Molecular dynamics simulations of fullerene and silica nanoparticles diffusion coefficients in air

Swiss Federal Institute of Technology Zürich

Katerina S. Karadima[1-2], Dimitrios G. Tsalikis[1-2], Vlasis G. Mavrantzas[1-2], Sotiris E. Pratsinis[1]

[1]Department of Mechanical and Process Engineering, ETH Zurich, Zurich, 8092, Switzerland

[2]Department of Chemical Engineering, University of Patras & Institute of Chemical Engineering Sciences (ICE-HT/FORTH), Patras, 26504, Greece

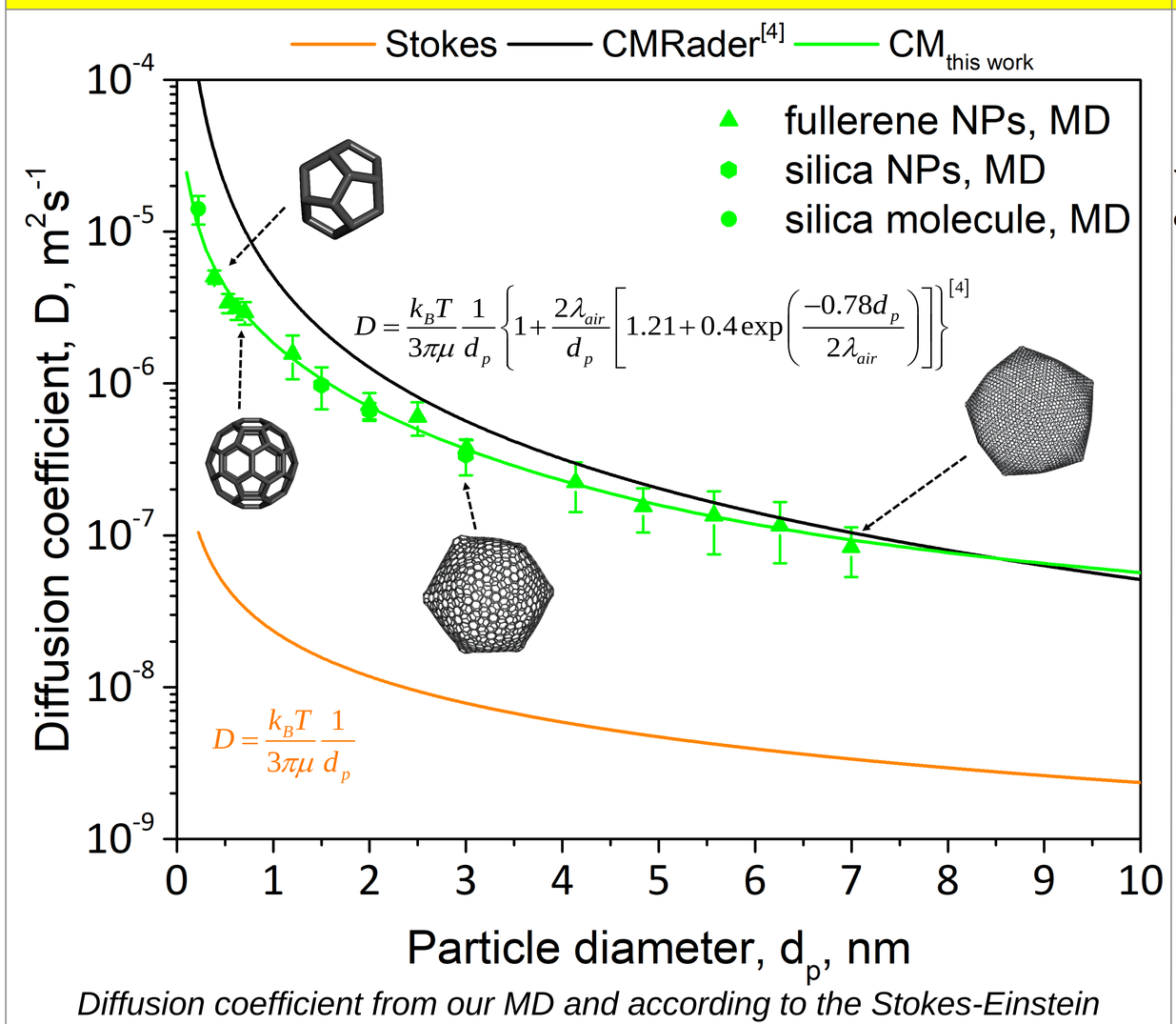
aikaradi@ptl.mavt.ethz.ch

PTL www.ptl.ethz.ch

Motivation

