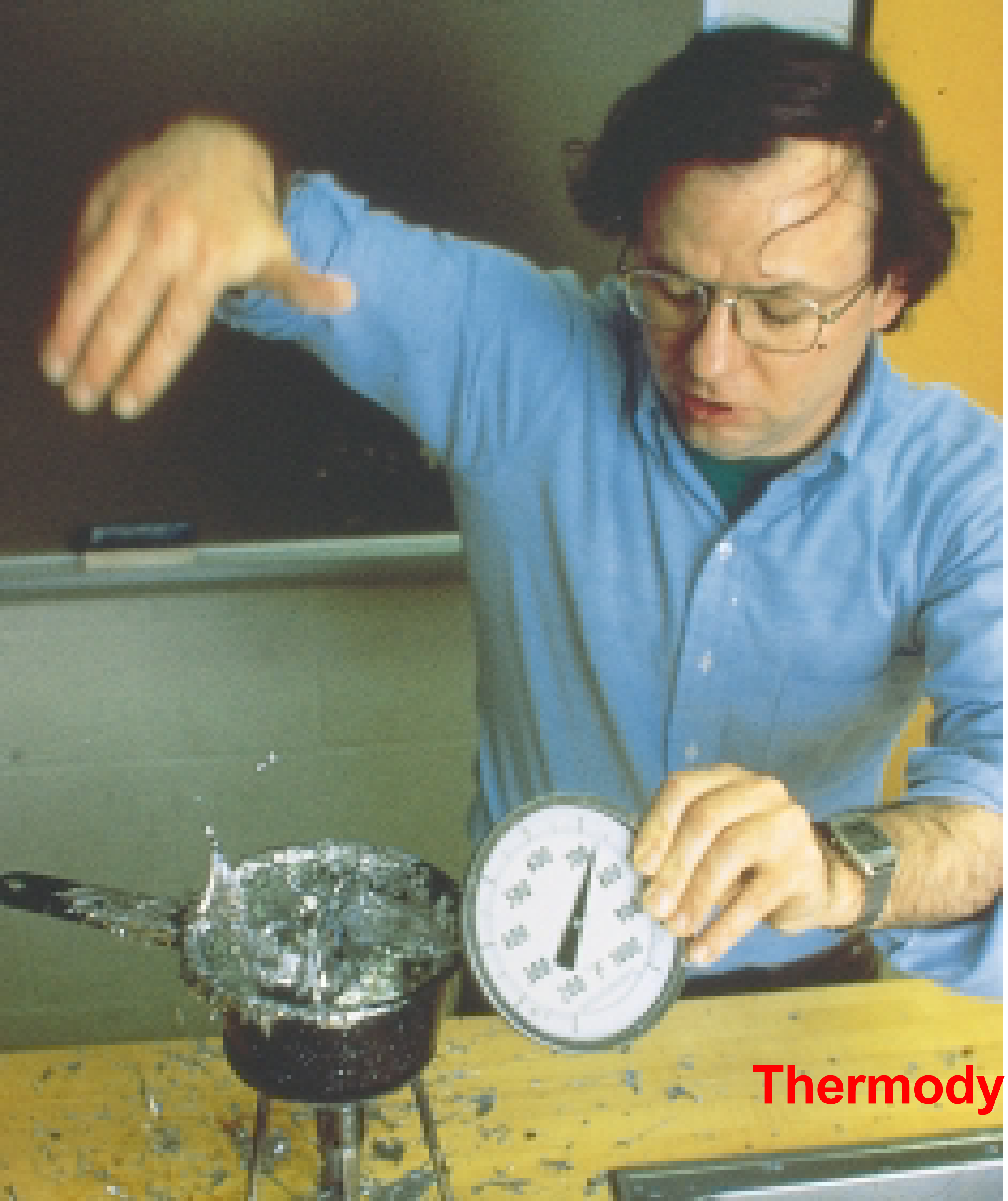
Leidenfrost effect (Hermann Boerhaave 1732, Gottlieb Leidenfrost 1756 „A Track on some qualities of common water” (in latin))



vapor

liquid

Hot stage



750 F
(400 C)

**Jearl Walker
puts his hand into
the molten lead
(at Cleveland State
University)**

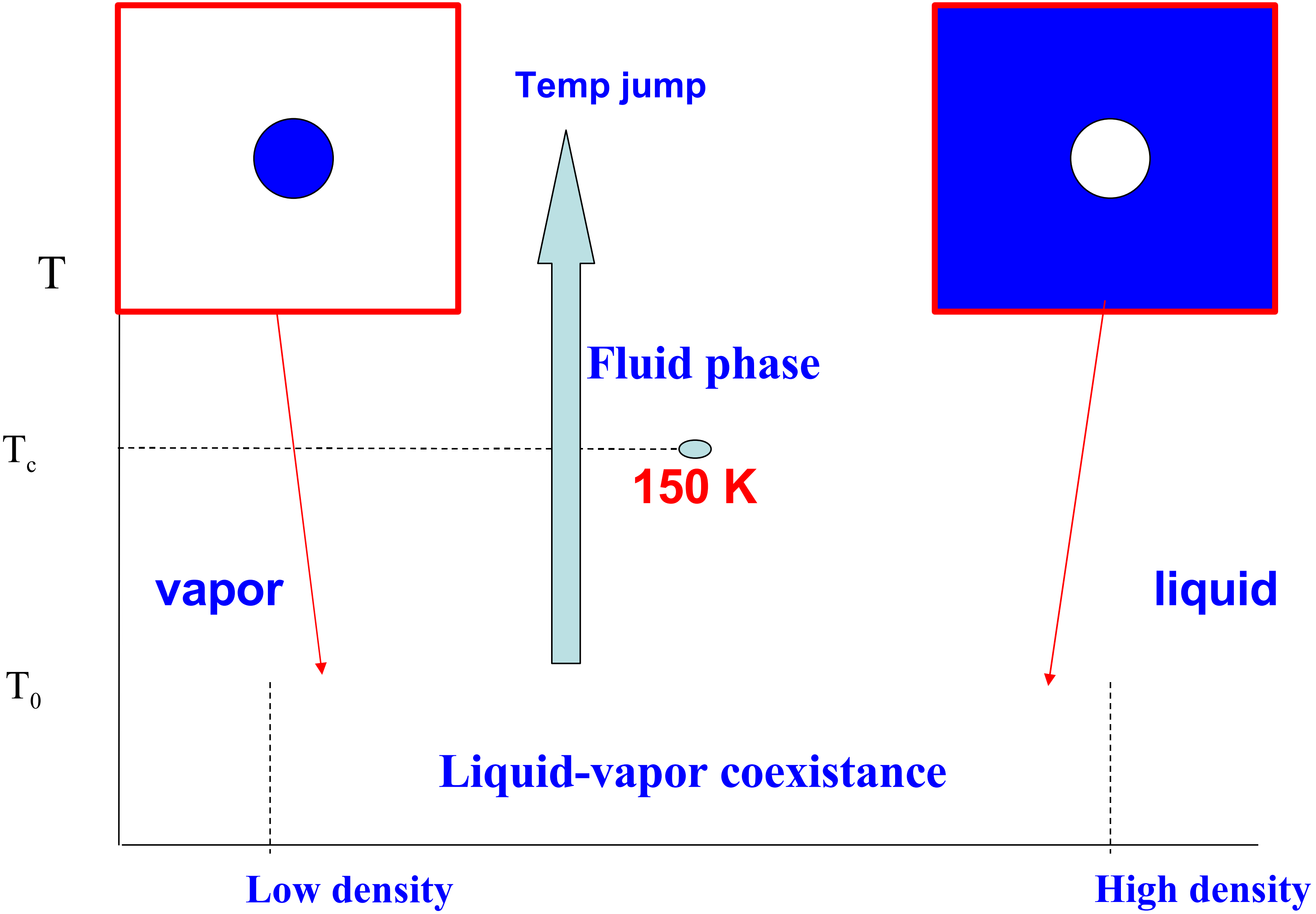
**He tried with
dry fingers and …….**

Thermodynamics is hot and cool

ARGON
Critical temperature 150.6 K
Time scale 3 picoseconds
Length scale 0.5 nanometer

In atomic simulations for argon the time scale is 10 femtoseconds and spatial scale is 0.1 nanometers or less.

Fixed volume and density



Temp jump

T

Fluid phase

T_c

150 K

vapor

liquid

T_0

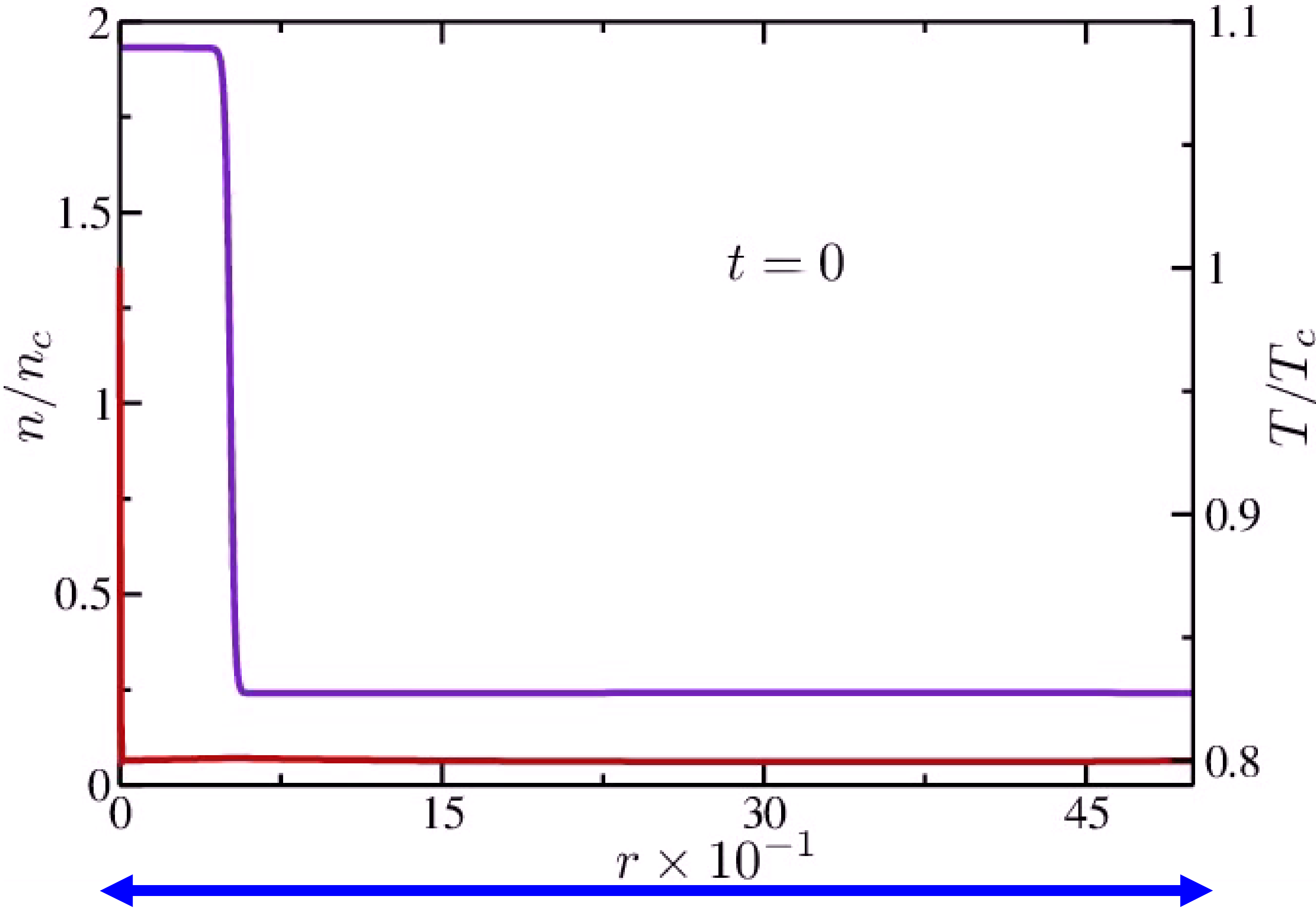
Liquid-vapor coexistance

Low density

High density

Method: Hydrodynamics + Irreversible thermodynamics in two phase region and van der Waals equation of state

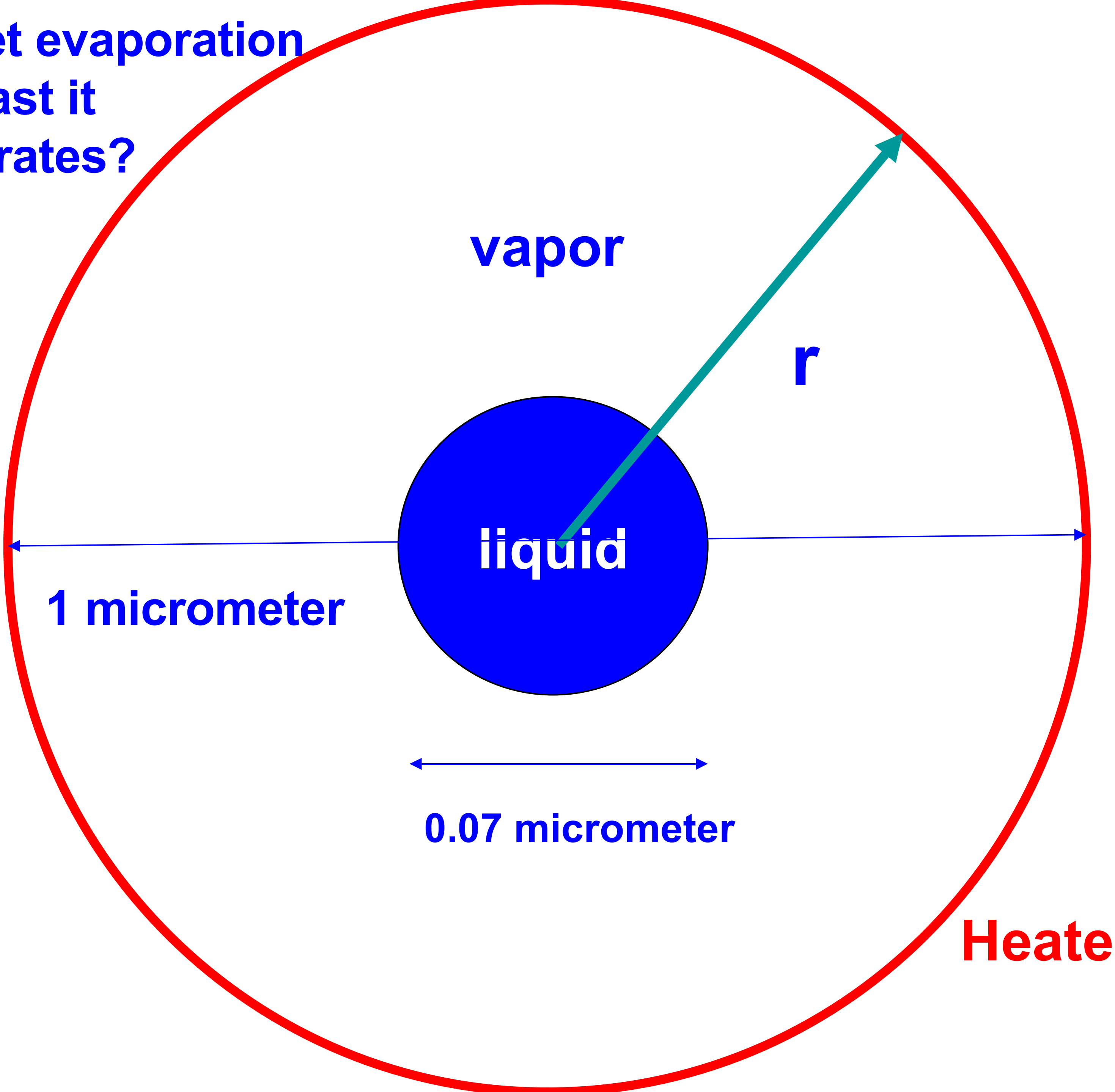
t=1 is 3 picoseconds
r=1 is 0.5 nanometer



