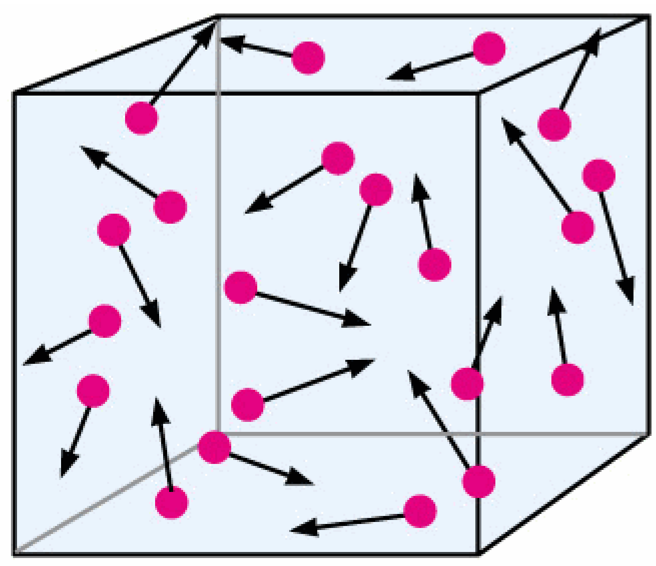
The impact of inelastic collisions on the mean free path in air

D.G. Tsalikis,[1] V.G. Mavrantzas[1,2] & S.E. Pratsinis[1]

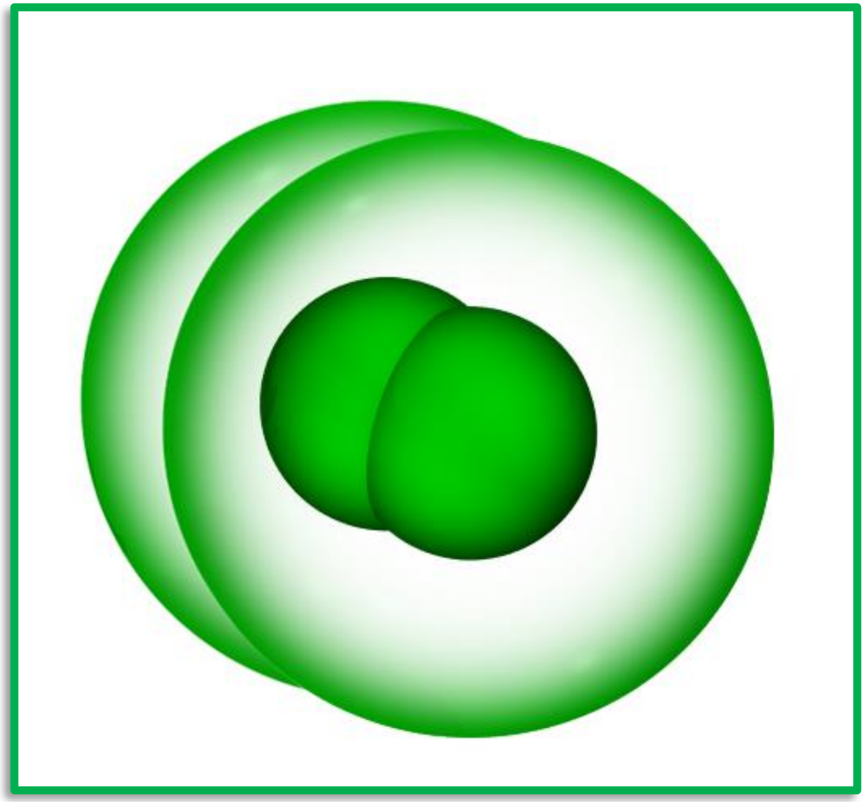
[1]Particle Technology Laboratory, ETH Zürich, Switzerland

[2]University of Patras & FORTH-ICE/HT, Greece

Kinetic Theory of Gases[1]: Perfect Spheres & Elastic Collisions



Air: Diatomic molecules (N_2, O_2) with finite force fields around them



Aerosol diffusion, coagulation etc. in the free-molecule regime & at the nanoscale

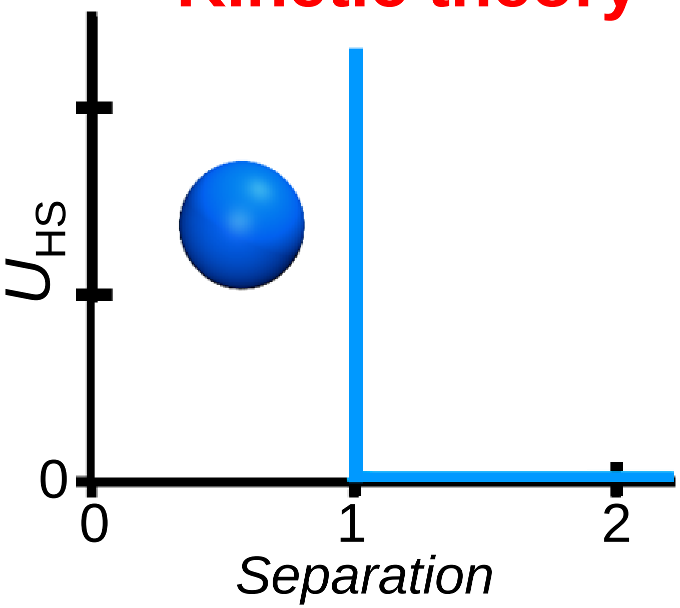
The goal:

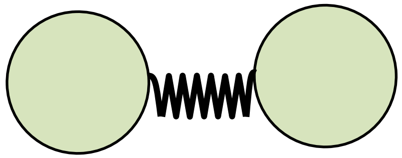
Determine the significance of these assumptions on the mean free path that defines the size regime of aerosol dynamics

1. J.C.M.A. Maxwell, *The London, Edinburgh, and Dublin Philos. Mag. and J. of Science* **19**, 19-32 (1860).

Simulation strategy for Molecular Dynamics:

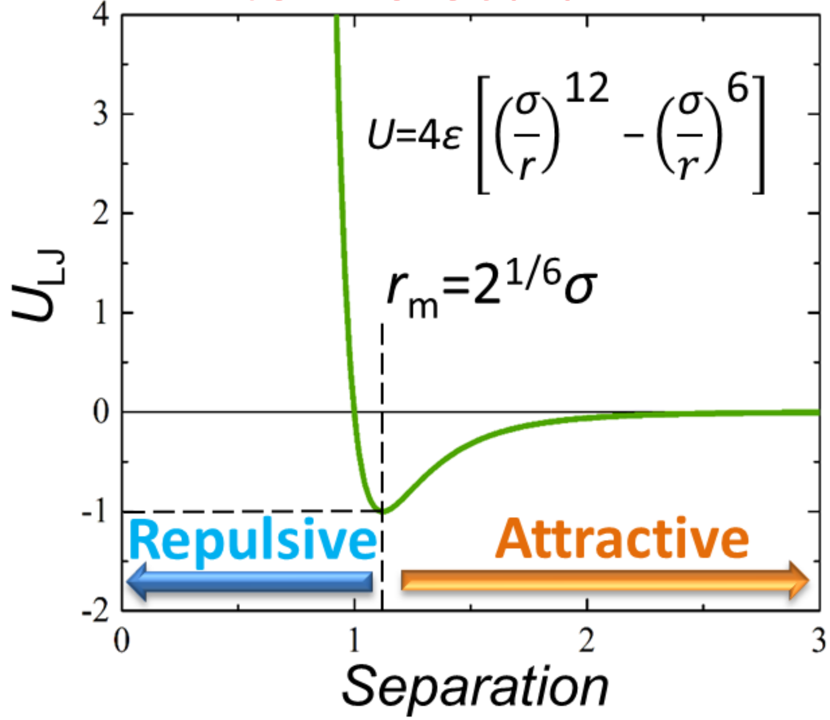
Kinetic theory[1]





Intramolecular

Intermolecular



- ✓ Fully Atomistic (FA) → Diatomic N_2/O_2 + inelastic collisions (Potential)

Additional simulations at reduced cases:

- ✓ The Hard-Sphere (HS) → spheres + elastic collisions (classic Kinetic Theory)
- ✓ Lennard-Jones (LJ) → spheres+ inelastic collisions (Potential)

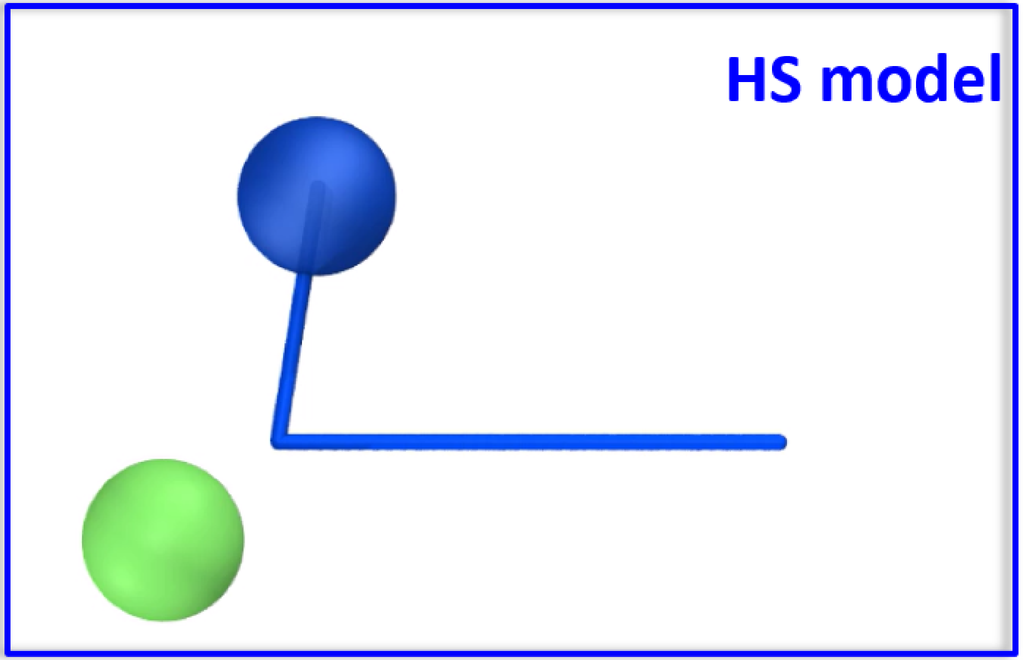
[1]. J.C.M.A. Maxwell, *The London, Edinburgh, and Dublin Philos. Mag. and J. of Science* **19**, 19-32 (1860).