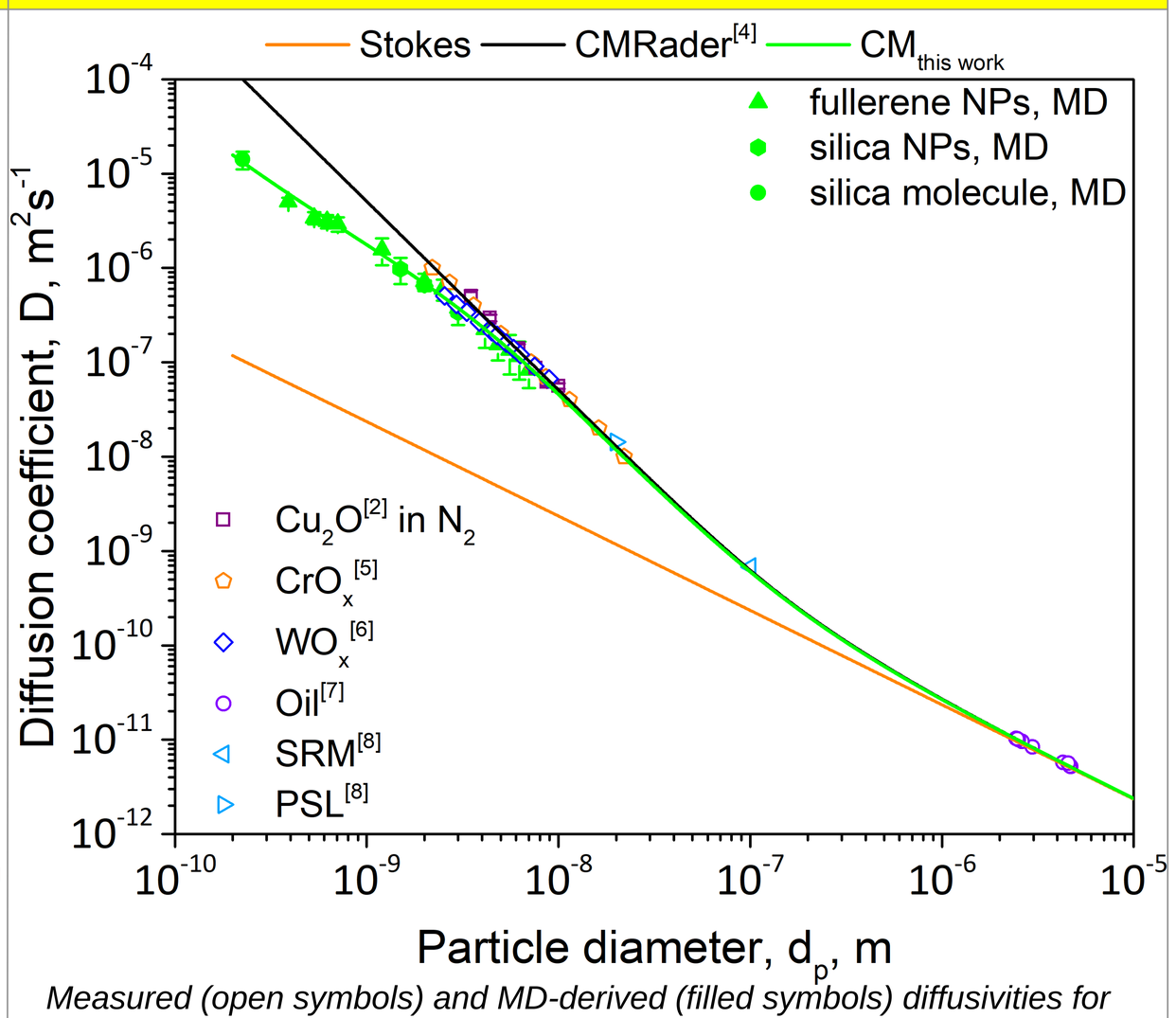
Several corrections to the kinetic theory or Stokes-Einstein relation for particle diffusivity have been proposed[1]. However, discrepancies are often reported[2], even for correlations on the same particle size regime. Here molecular dynamics (MD) simulations are employed to determine the diffusion coefficient of various fullerene and silica nanoparticles (NPs) in air since MD unravel the fundamentals of processes dominating aerosol dynamics, thus facilitating the understanding of natural phenomena and accelerating process scale-up and innovation[3].