0.25 micrometer

Temperature jump 30 K

Droplet evaporation
How fast it evaporates?



vapor

r

liquid

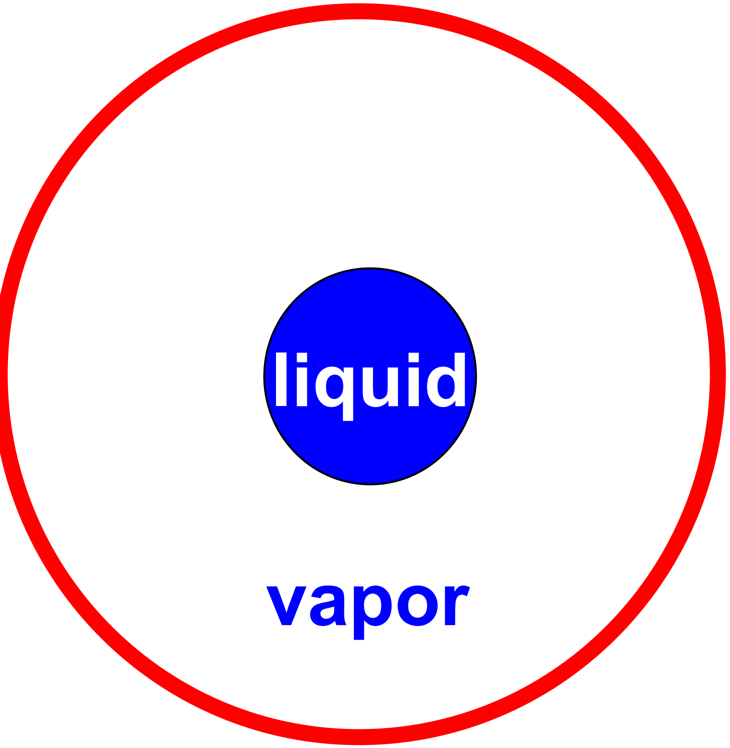
1 micrometer

0.07 micrometer

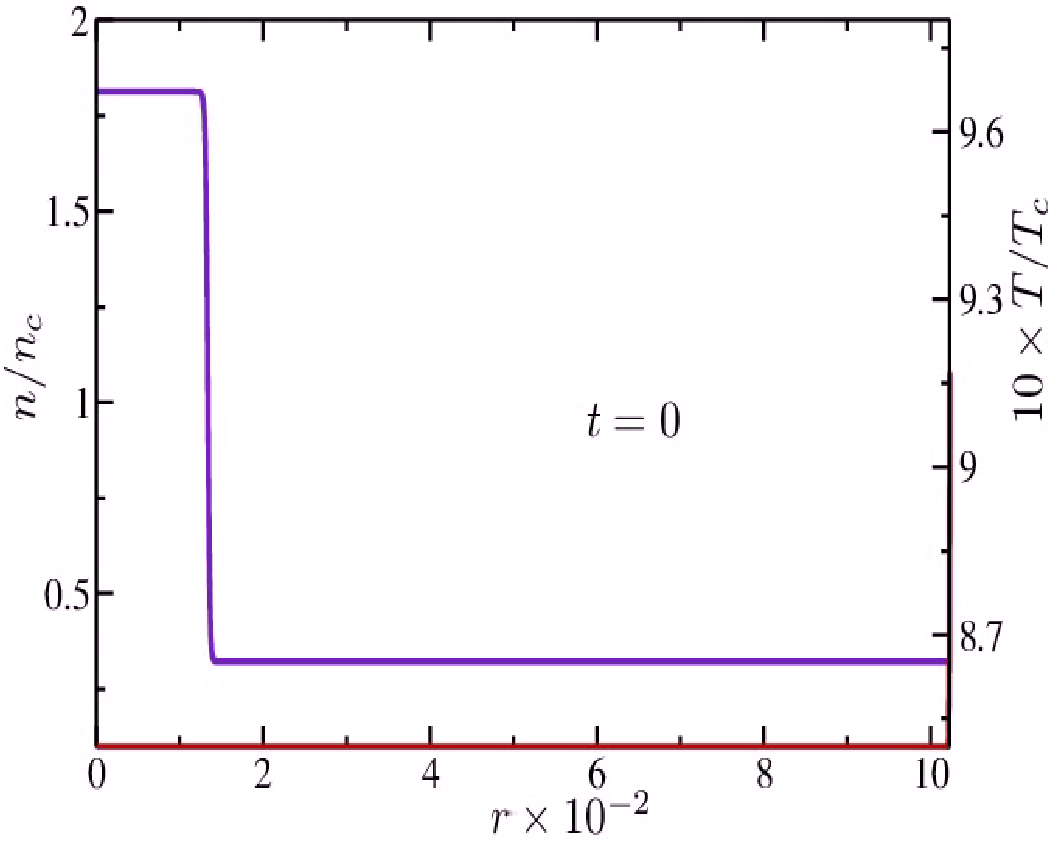
Heated walls

Ken Suslick

Evaporation – short times



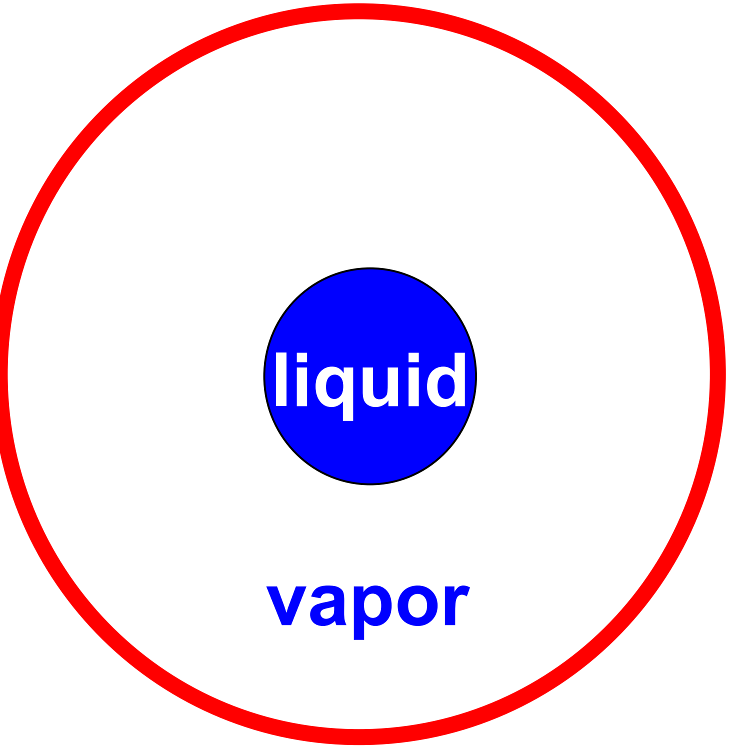
Waves heat up the droplet



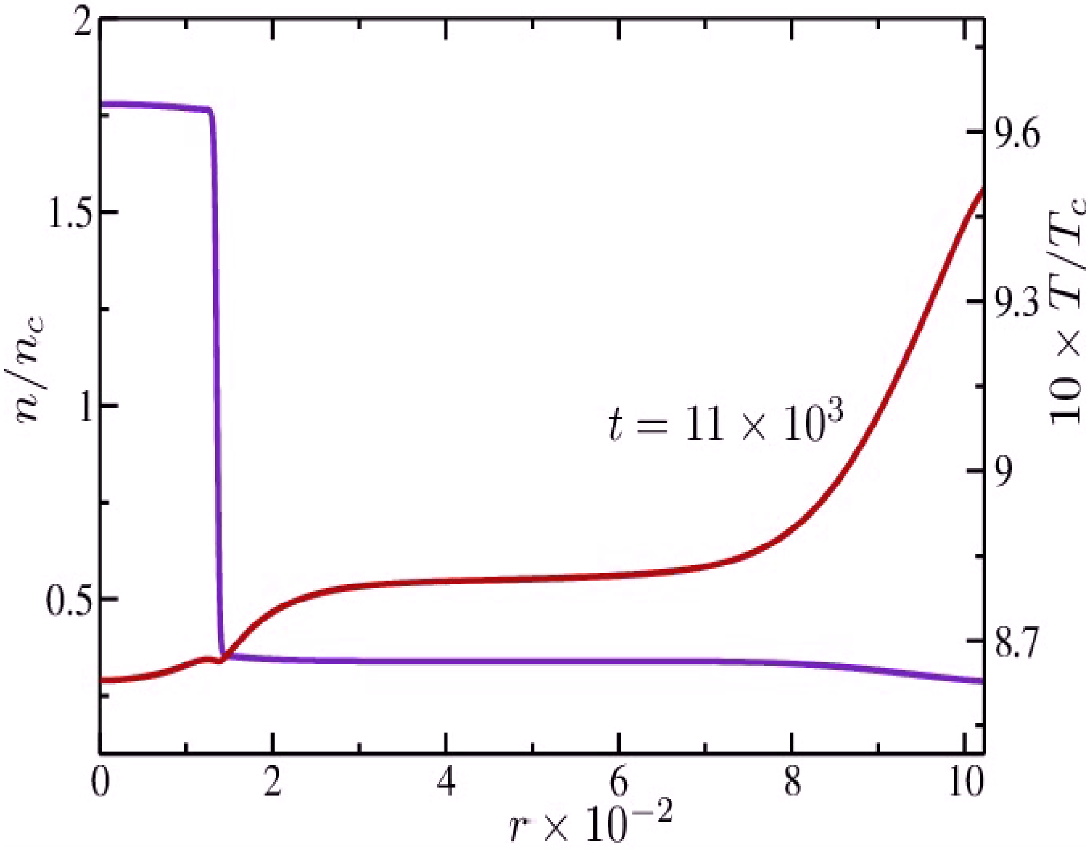
1 micrometer

time scale 3 ps
length scale 0.5 nm

Evaporation – long times (main stage)



