Mean free path of air: The impact of inelastic molecular collisions

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Motivation

- Molecular collisions in the gas phase determine the key transport properties of gases while the gas mean free path and particle size largely control aerosol behavior.[1]
- The kinetic theory of gases provides analytical expressions for their principal transport properties of diffusivity, D, viscosity, η, and thermal conductivity, κ.[1,2]
- However, the kinetic theory assumes gas molecules as perfect spheres undergoing random elastic collisions.
- Very soon it was noticed that the temperature scalings for transport properties predicted by the kinetic theory were not accurate.[3]

Here we relax the basic assumptions (molecular shape and potential between molecules) through molecular dynamics simulations.

✓ Oxygen and nitrogen are modelled as diatomic molecules interacting via a fully atomistic potential (FA), including bond stretching and Lennard-Jones interactions.[4]

✓ Two additional simpler cases (in both molecules assumed spherical) are examined: a) application of a hard sphere (HS model) potential to enable a comparison with kinetic theory and b) of a Lennard-Jones potential (LJ model) to examine the impact of the potential separately.

Kinetic theory and variants

Kinetic theory: a) $\lambda_{\text{Jennings}} = \sqrt{\pi/8}\cdot\dfrac{\eta}{f}\cdot\dfrac{1}{\sqrt{\rho P}}$ [5]

b) Chapman-Enskog: $d_{\text{ref}} = \left(\dfrac{5}{16}\dfrac{\left(mk_B T_{\text{ref}}/\pi\right)^{1/2}}{\eta_{\text{ref}}}\right)^{1/2}$, and $\lambda_{\text{C-E}} = \left\{2^{1/2}\pi d_{\text{ref}}^2\, n\left(\dfrac{T_{\text{ref}}}{T}\right)^{\omega-\frac{1}{2}}\right\}^{-1}$ [3]

Variants of the kinetic theory:[6-8]

a) Variable Hard Sphere (VHS) model [6]: $d_{\text{ref, VHS}} = \left(\dfrac{15\left(mk_B T_{\text{ref}}/\pi\right)^{1/2}}{2(5-2\omega)(7-2\omega)\eta_{\text{ref}}}\right)^{1/2}$, and $\lambda_{\text{VHS}} = \left\{2^{1/2}\pi d_{\text{ref,VHS}}^2\, n\left(\dfrac{T_{\text{ref}}}{T}\right)^{\omega-\frac{1}{2}}\right\}^{-1}$

b) Variable Soft-Sphere (VSS) model [7,8]: $d_{\text{ref, VSS}} = \left(\dfrac{5(a+1)(a+2)\left(mk_B T_{\text{ref}}/\pi\right)^{1/2}}{4a(5-2\omega)(7-2\omega)\eta_{\text{ref}}}\right)^{1/2}$, and $\lambda_{\text{VSS}} = \left\{2^{1/2}\pi d_{\text{ref, VSS}}^2\, n\left(\dfrac{T_{\text{ref}}}{T}\right)^{\omega-\frac{1}{2}}\right\}^{-1}$

with ω, being the viscosity scaling factor, m the molar mass, T_{ref} the reference temperature for which the dynamic viscosity η_{ref} is known, and α a softness parameter ($\alpha \geq 1$)

c) Expressions for the mean free path based on transport properties (dynamic viscosity and diffusivity):

VHS model [7]: $\lambda_\eta = (8\eta/15)(3-\omega)(2-\omega)\left(2\pi m k_B T\right)^{1/2}/n$