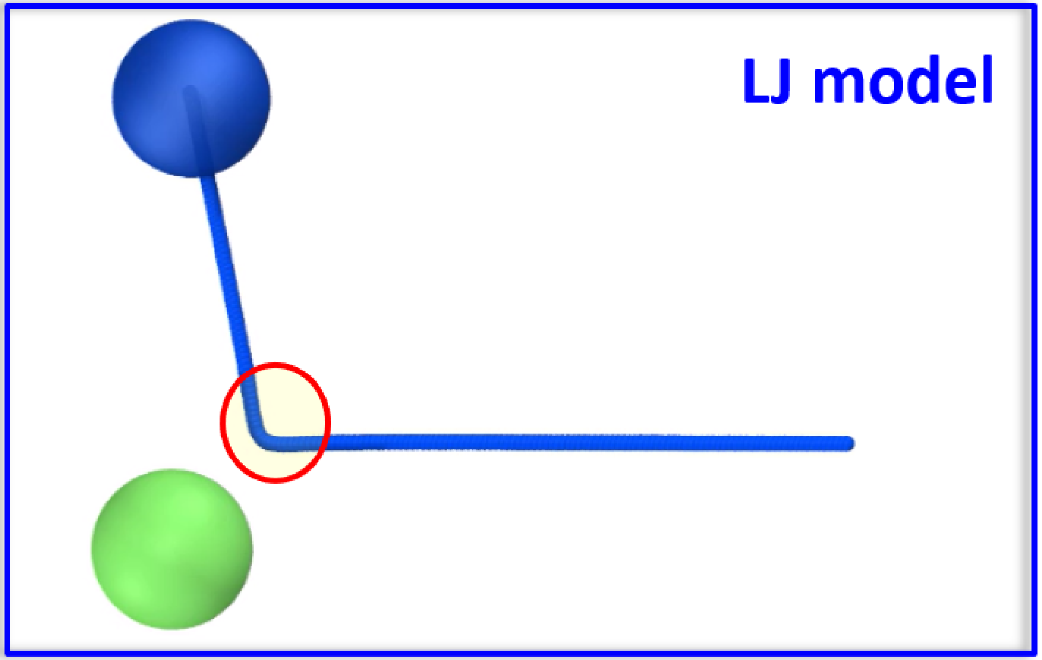
Rigorous validation

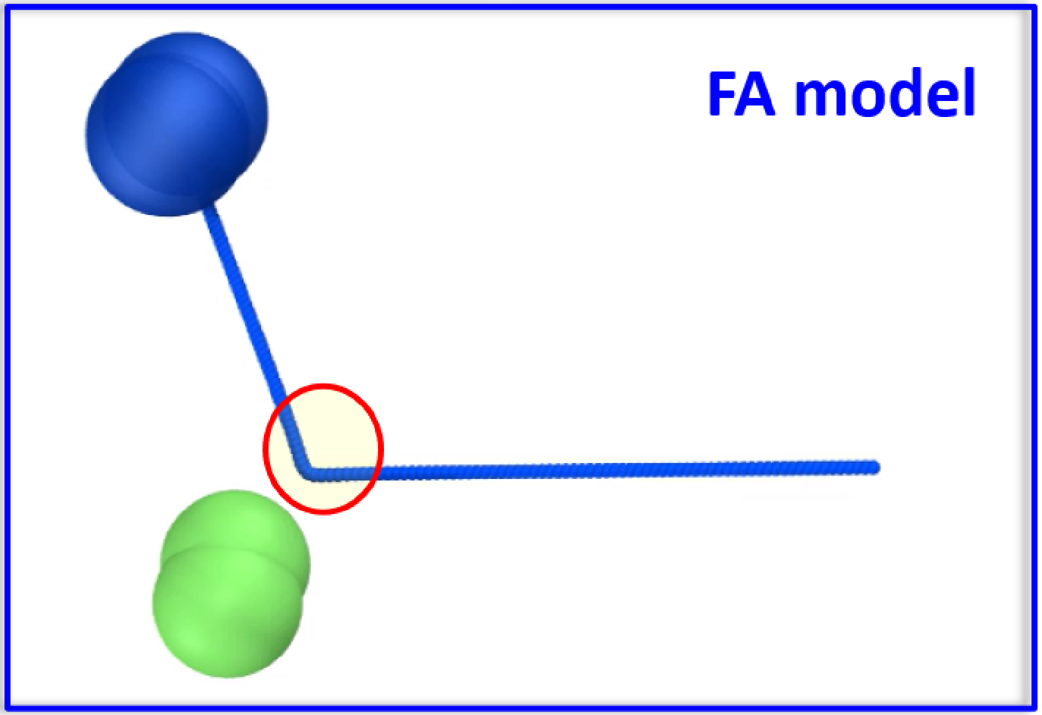
	Density[1] kg/m³	Diffusivity[2] cm²/s	Viscosity[3-5] µPas
Exp. data	1.177	0.203	18.5
KT	1.172	0.179	18.2
HS model	1.170 ± 0.01	0.185 ± 0.005	18.0 ± 0.5
LJ //	1.180 ± 0.01	0.200 ± 0.005	18.1 ± 0.5
FA //	1.180 ± 0.01	0.203 ± 0.005	18.1 ± 0.5

[1] Engineering ToolBox. Air - Density at varying pressure and constant temperatures (2004).
[2] J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, M.G. Mayer, *Molecular theory of gases and liquids* (Wiley New York, 1964).
[3] E.L. Cussler, *Diffusion: Mass Transfer in Fluid Systems* (Cambridge University Press, Cambridge, 2009).
[4] J. Kestin, W. Leidenfrost, Physica 25, 1033-1062 (1959).
[5] J. Kestin, J. Whitelaw, Int. J. Heat Mass Transfer 7, 1245-1255 (1964).