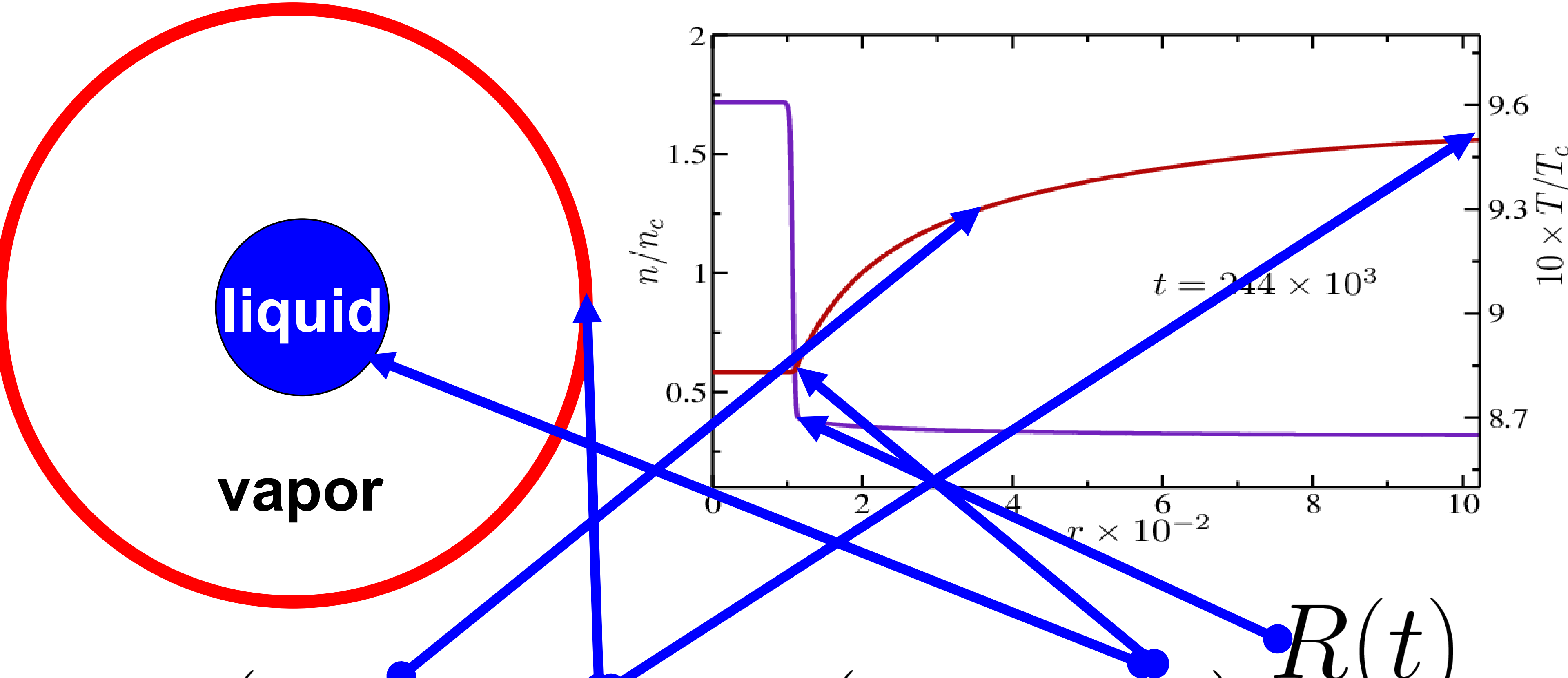
1 micrometer



time scale 3 ps

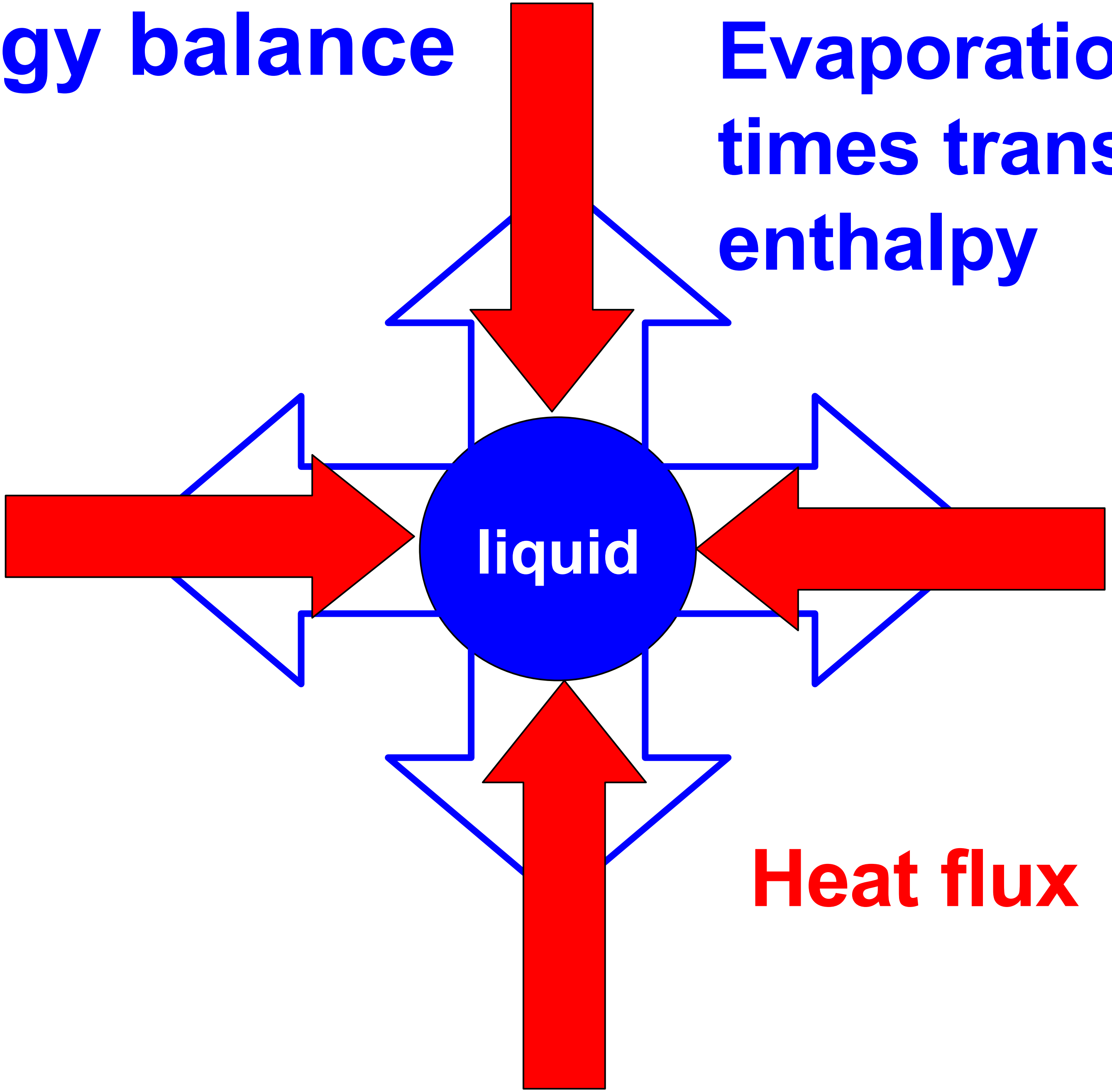
length scale 0.5 nm

Quasi-stationary temperature profile



$$T_v(r,t) = T_w - (T_w - T_l)\frac{R(t)}{r}$$

Energy balance



Evaporation flux times transition enthalpy

Heat flux

$$\begin{aligned} H &= n_l \left[u_l - \partial_t R(t) \right] \\ &= n_v \left[u_v - \partial_t R(t) \right] \approx -n_l \partial_t R(t) \end{aligned}$$