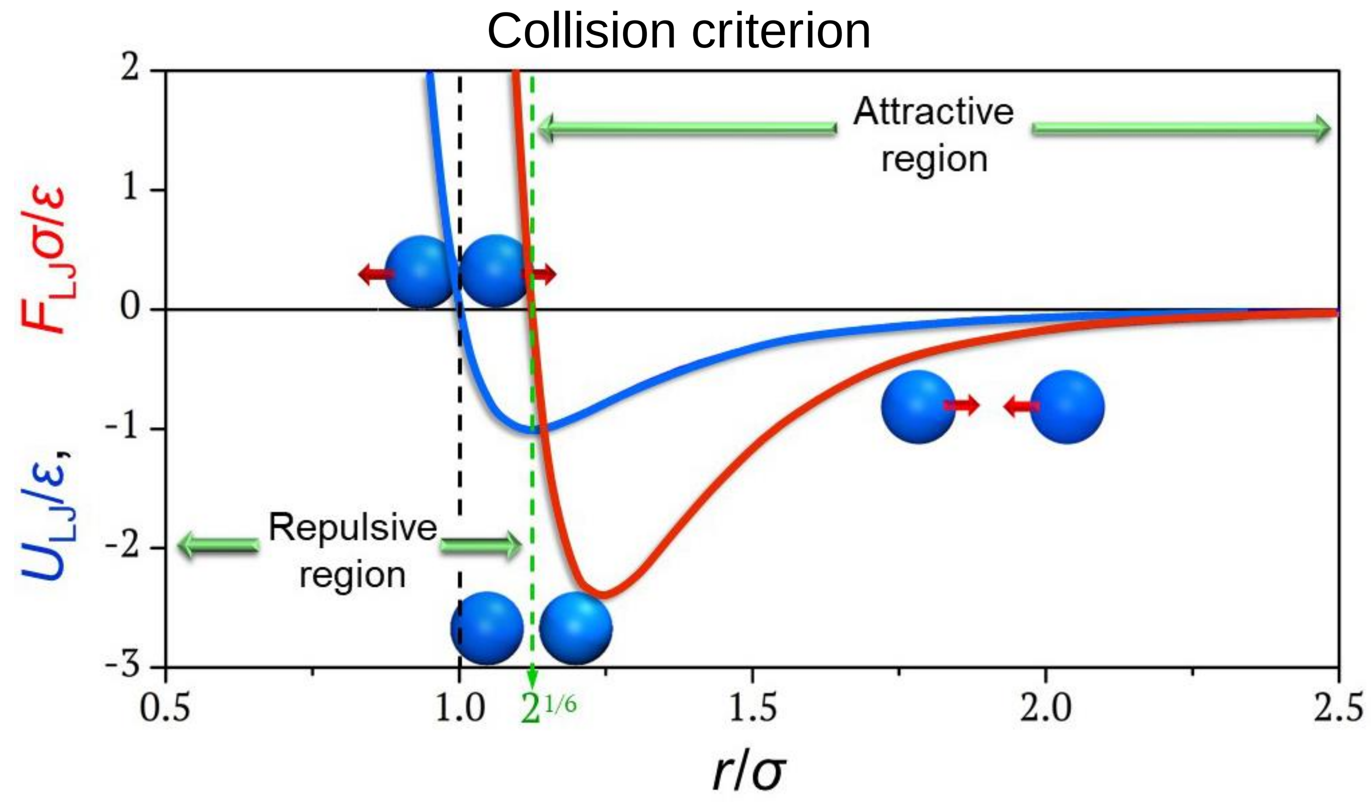
VHS model [7]: $\lambda_D = (4D/3)(2-\omega)\left(2\pi k_B T/m\right)^{1/2}$

Mean free path of air from the various models at T = 300 K and P =1 atm

Mean free path (nm)					
$\lambda_{\text{Jennings}}$	$\lambda_{\text{C-E}}$	λ_{VHS}	λ_η	λ_D	λ_{VSS}
67.3	66.3	53.6	31.4	45.3	55