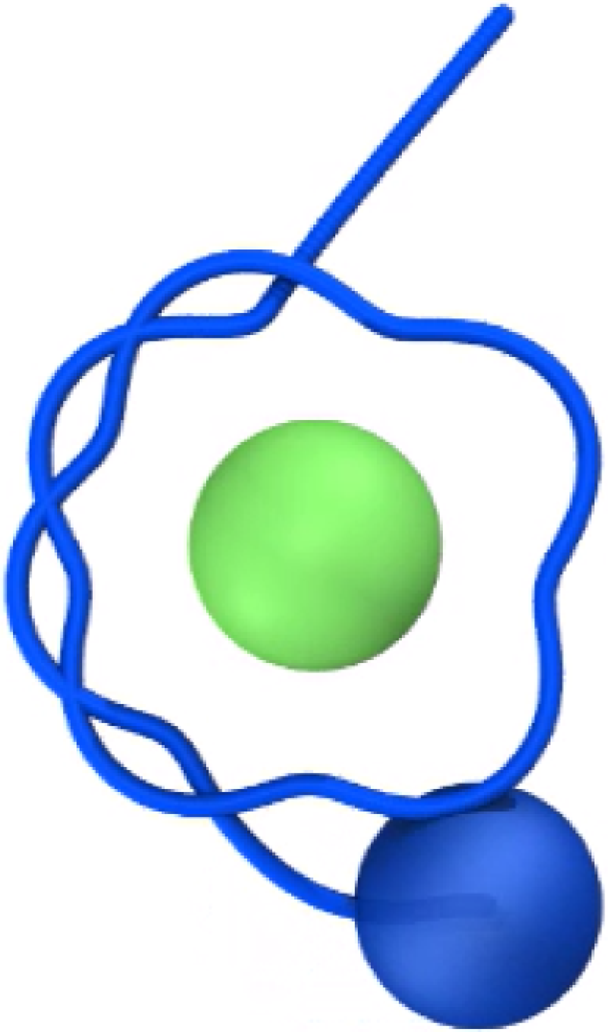
Mechanics of collisions







Accounting for force field & shape → to spurious collisions
Case 1: Lennard - Jones molecules

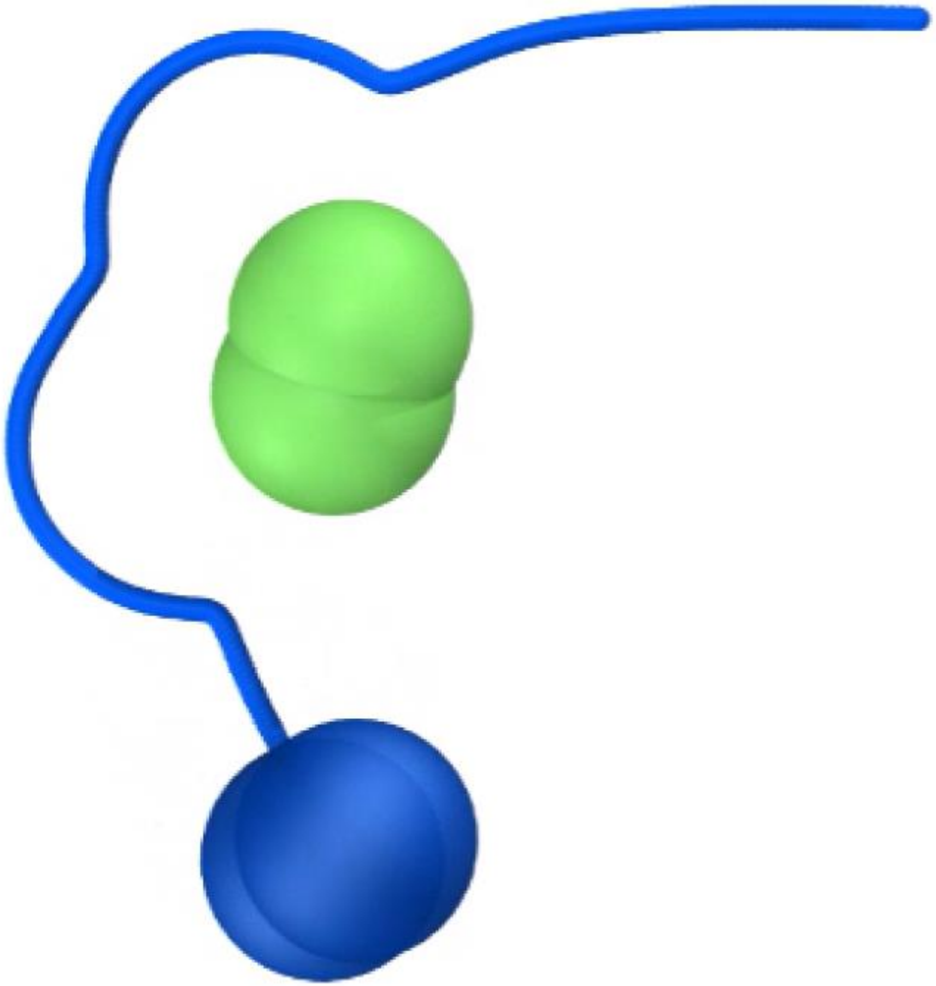


Spurious collisions:
Successive collisions between the same pair of molecules.

Seven spurious collisions!