Diffusion coefficients for fullerene and silica particles at 298 K



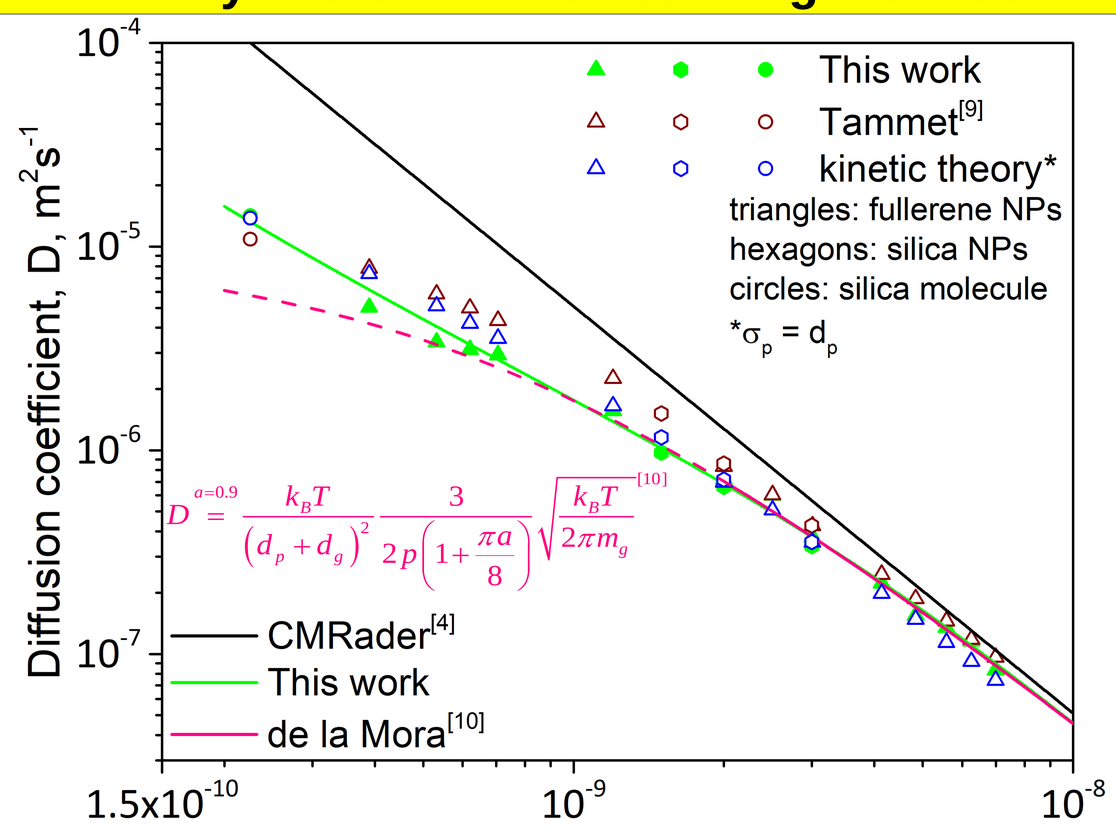
Diffusion coefficient from our MD and according to the Stokes-Einstein equation without (orange) and with (black) the Cunningham-Millikan (CM) slip correction[4], and the equation proposed here ($CM_{this\ work}$, green).

Measured diffusivity coefficients in the transition to free molecule regime vs. theory/experiments