Collision detection

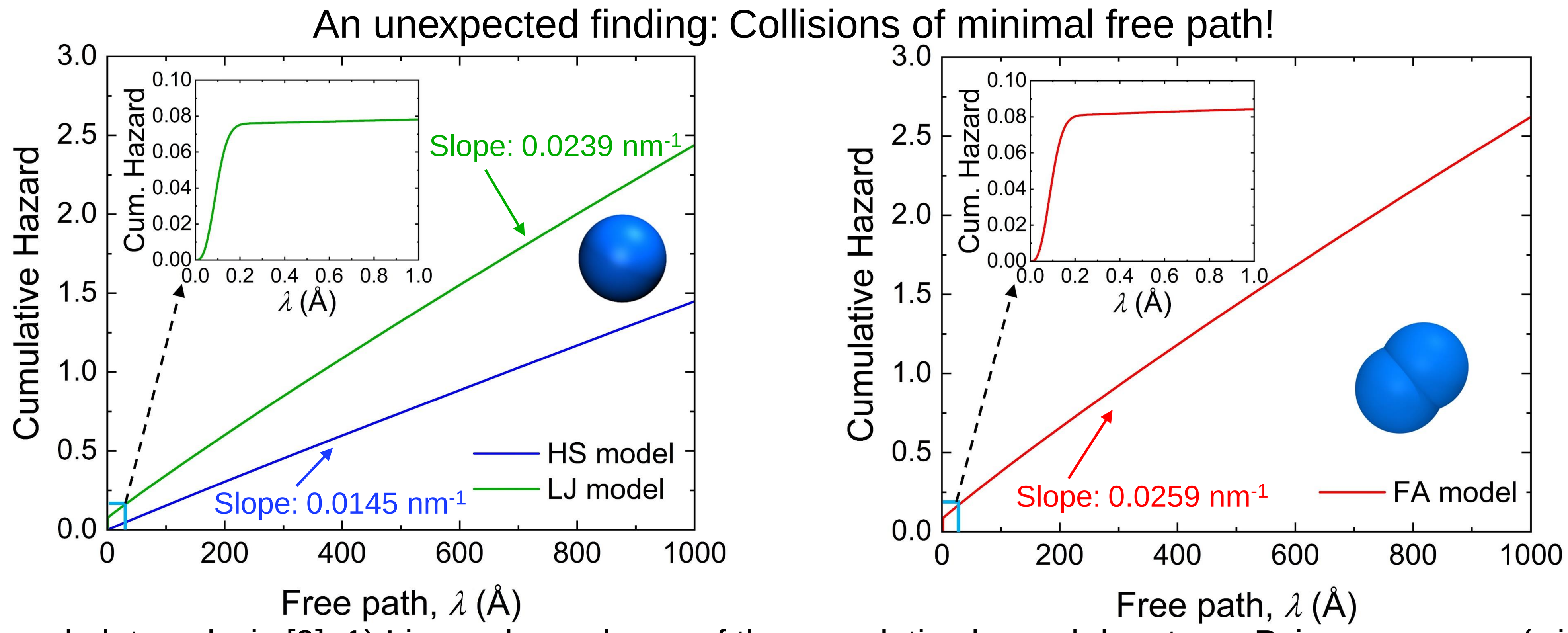
Collision criterion



Collision distance, r_m: $r_m = 2^{1/6}$ (vertical green dashed line).

The distance where the inter-atomic force between the becomes zero as it changes sign from negative (attractive) at $r_m/\sigma > 2^{1/6}$ to positive (repulsive) at $r_m/\sigma < 2^{1/6}$.

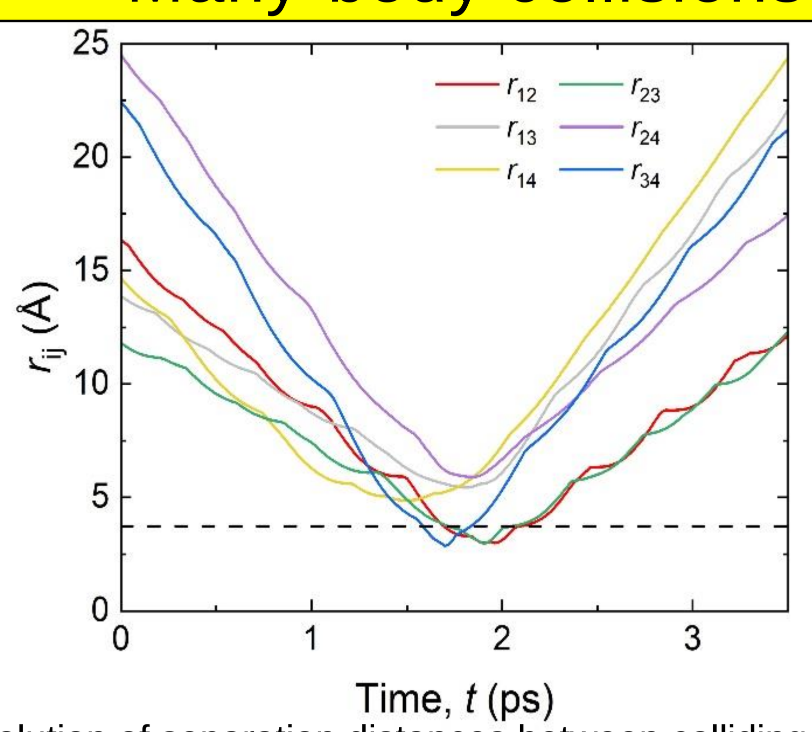
An unexpected finding: Collisions of minimal free path!