Particle flux

Energy balance

$$\ell H = \kappa \partial_r T_v(r,t)\big|_{r=R(t)}$$

temperature gradient at the interface

Latent heat

Heat conductivity

Radius R versus time t

Wall temperature

Single fitting parameter

$$R^2(t) = R^2\Big|_{t=0} - t\frac{2\kappa_v}{\ell n_l}(T_w - T_l)$$

Liquid temperature

We use NIST data base to get the numbers

Heat conductivity
of vapor at
the interface

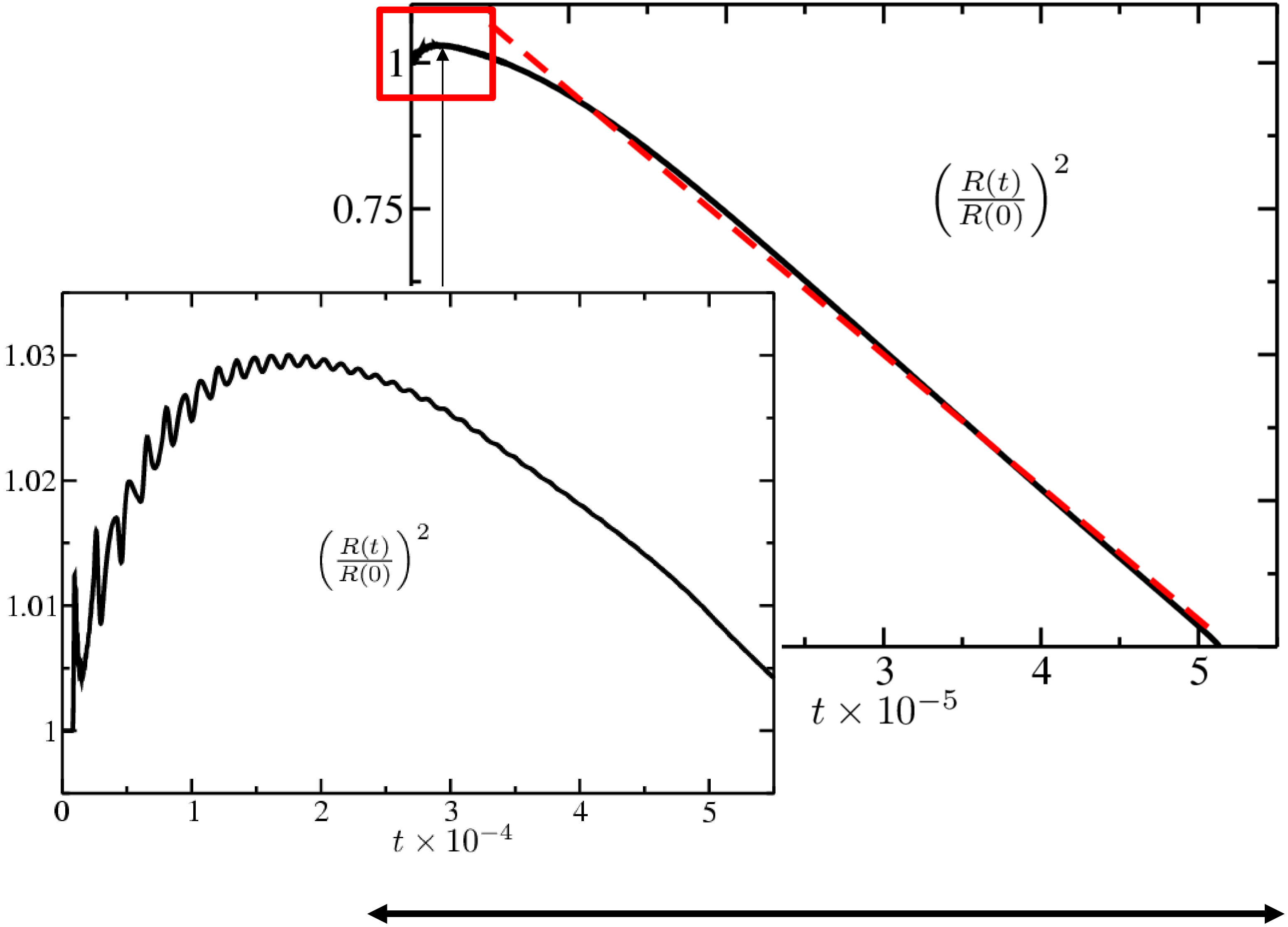
radius

Initial radius

Latent heat per mole

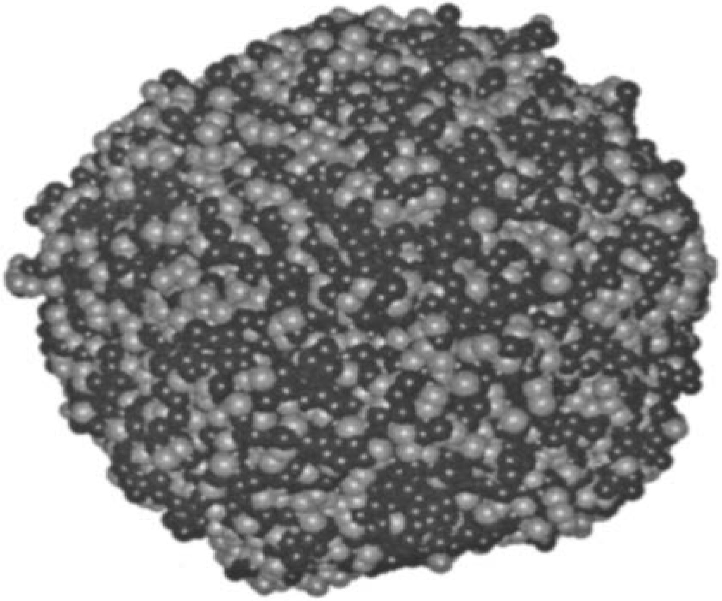
Liquid density

R(t=0)=66.8 nm

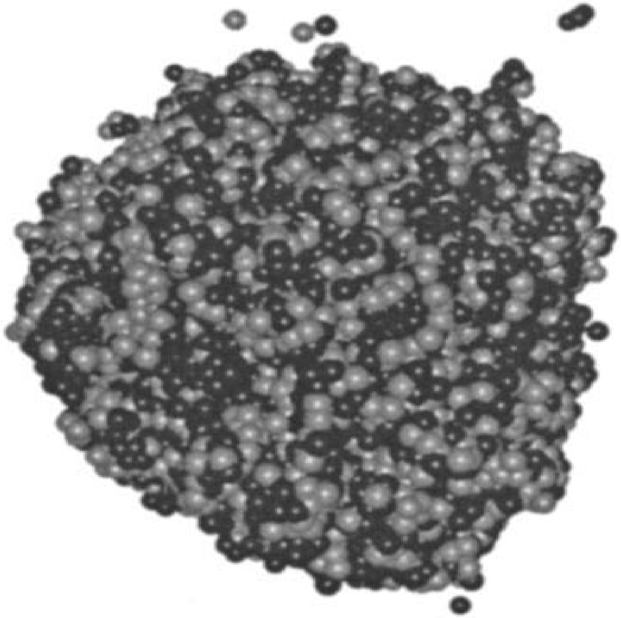


1.5 microseconds

Evaporation in a nanoscale

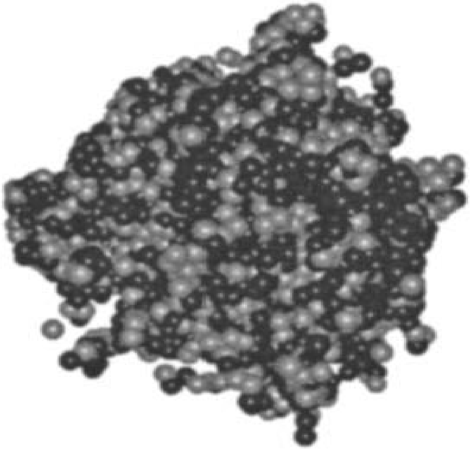


200 ps



800 ps

1800 ps