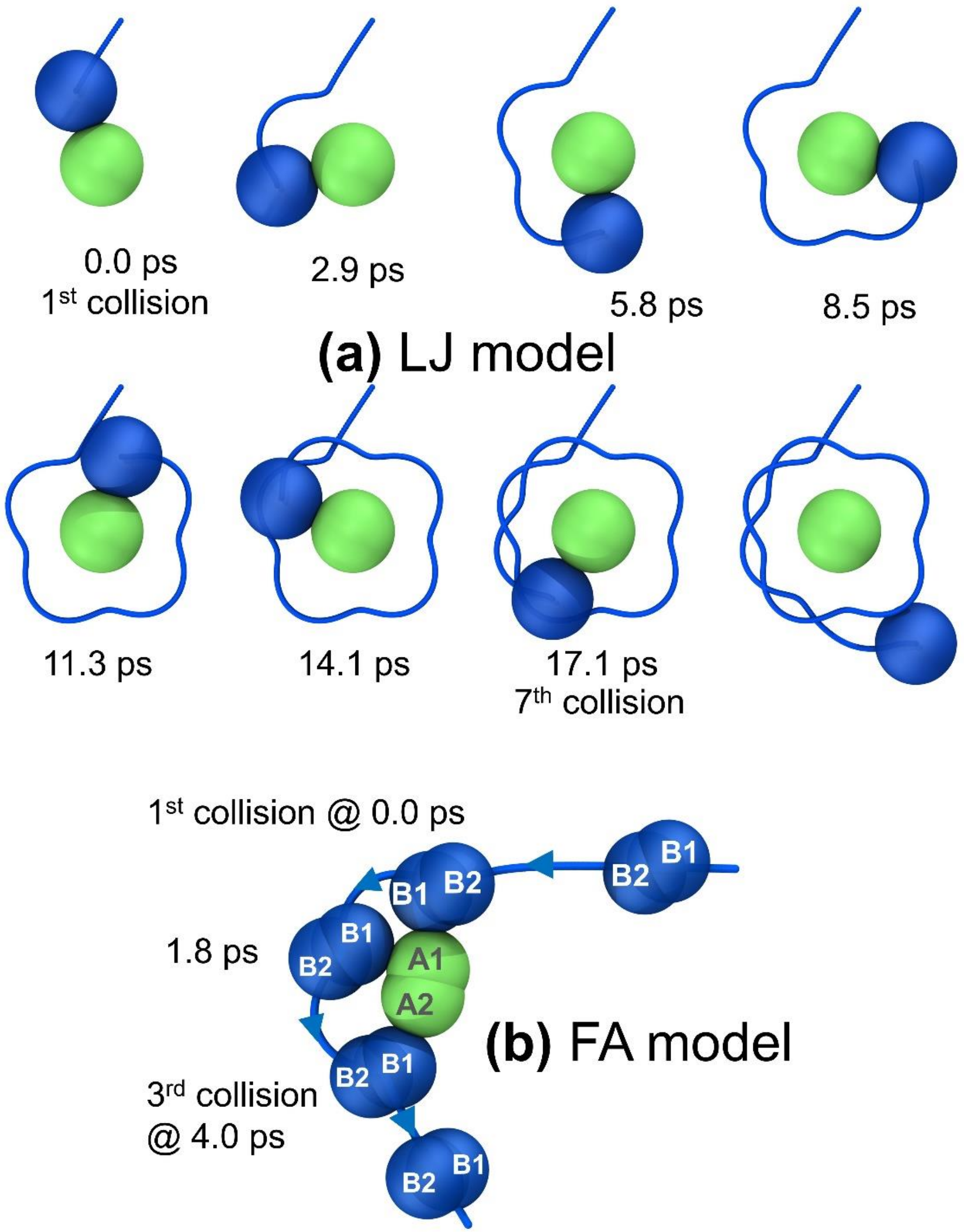
Accounting for force field & shape → to spurious collisions
Case 2: The real thing (FA model)

Spurious collisions:
Successive collisions between the same pair of molecules.