Hazard plot analysis [9]: 1) Linear dependence of the cumulative hazard denotes a Poisson process (with a rate equal to the slope of the curve), 2) Non-linear dependence implies correlated (not random) events

- A significant fraction of very short paths is observed occurring at a very high rate
- Most of free paths follow an exponential distribution.
- For the HS model, no correlated short paths are observed

Many-body collisions

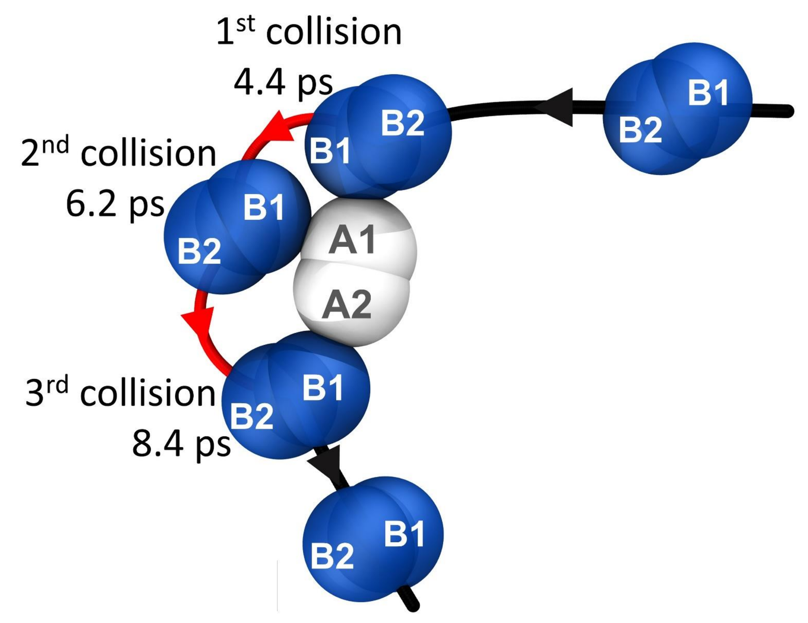


The evolution of separation distances between colliding pairs of nitrogen atoms 1, 2, 3 and 4 in a 4-body collision.

Black line: nitrogen collision threshold distance.