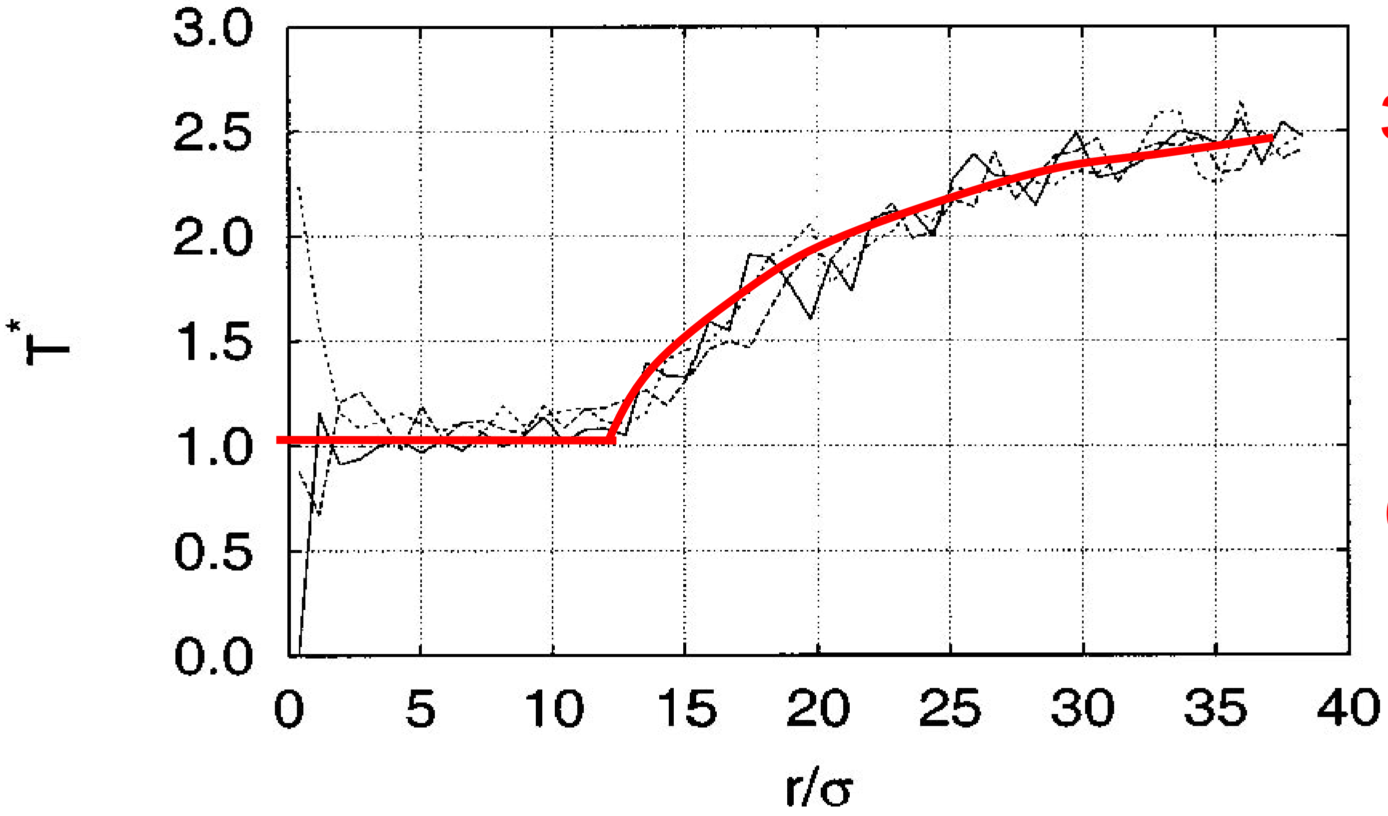
1400 ps

50000 argon atoms

100K → 300K

Walther, Kousmatos, 2001

The same temperature profile in a nanoscale as in the microscale

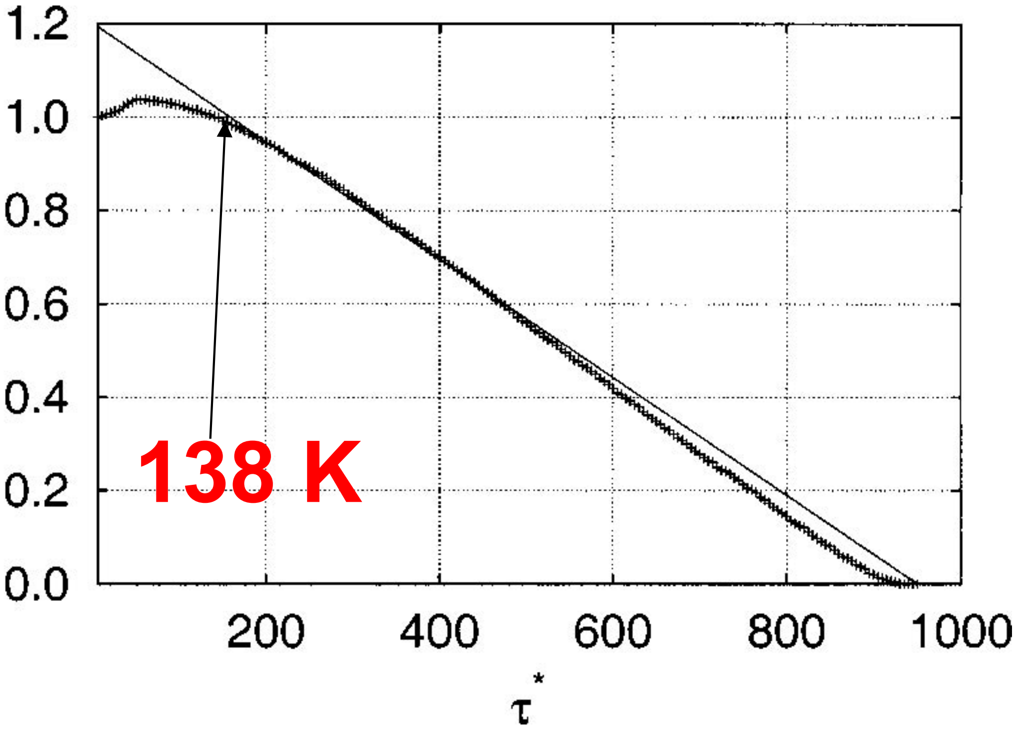


300 K

138 K
(100 K)

Walther, Kousmatos, 2001

100 K → 300 K



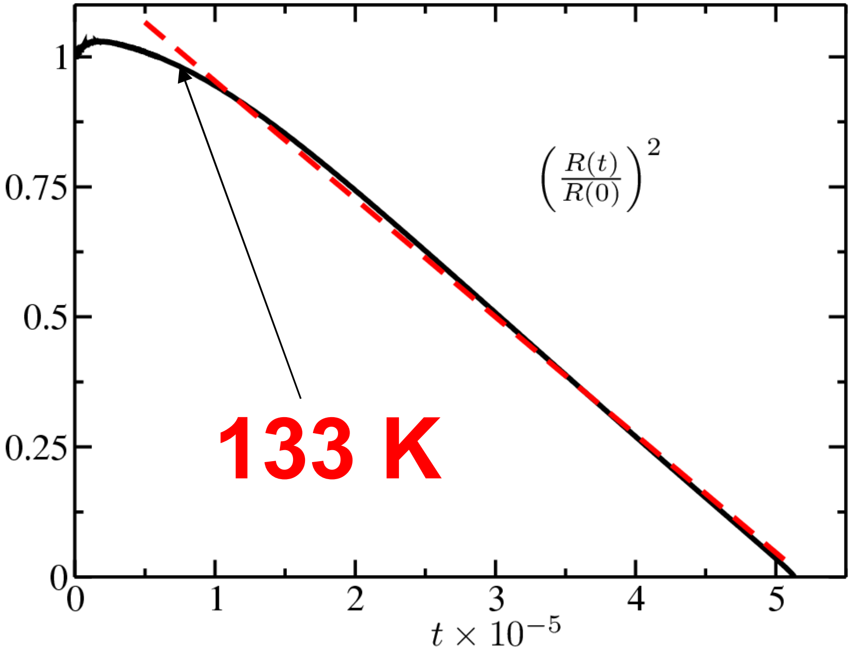
138 K

1.8 ns

R(0)=8.8 nm

L=52 nm

128 K → 143 K



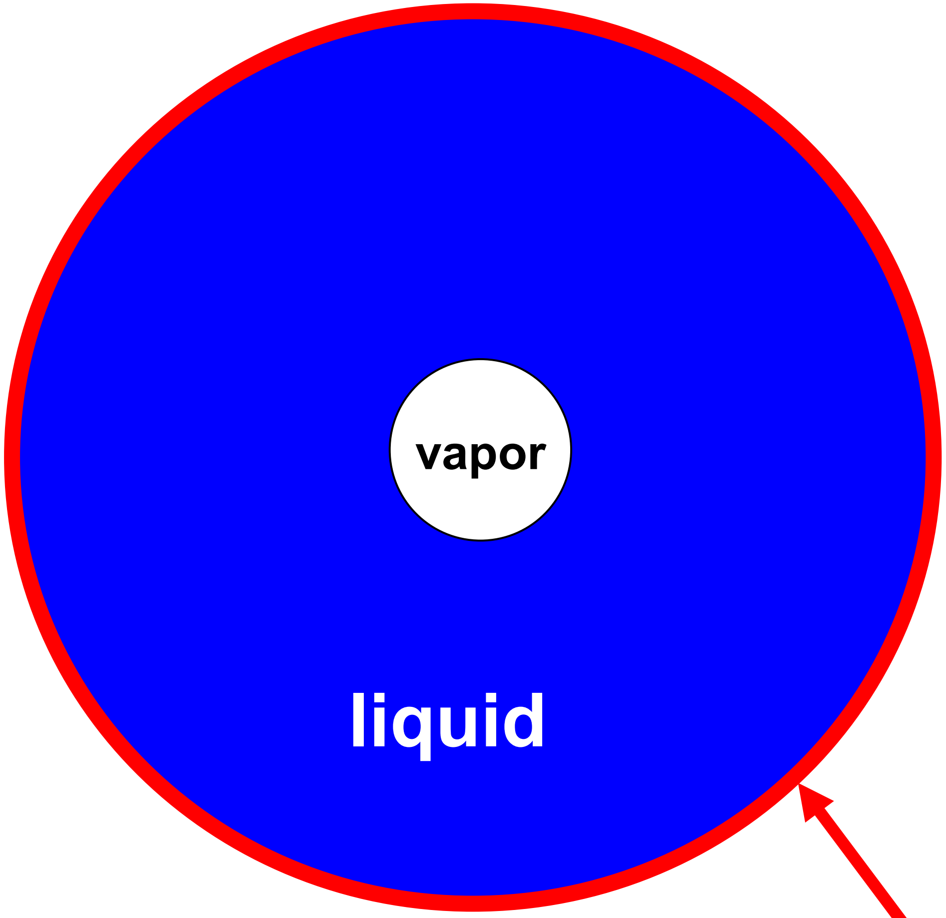
133 K

1 500 ns

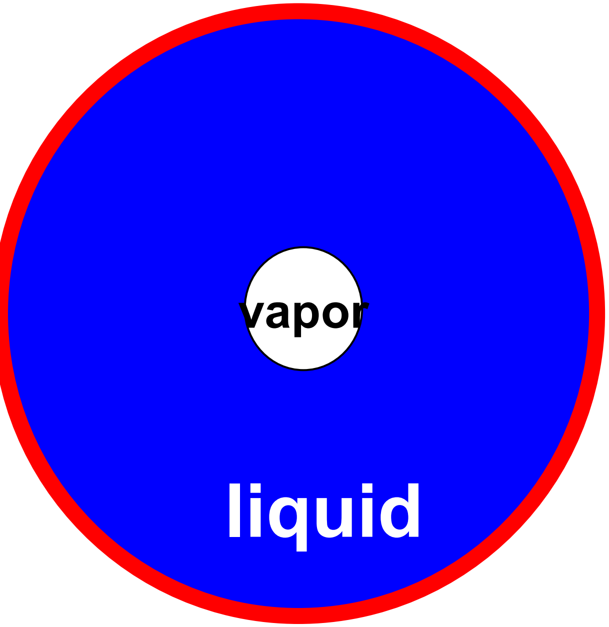
R(0)=66.8 nm

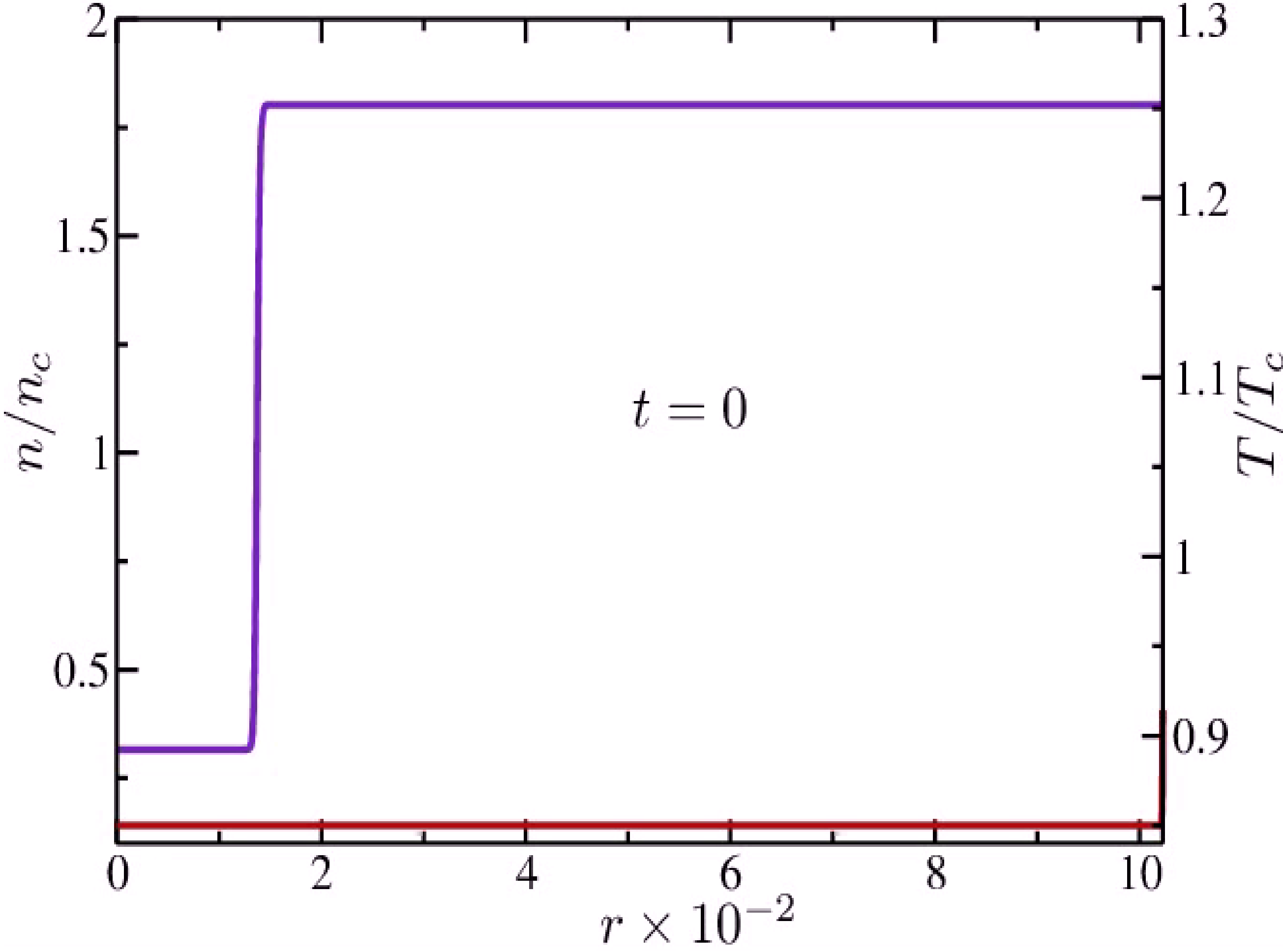
L=1000 nm

Condensation in a microscale



Heated walls



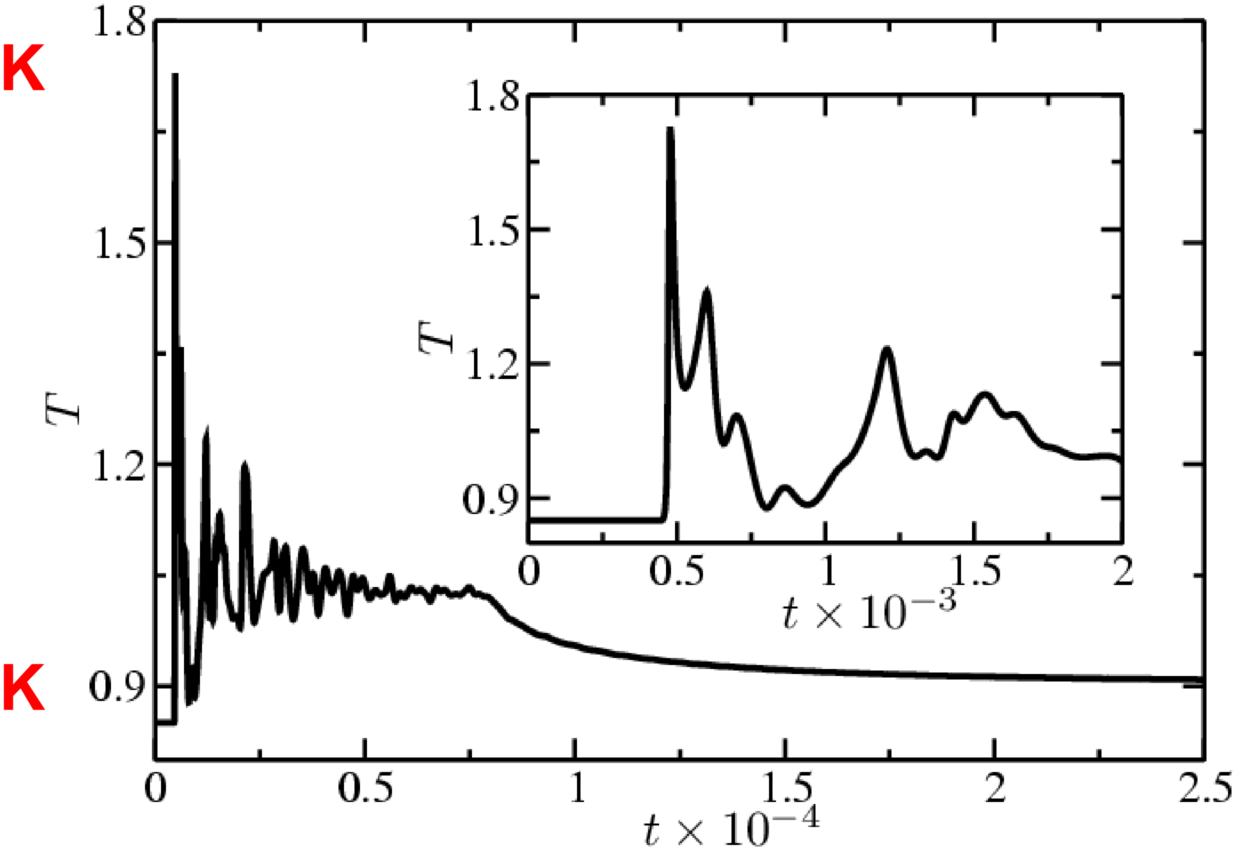


Condensation is complete in 30 ns

Two orders of magnitude faster than evaporation

It is never quasi-stationary.