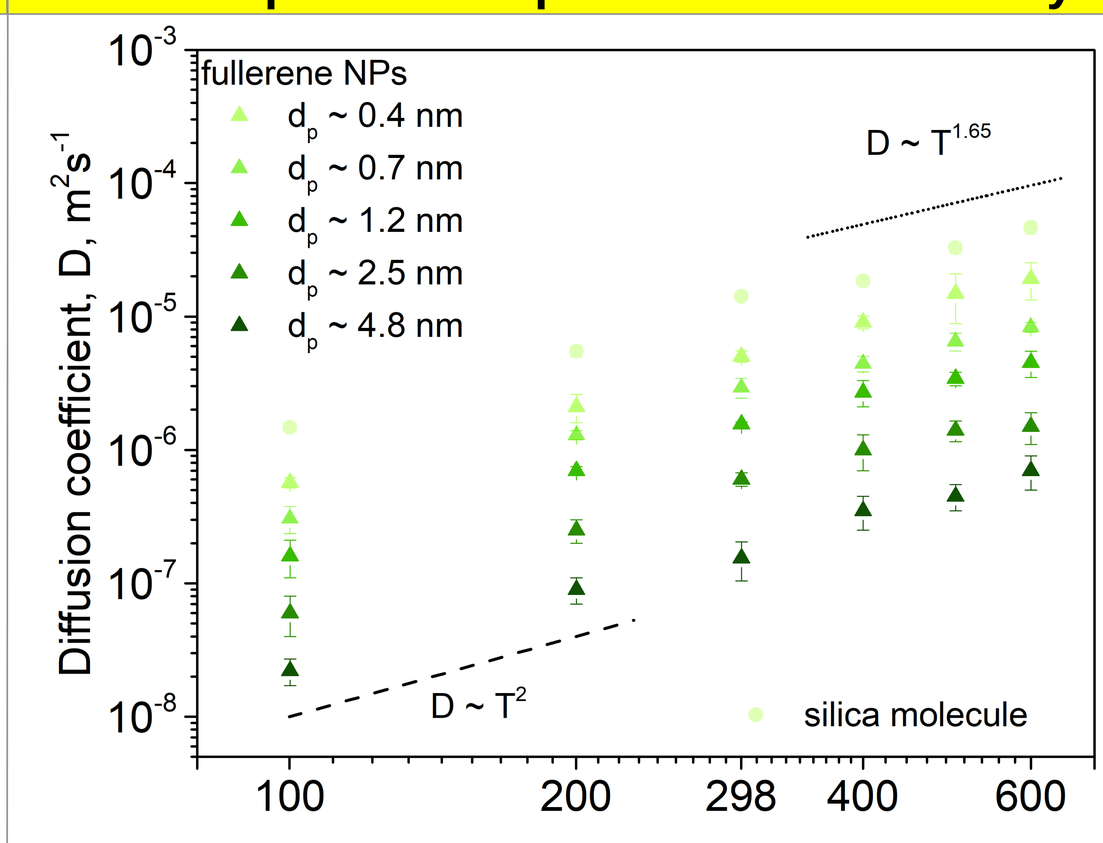
Measured (open symbols) and MD-derived (filled symbols) diffusivities for various materials with the Stokes-Einstein w/ & w/o the Cunningham-Millikan correction and the present MD-derived correlations (lines) at 298 K & 1 atm.

Diffusivity in the free molecule regime vs. theory



MD-derived (green symbols) diffusivities and predictions according to the kinetic theory and equations proposed in bibliography[4],[9]-[10]. de la Mora's eq. fails as particle approaches the molecular size, since it assumes rigid bodies and almost specular reflection as a modification of Epstein's formula[10].

Temperature dependence of diffusivity



The temperature dependence of the MD-derived diffusion coefficients for fullerenes with d_p = 0.4, 0.7, 1.2, 2.5 and 4.8 nm and silica molecule. Power laws, $D \sim T^k$, for low and high temperatures[11] are also depicted.

References

[1] Hinds, W.C. (1999) *Aerosol technology*, John Wiley & Sons.
[2] Rudyak, W.Ya., Krasnolutskii, S.L., Nasibulin, A.G. and Kauppinen, E.I. (2002) *Dokl. Phys.* **47**, 758-761.
[3] Mavrantzas, V.G. and Pratsinis, S.E. (2019) *Curr. Opin. Chem. Eng.* **23**, 174-183.
[4] Rader, D.J. (1990) *J. Aerosol Sci.* **21**, 161-168.
[5] Pedder, M.A. (1971) *J. Phys. D: Appl. Phys.* **4**, 531-539.
[6] Rudyak, W.Ya., Dubtsovc, S.N. and Baklanovc, A.M. (2009) *Aerosol Sci.* **40**, 833-843.
[7] Allen, M.D. and Raabe, O.G. (1982) *J. Aerosol Sci.* **13**, 537-547.
[8] Kim, J.H, Mulholland, G.W., Kukuck, S.R. and Pui, D.Y.H. (2005) *J. Res. Natl. Inst. Stand. Technol.* **110**, 31-54.
[9] Tammet, H. (1995) *Aerosol Sci.* **26**, 459-475.
[10] de la Mora, J.F., de Juan, L., Liedtke, K. and Schmidt-Ott, A. (2003) *J. Aerosol Sci.* **34**, 79-98
[11] Bird, R.B., Stewart, W.E. and Lightfoot, E.N. (2002) *Transport Phenomena*, 2nd ed., John Wiley & Sons.

Conclusions

1. Diffusivities of fullerene and silica particles with d_p = 0.4-7.0 nm and silica molecule were determined by MD simulations.
2. A new formulation for the particle diffusion coefficient was proposed all the way from the continuum to the free molecular regime.
3. Our results provide insights of the diffusion behaviour of NPs with a diameter smaller than 2 nm.
4. The diffusivity temperature dependence of the silica molecule and several fullerene particles was estimated with MD simulations in the temperature range of 100-600 K and provided a scaling exponent close to 2 and 1.65 for low and high temperatures respectively[11].

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