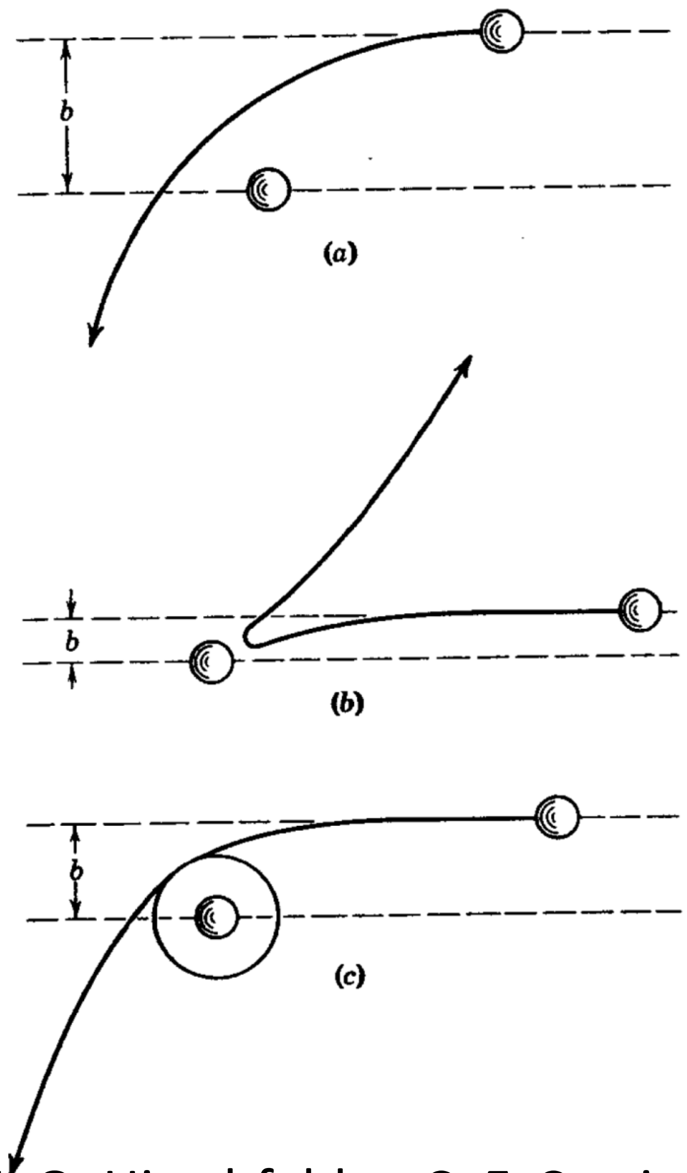


Three spurious collisions!

Accounting for force field & shape → to complex collisions

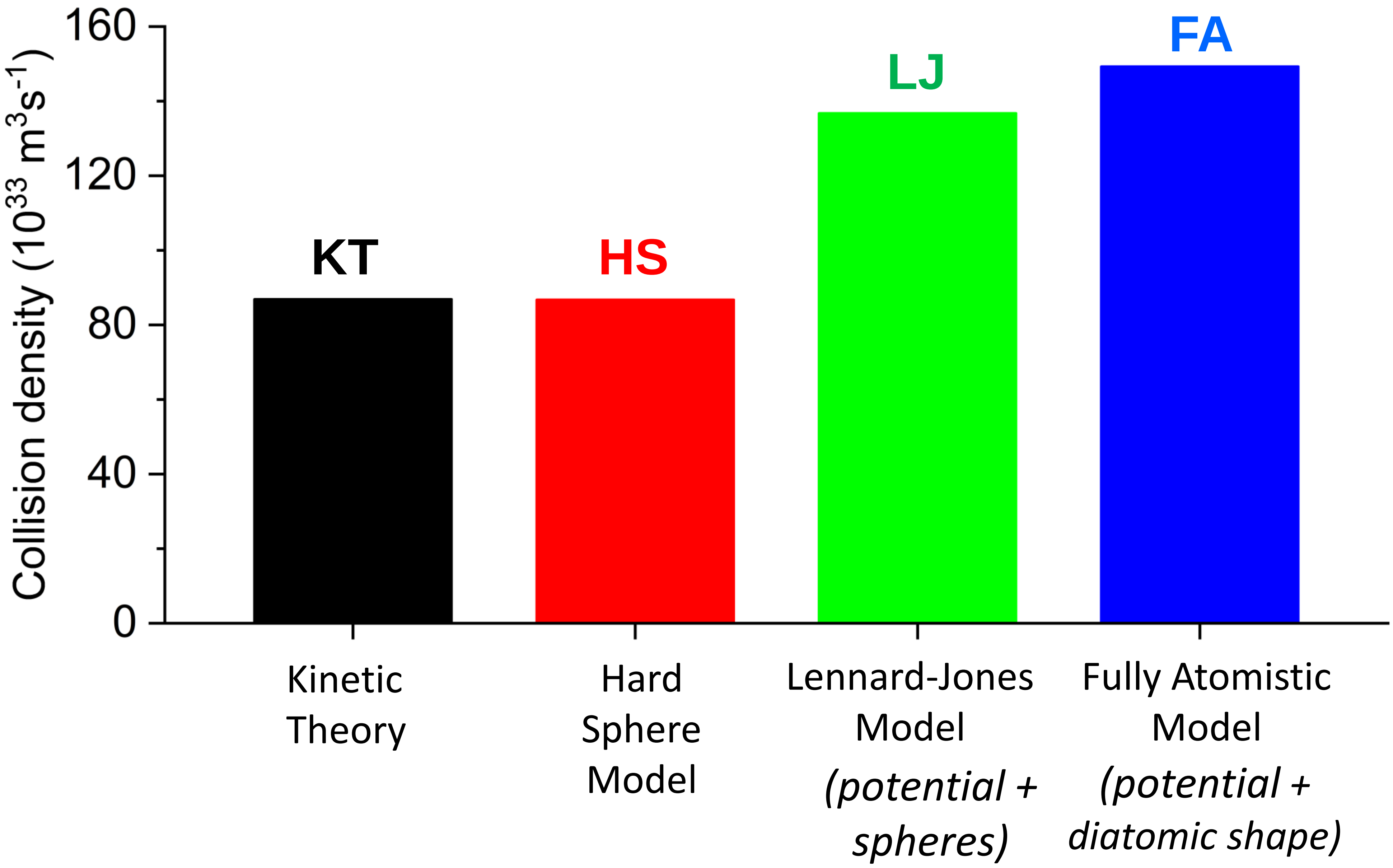


Is this really new?