Evolution of temperature in time in a middle of a bubble

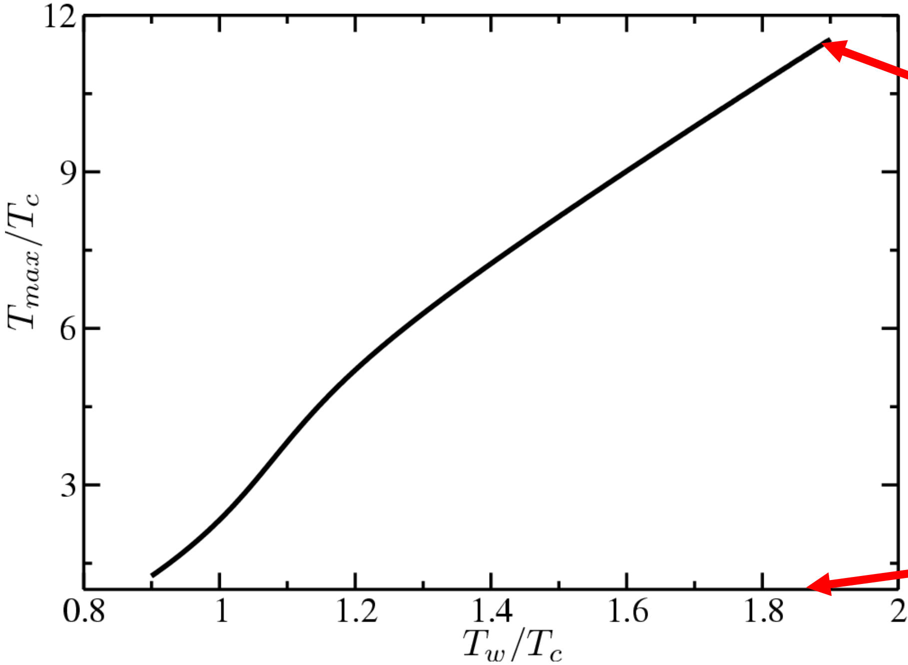


270 K

138 K

time

Maximal temperature inside a vapor bubble



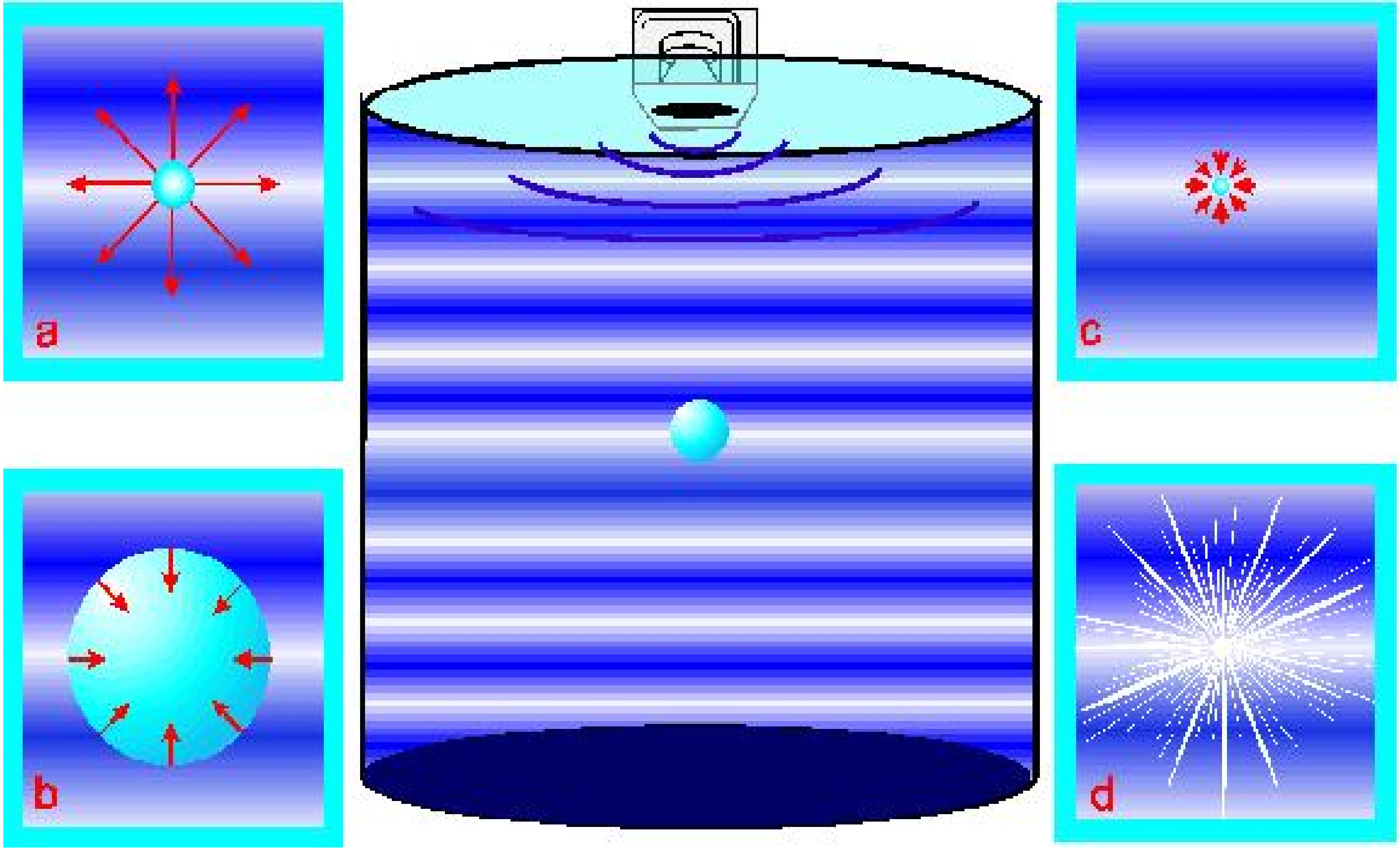
1800 K

280 K

Wall temperature

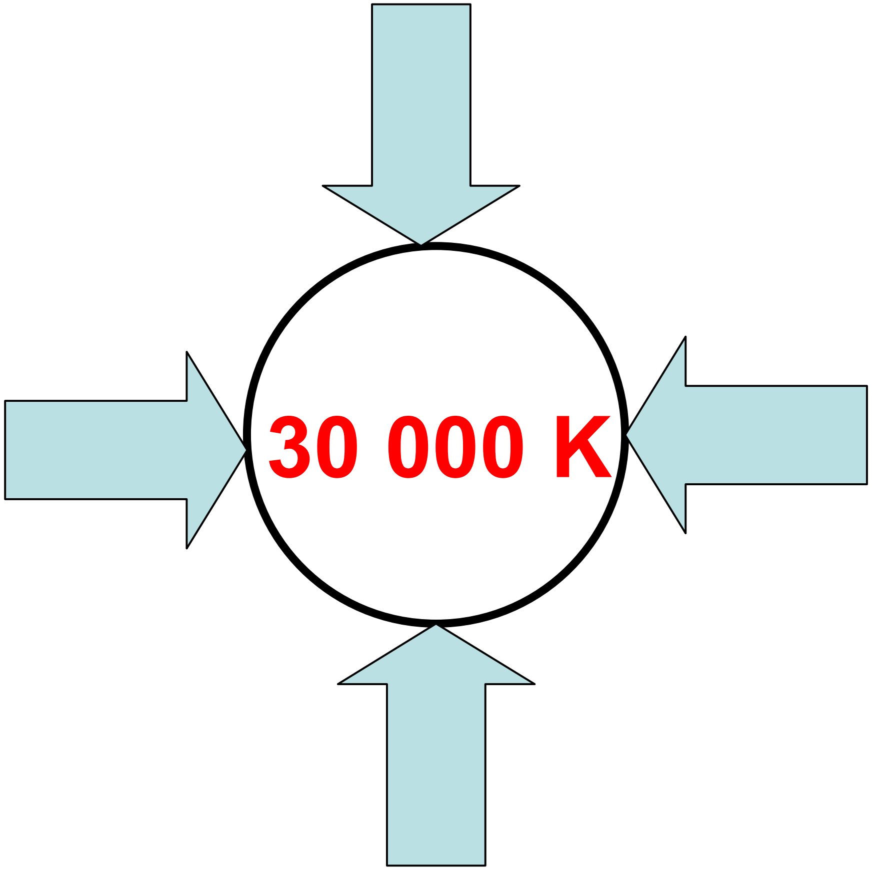
Focusing of wave energy

sonoluminescence



@nature

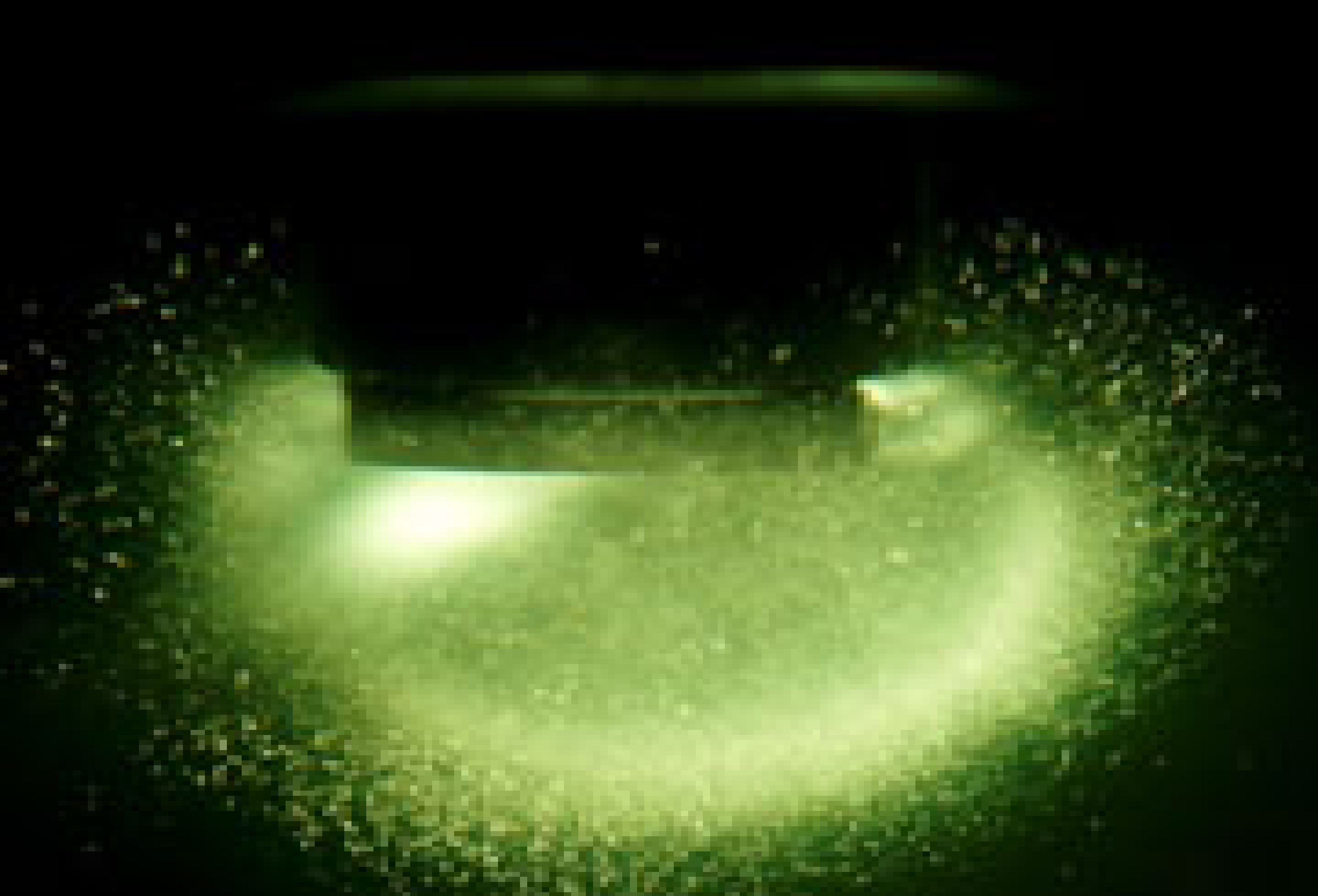
Sonoluminescence and sonochemistry



30 000 K

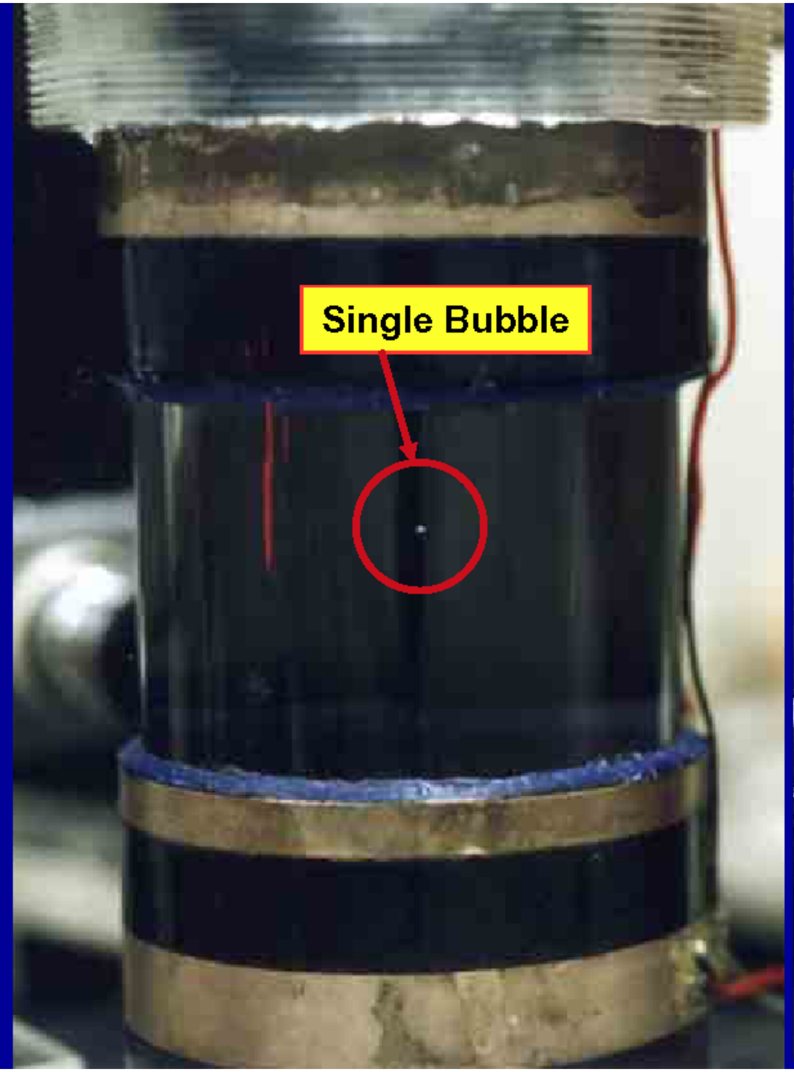
Focusing wave energy

Focused energy in a form of shock wave heats the bubble

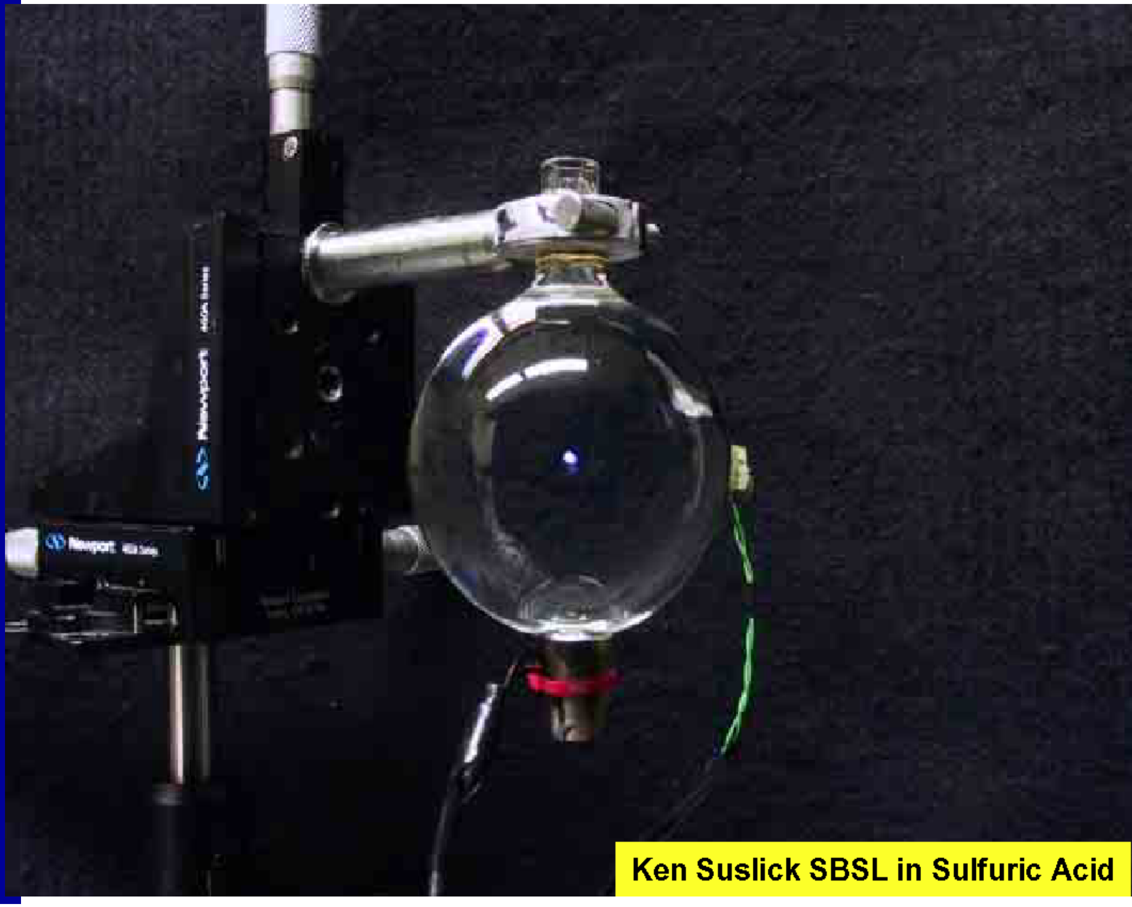


Most intense burst of light: U of Illinois, chemistry
Flannigan and Suslick

Star in a jar

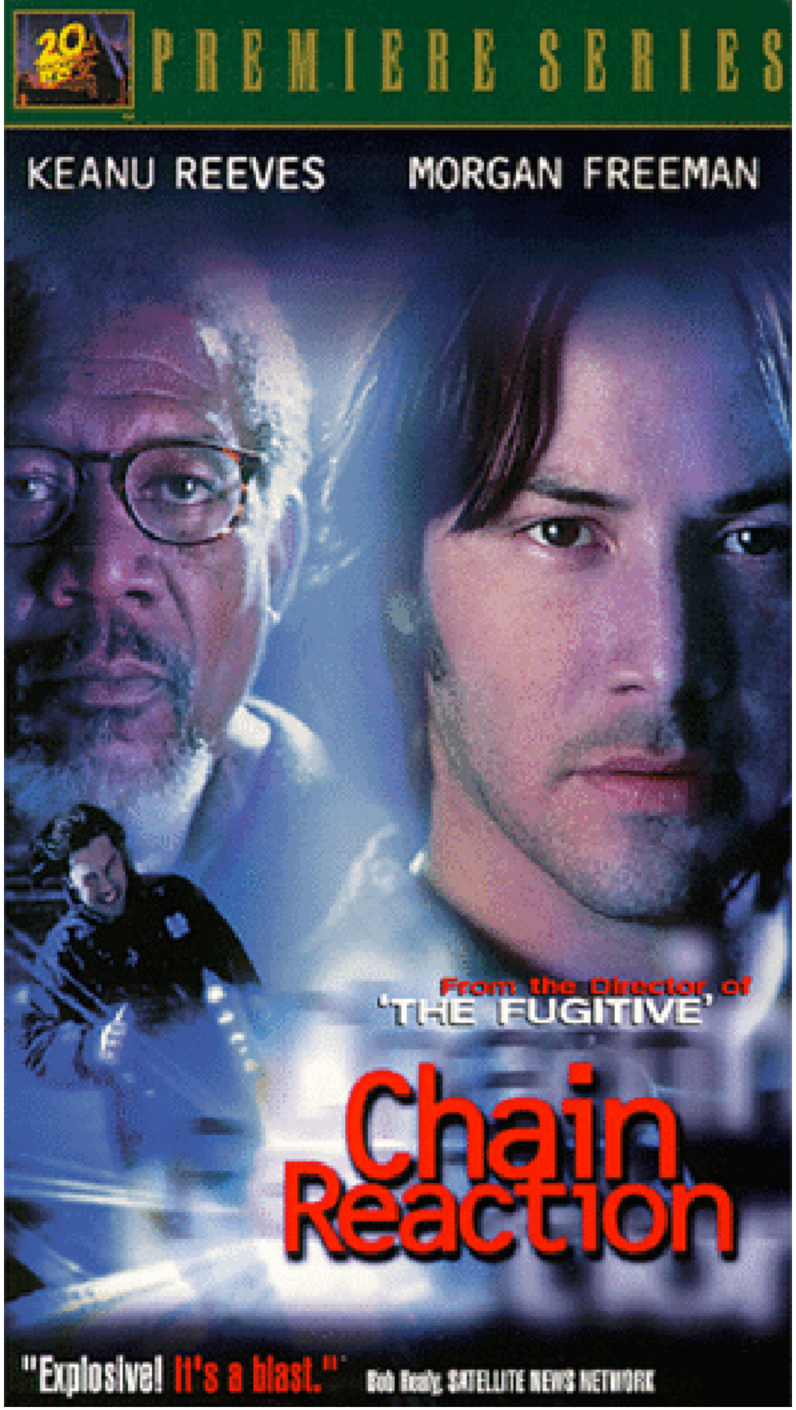


L.A.Crum



5 parts in 10^{11}

50 ps duration of light pulses, temp 30 000 K and synchronization of pulses lead to interesting physics and chemistry



Hollywood discovered sonoluminescence in 1996 more than 60 years after its discovery in science

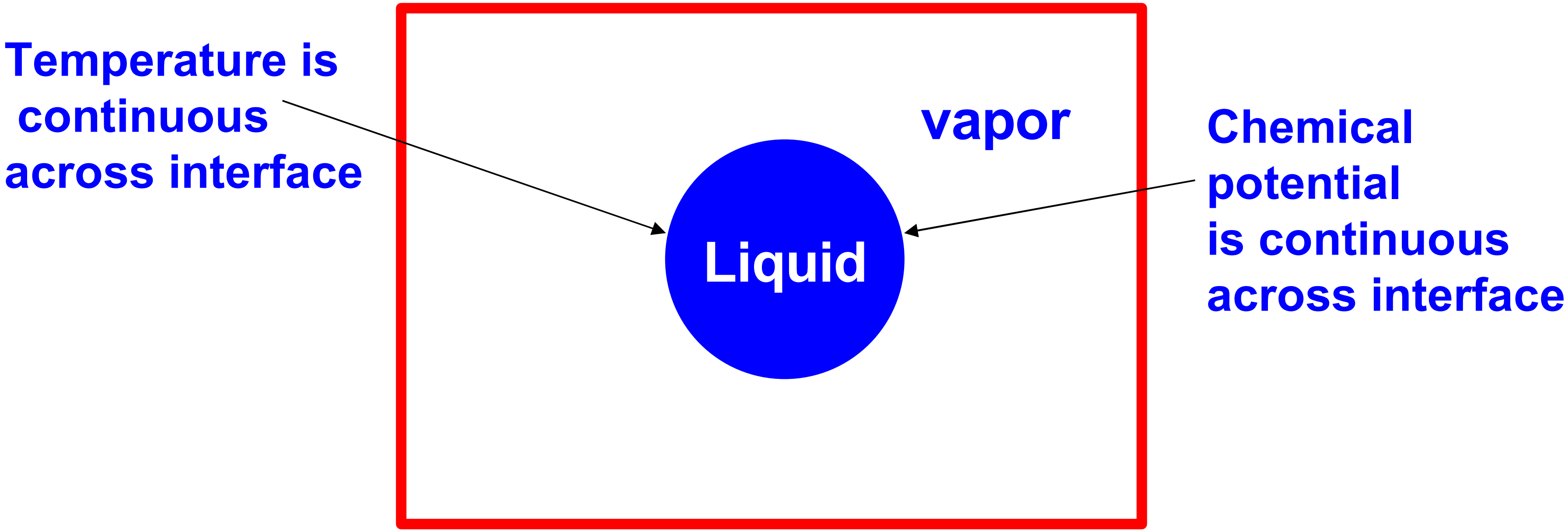
In 1933 Marinesco and Trillat and in 1934 Frenzel and Schultes observed darkening of a photographic plate by acoustic waves in a water bath

Star Trek and wormholes

Simple formula works in nano and microscale

$$R^2(t) = R^2\Big|_{t=0} - t\frac{2\kappa_v}{\ell n_l}(T_w - T_l)$$

Boundary conditions at the interface



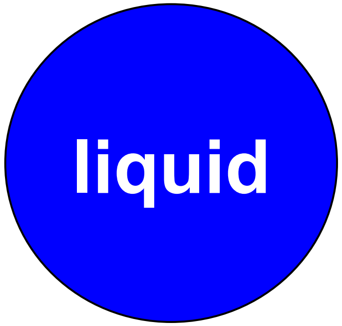
Temperature is continuous across interface

Chemical potential is continuous across interface

Condensation of bubbles can be used as a high-temperature, fast chemical microreactor at ambient temperature