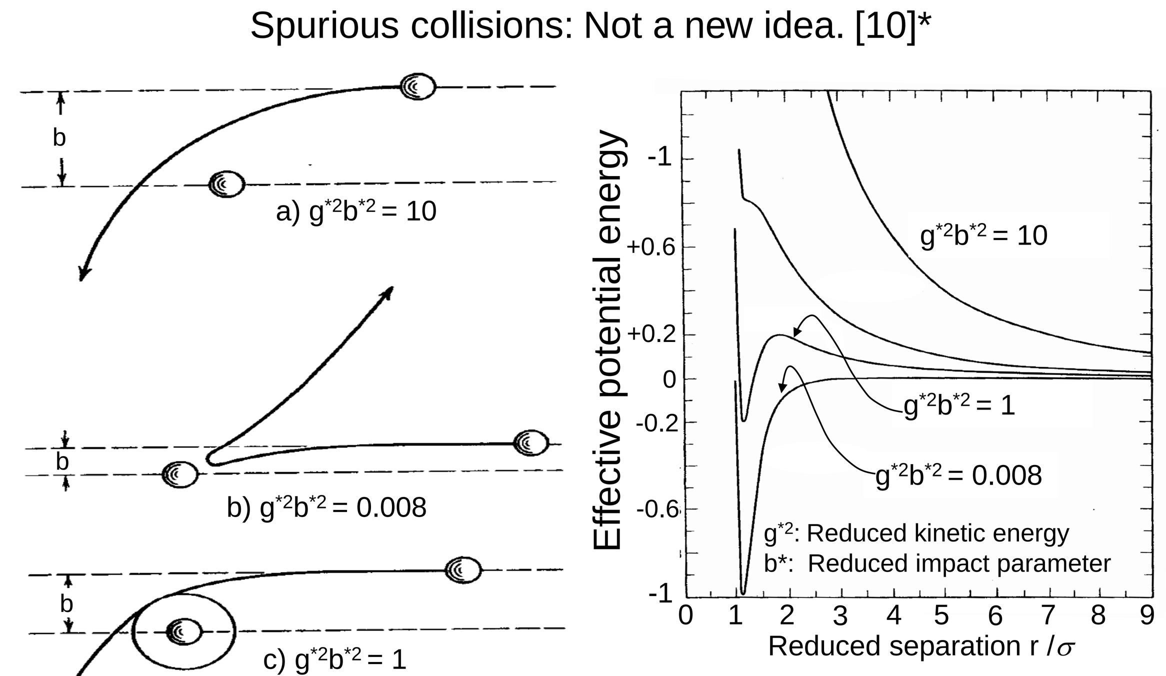
Spurious collisions

Spurious collisions: Successive collisions between the same pair of molecules, without another molecule intervening in their interaction.



Have to be considered as one collision, otherwise the collision densities would be largely overestimated.

Spurious collisions: Not a new idea. [10]*



*"Molecular Theory of Gases and Liquids" of J. O. Hirschfelder, C. F. Curtiss and R. B. Bird. pages 554-6, Figures 8.4-1, & 8.4.2, 1964

Collision densities

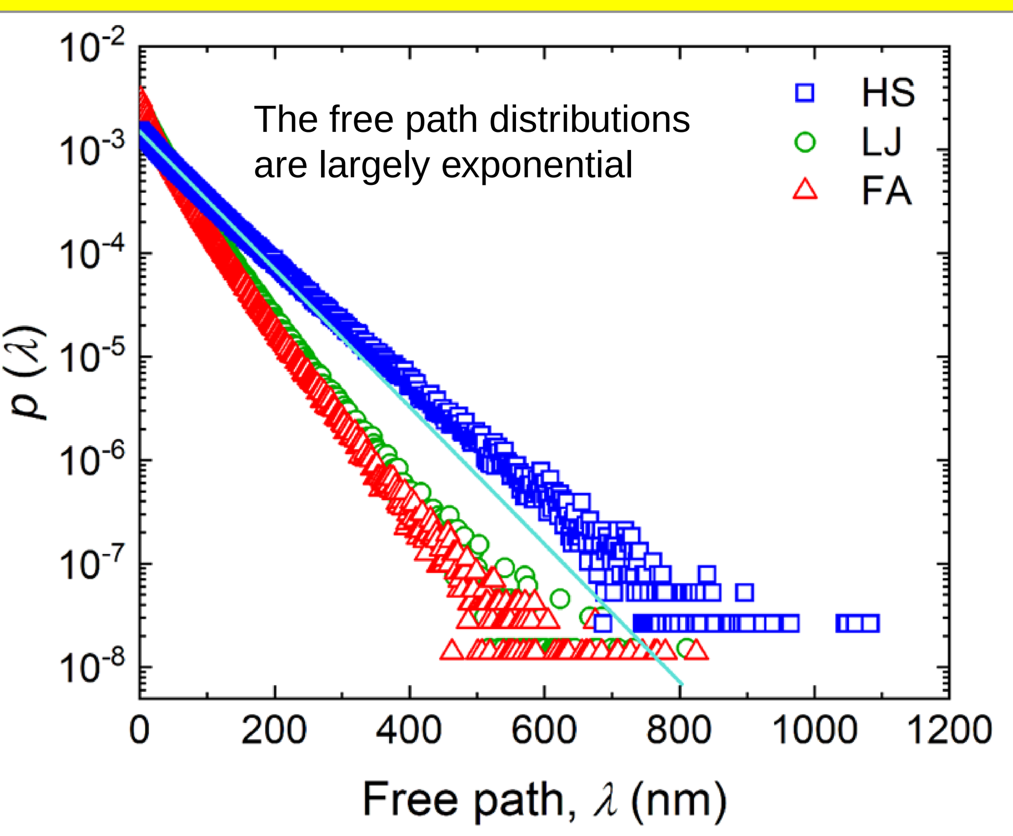
Collision densities (after detecting and excluding spurious collisions) by the HS, LJ, and FA models in comparison to kinetic theory of gases that assumes purely elastic spheres.