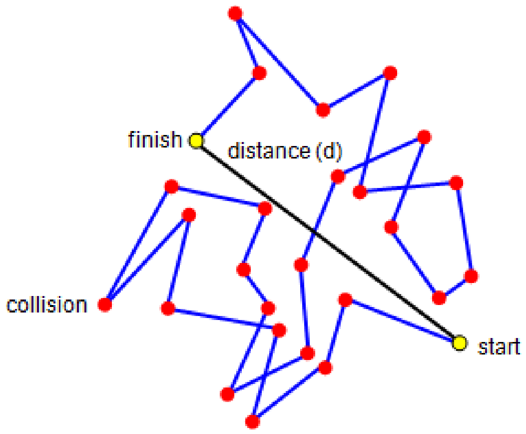


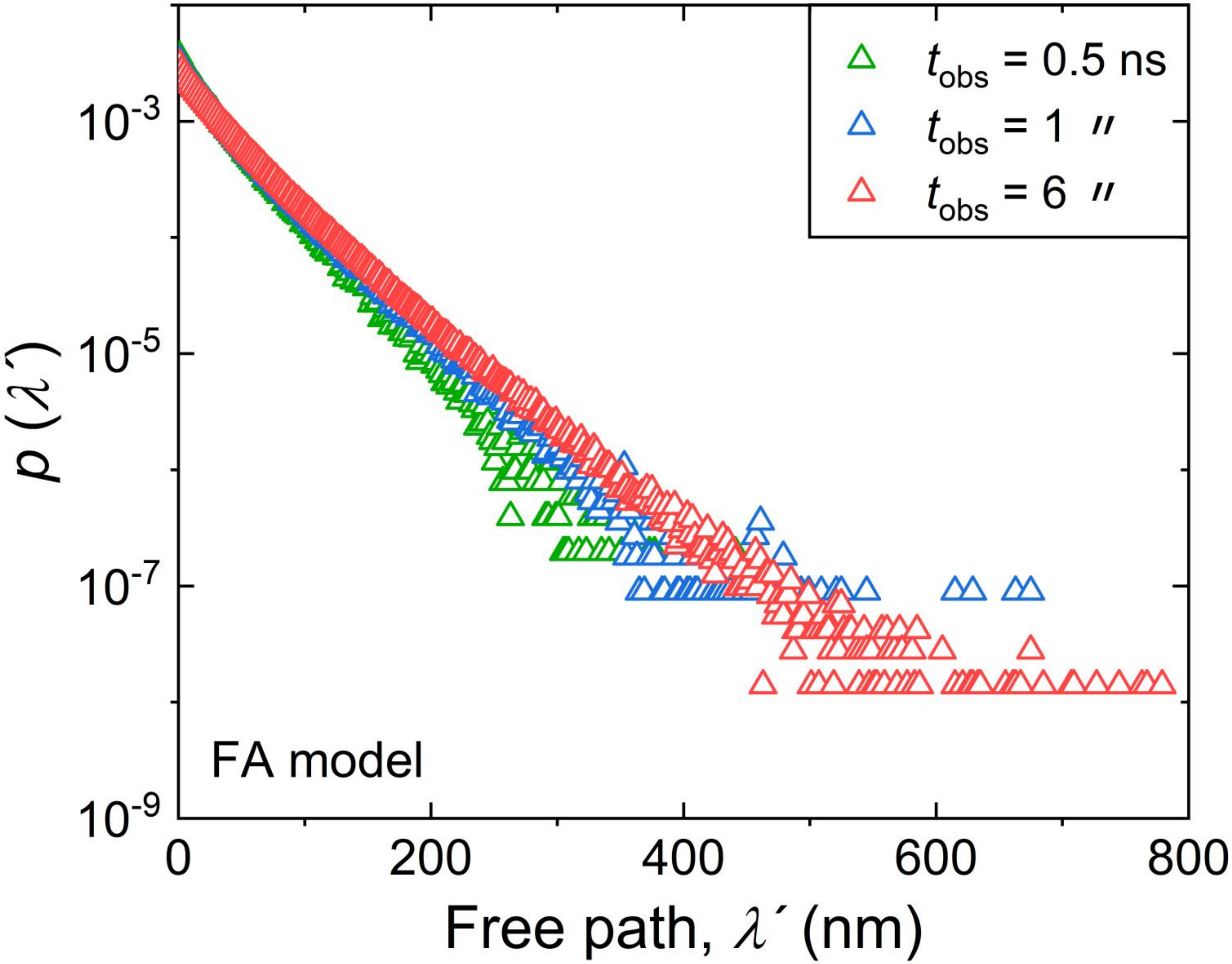
"Molecular Theory of Gases and Liquids" of J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, p. 556, Figure 8.4-2, 1954