But energy balance applies once again

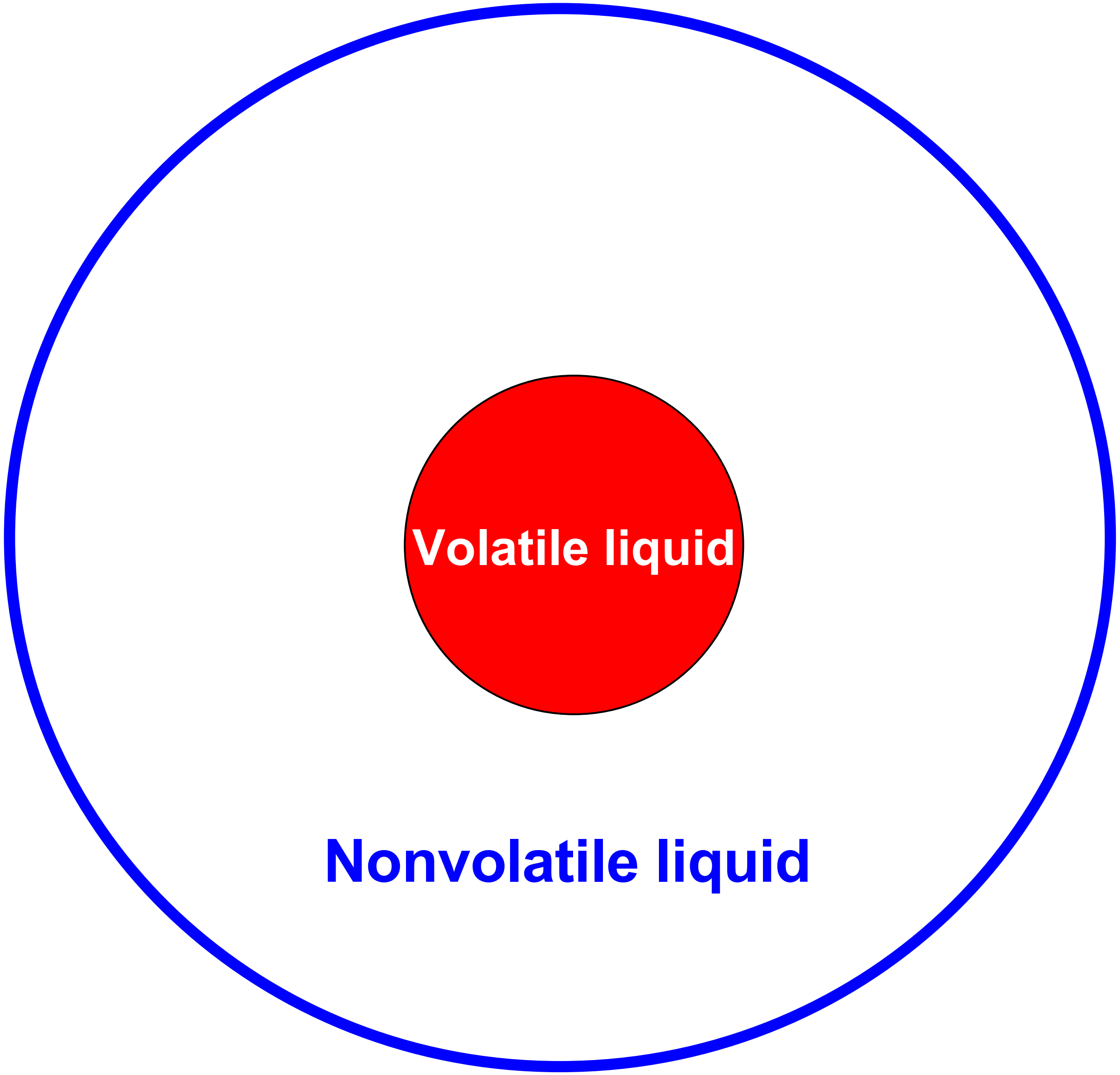
Vacuum



Latent heat/heat capacity=few hundreds K

In the process of evaporation the liquid droplet will freeze

Suppressing boiling

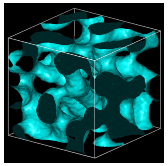


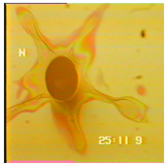
Volatile liquid

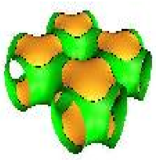
Nonvolatile liquid

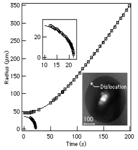

E.Kornienko

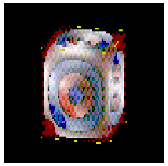
www.ichf.edu.pl/Dep3.html

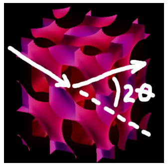


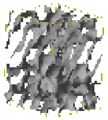


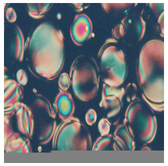


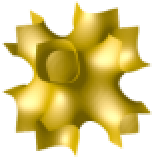












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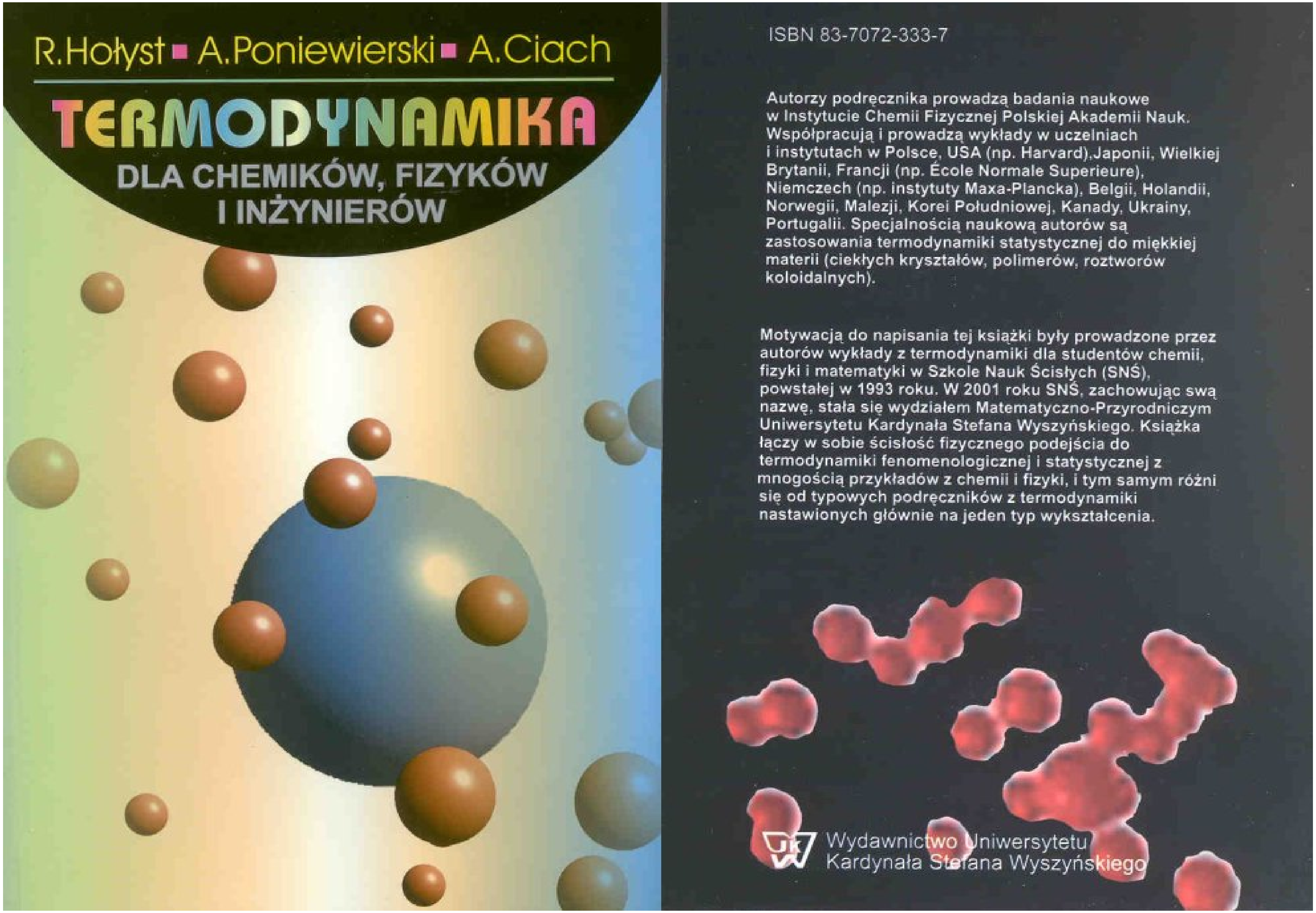


R.Hołyst ▪ A.Poniewierski ▪ A.Ciach

TERMODYNAMIKA

DLA CHEMIKÓW, FIZYKÓW
I INŻYNIERÓW

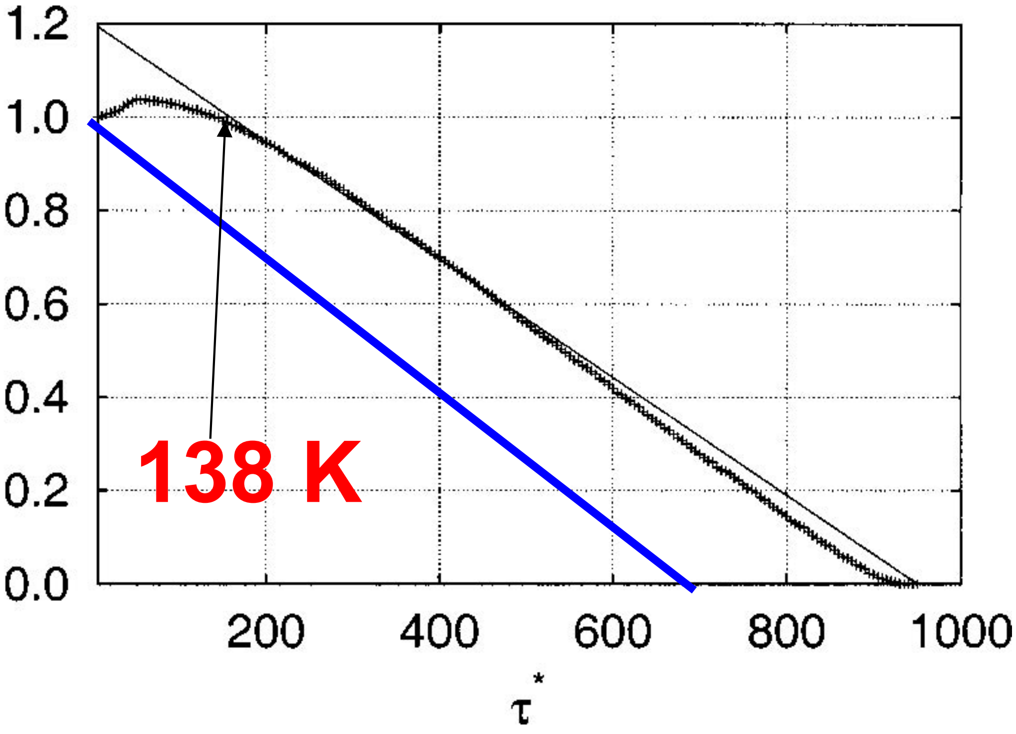
ISBN 83-7072-333-7

Autorzy podręcznika prowadzą badania naukowe w Instytucie Chemii Fizycznej Polskiej Akademii Nauk. Współpracują i prowadzą wykłady w uczelniach i instytutach w Polsce, USA (np. Harvard),Japonii, Wielkiej Brytanii, Francji (np. École Normale Superieure), Niemczech (np. instytuty Maxa-Plancka), Belgii, Holandii, Norwegii, Malezji, Korei Południowej, Kanady, Ukrainy, Portugalii. Specjalnością naukową autorów są zastosowania termodynamiki statystycznej do miękkiej materii (ciekłych kryształów, polimerów, roztworów koloidalnych).

Motywacją do napisania tej książki były prowadzone przez autorów wykłady z termodynamiki dla studentów chemii, fizyki i matematyki w Szkole Nauk Ścisłych (SNŚ), powstałej w 1993 roku. W 2001 roku SNŚ, zachowując swą nazwę, stała się wydziałem Matematyczno-Przyrodniczym Uniwersytetu Kardynała Stefana Wyszyńskiego. Książka łączy w sobie ścisłość fizycznego podejścia do termodynamiki fenomenologicznej i statystycznej z mnogością przykładów z chemii i fizyki, i tym samym różni się od typowych podręczników z termodynamiki nastawionych głównie na jeden typ wykształcenia.