	Collision densities (10^{33} m^{-3}s^{-1})			
	oxygen - oxygen	nitrogen – nitrogen	nitrogen - oxygen	Total
Kinetic theory	3.14	57.0	26.8	86.94
HS model	3.2 ± 0.1	56.9 ± 1.6	26.7 ± 0.6	86.8 ± 1.7
LJ model	5.3 ± 0.1	88.3 ± 2.4	43.3 ± 1.0	136.8 ± 2.6
FA model	5.8 ± 0.2	96.1 ± 2.7	47.4 ± 1.2	149.3 ± 3.0

The HS model in an excellent agreement with the kinetic theory.

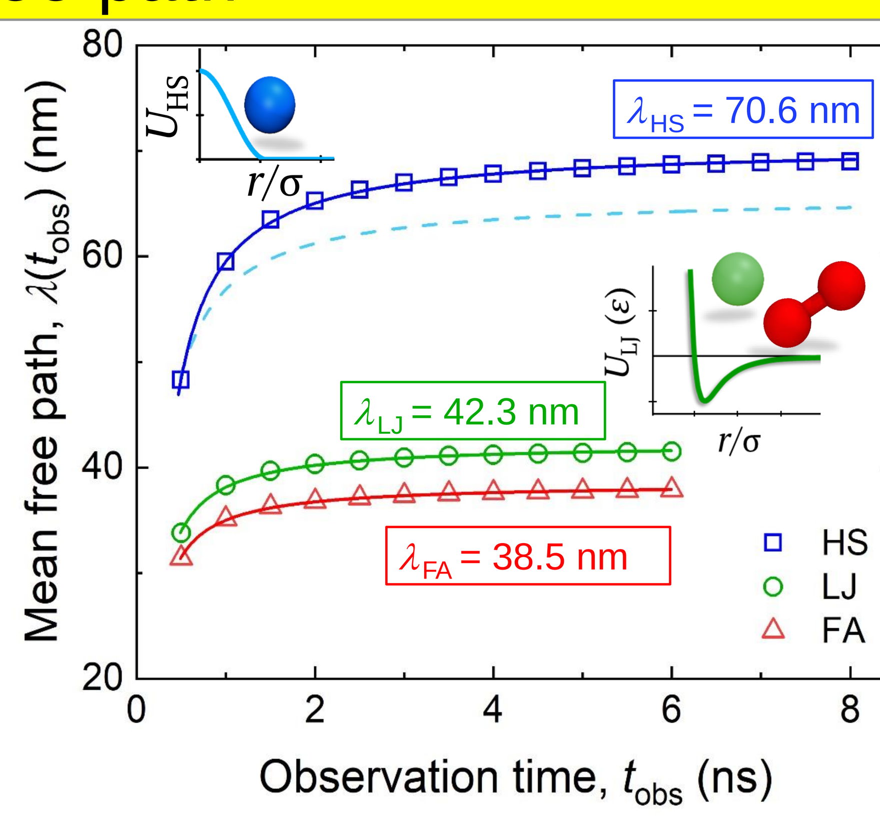
The collision densities from LJ and FA models are significantly enhanced compared to those of the kinetic theory.

Mean free path



Probability distributions $p(\lambda)$ of free paths λ from the HS, LJ , and FA models.

Solid line: Best fit to the HS data is following the kinetic theory of gasses.



Symbols: Mean free path as a function of observation time by directly averaging over the corresponding density distributions of free paths.

Solid lines: Best fits to the MD data with a hyperbolic function.

Broken line: Regressing the distribution with an exponential function and then computing the average of this function.

References

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Conclusions

- The collision densities and the corresponding λ as determined by the HS model were in agreement with kinetic theory.
- When O_2 and N_2 when treated as diatomic molecules experiencing both repulsive and attractive interactions, their λ is considerably smaller than that from the classic kinetic theory of gasses.
- The new value of the mean free path of air reported here (after detecting and excluding spurious collisions) is 38.5 nm, almost 43% smaller than the currently known and widely used value of 67.3 nm at 300 K and 1 atm.
- Particle transport in the continuum regime can be safely used at smaller particles than today.