Number of genuine collisions by KT & three models

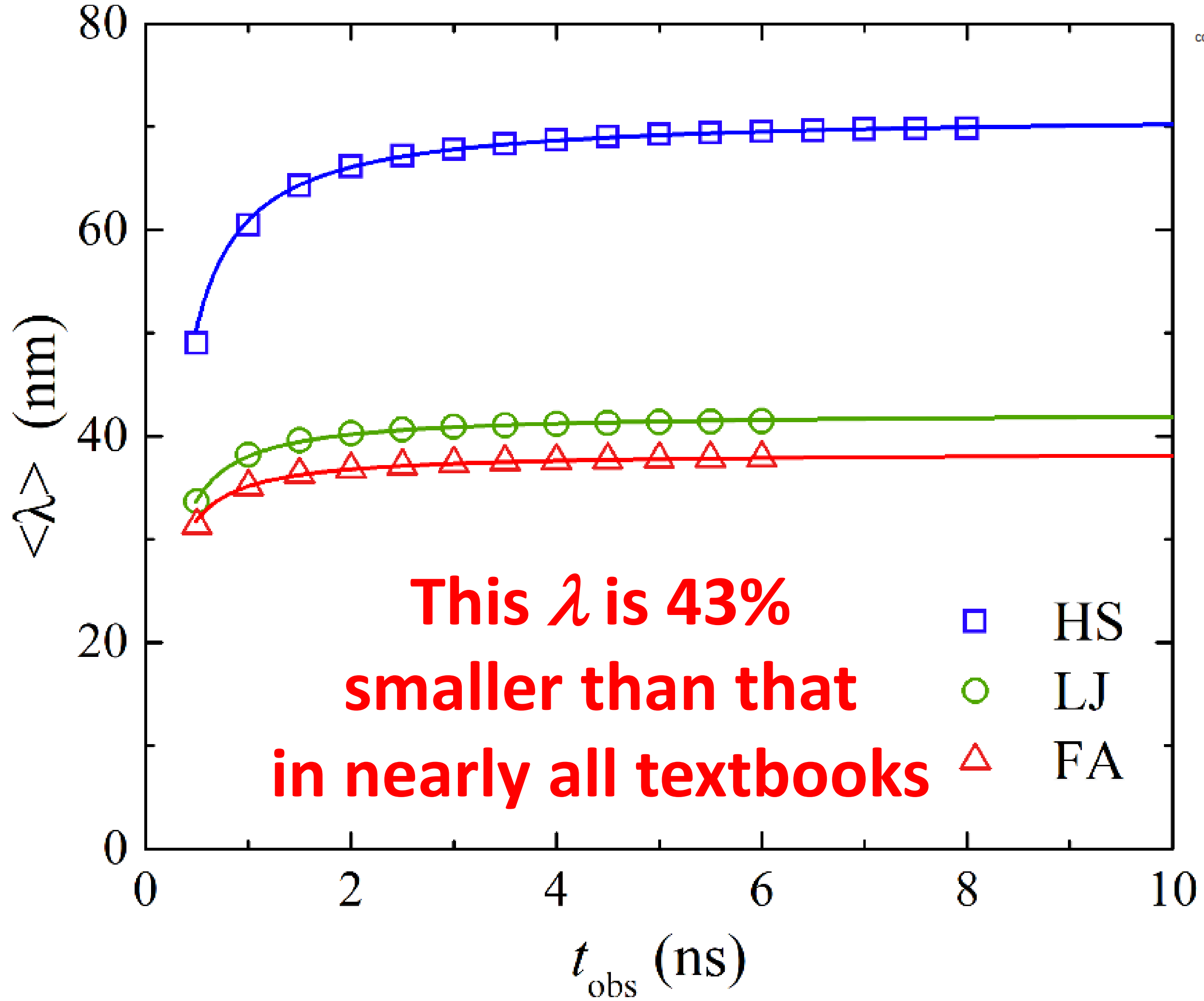


Evolution of the free path probability distribution

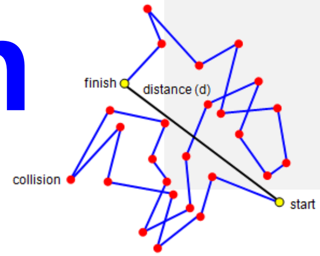




Mean free path



This λ is 43% smaller than that in nearly all textbooks

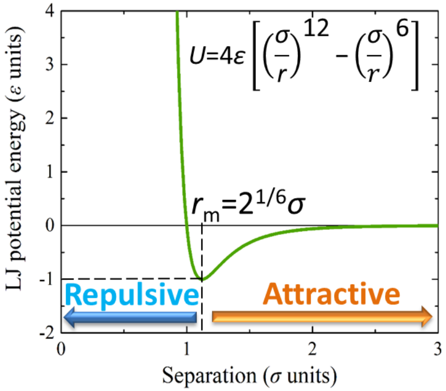


	Mean free path $\langle\lambda\rangle$ (nm)
Kinetic Theory	**67.6**
HS model	**70.6 ± 2.2**
LJ model	**42.3 ± 1.1**
FA model	**38.5 ± 1.0**

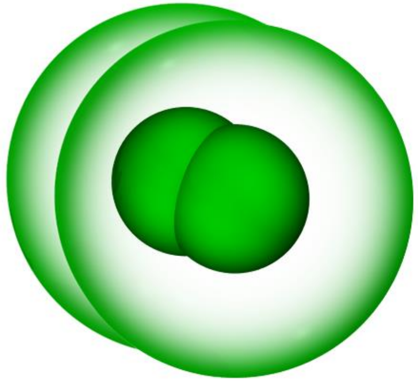
This λ does not depend on the parametrization of the MD force field.

So what?

- **Continuum → smaller sizes**
- **Subcritical cluster nucleation dynamics**
- **Diffusivity of nanoparticles**
- **Nanoparticle coagulation**
- **…………**



Summary



1. Relaxed the assumptions of KT (perfect spheres & elastic collisions) by fully atomistic MDs, for the first time to our knowledge.
2. Rigorous validation with the air density, viscosity & diffusivity.
3. Genuine collisions were distinguished from spurious ones.
4. Collision densities from the HS model are in agreement with KT!
5. By accounting for the **force field and the non-spherical shape** of O_2 & N_2, the mean free path of air at RT is **~38 nm,** 43% smaller than that in nearly all texts.

Dynamics of molecular collisions in air and its mean free path, *Physics of Fluids* **35**, 097131 (2023)

Thank you for listening!