Wydawnictwo Uniwersytetu
Kardynała Stefana Wyszyńskiego

100 K → 300 K

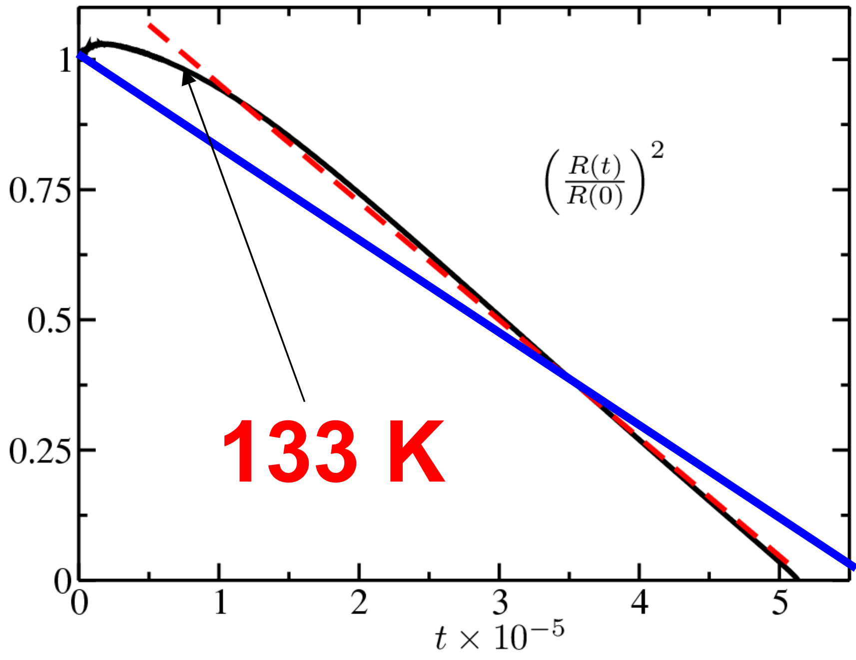


1.8 ns

R(0)=8.8 nm

L=14 nm

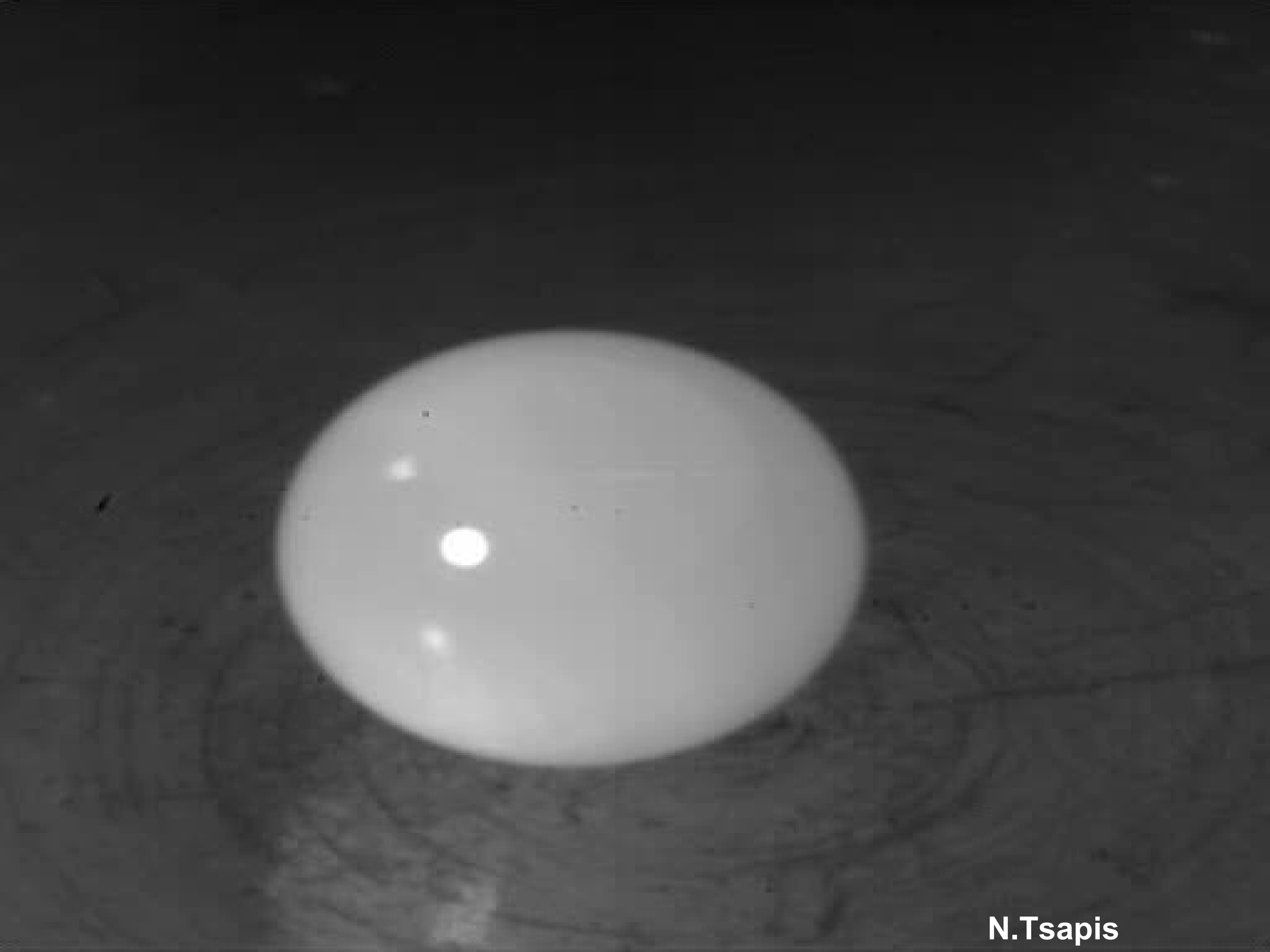
128 K → 143 K



1 500 ns

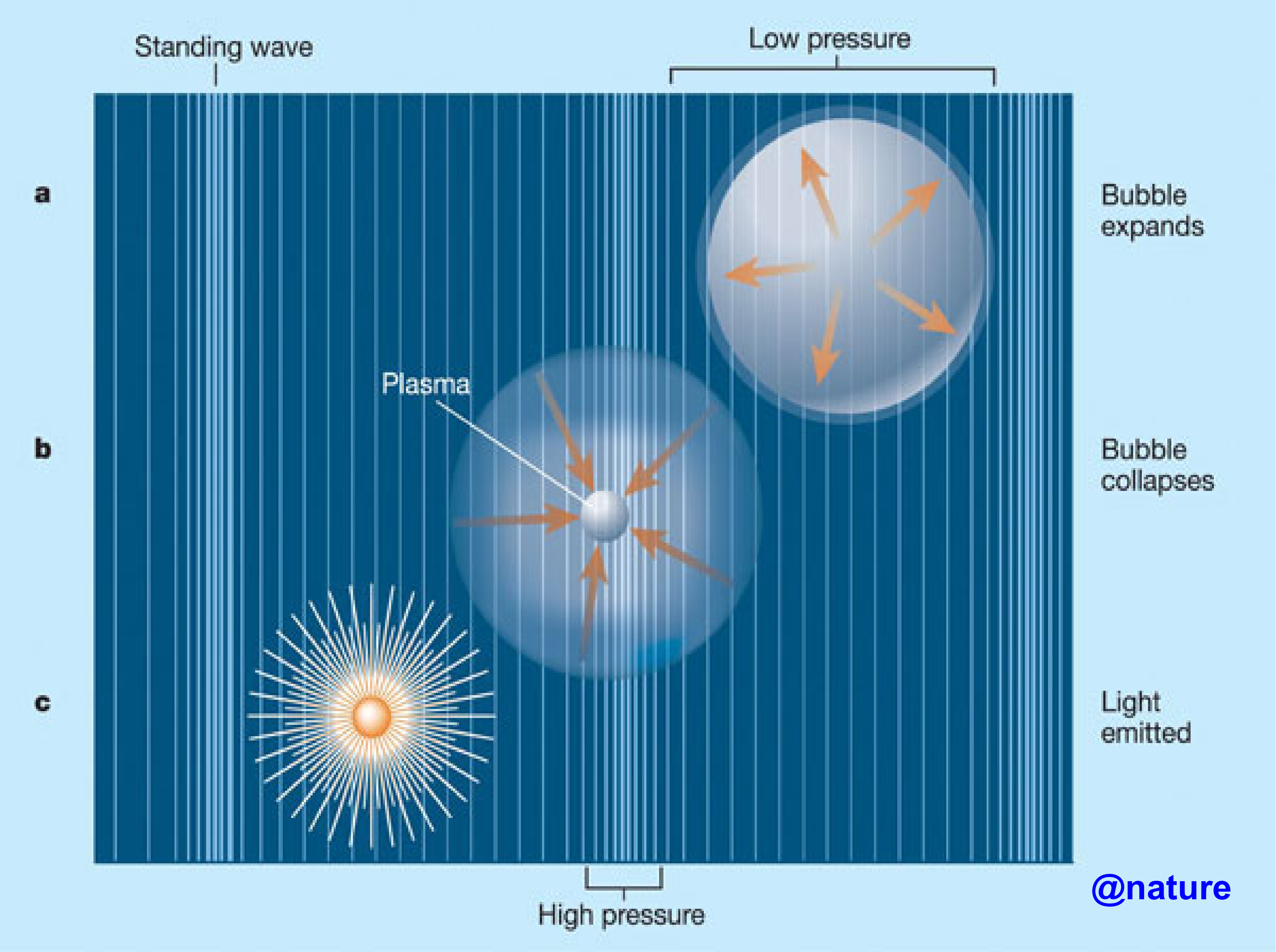
R(0)=66.8 nm

L=1000 nm



N.Tsapis

Compressing a vapor bubble



@nature

E.Kornienko

news bureau
UNIVERSITY OF ILLINOIS AT URBANA-CHAMPAIGN

Scientists measure energy dissipation in a single cavitating bubble

Flannigan and Suslick

$$R^2(t) = R^2\Big|_{t=0} - t\frac{2\kappa_v}{\ell n_l}(T_w - T_l)$$

Simple formula agrees within 30% with the results of the atomic simulations of argon in the nanoscale
and evaporation in a microscale

1.3 ns versus 1.8 ns
in nanoscale

1800 ns versus 1500 ns
in microscale

Irreversible thermodynamics:

2)Conservation of mass

3)Conservation of momentum

4)Conservation of energy

5)Van der Waals free energy(diffuse interface)

ARGON

Critical temperature 150.6 K

Time scale 3 picoseconds

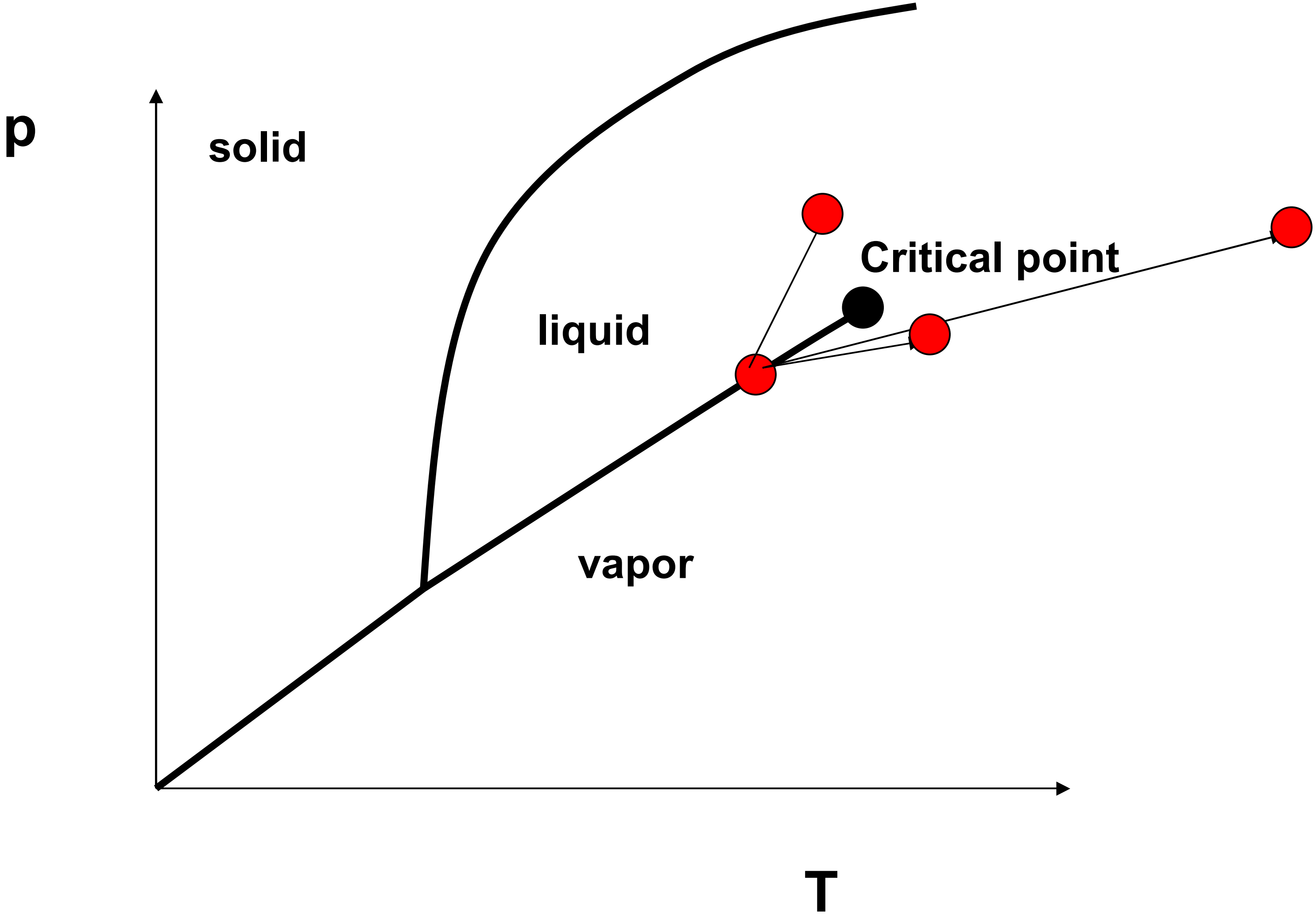
Length scale 0.5 nanometer

Constitutive equations:

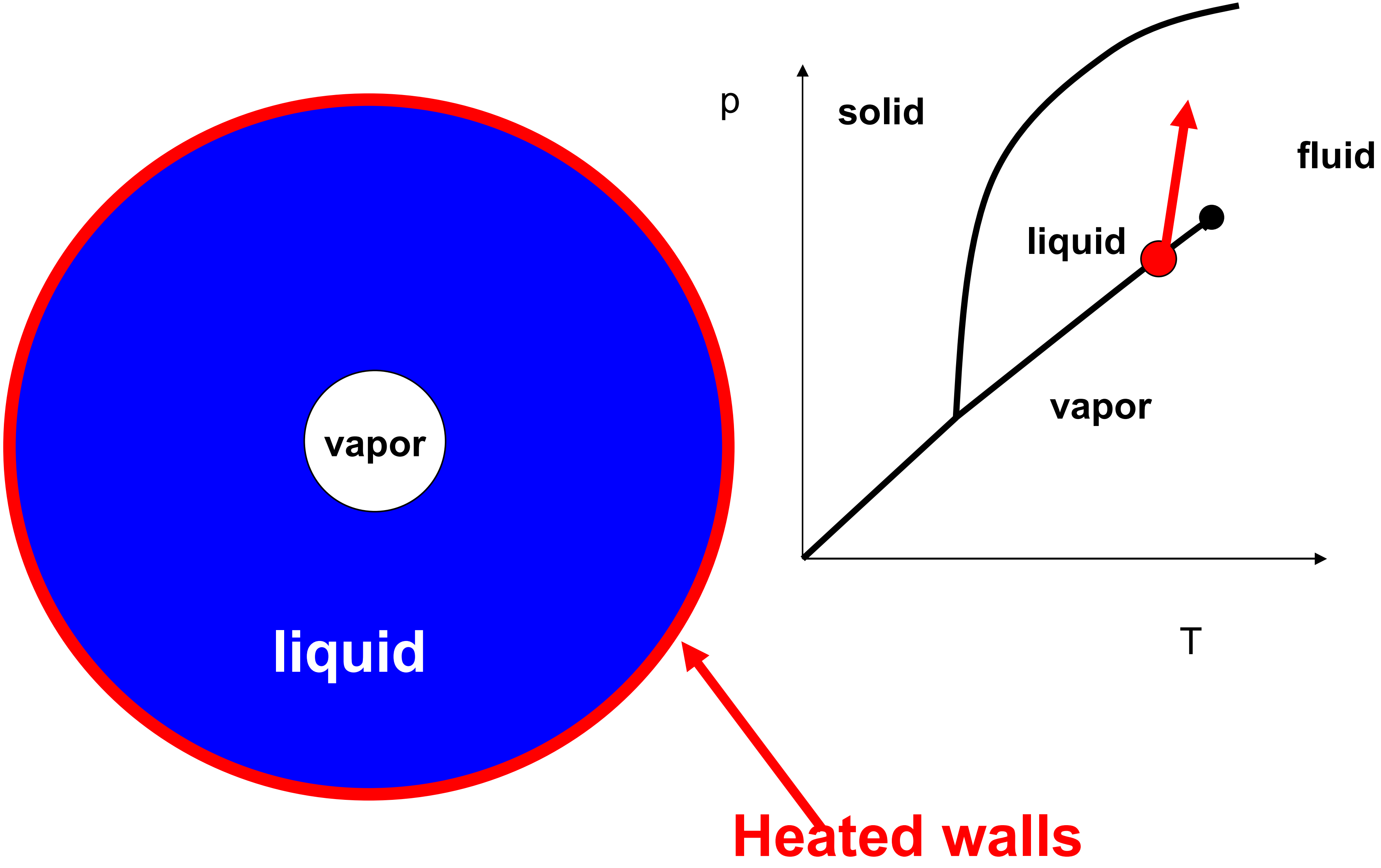
Heat flux, viscous stress tensor and capillary tensor,

Additionally we have to specify heat conductivity and viscosity (NIST web site)

In atomic simulations for argon the time scale is 10 femtoseconds and spatial scale is 0.1 nanometers or less.


p
solid
liquid
Critical point
vapor
T

Condensation in a microscale



Heated walls