Adsorption and Thermal Conductivity in Nanoporous Materials: Underlying Molecular Mechanisms and the Rattle Effect

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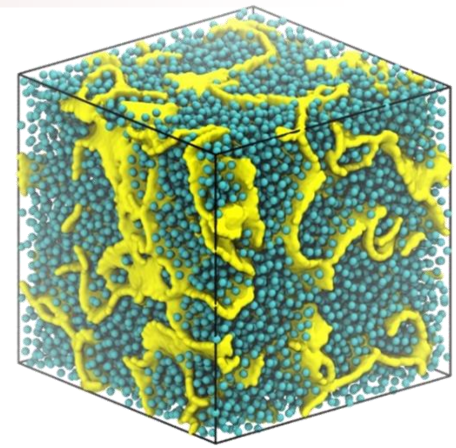
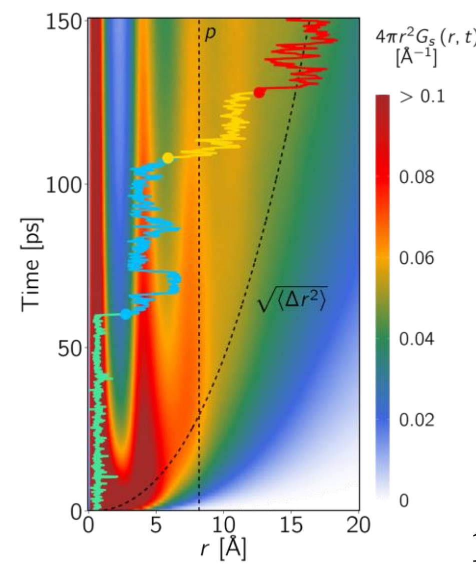
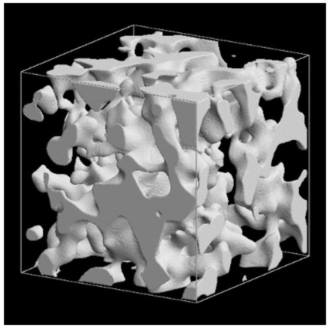
May 21, 2026





Nanoporous Materials



Courtesy of Levitz

Large surface areas (ex. ashes ~m^2/g) but larger surfaces can be reached ~1000 m^2/g

Nanoporous solids (with one dimension ~ *nm*) are of particular interest because D ~ ξ

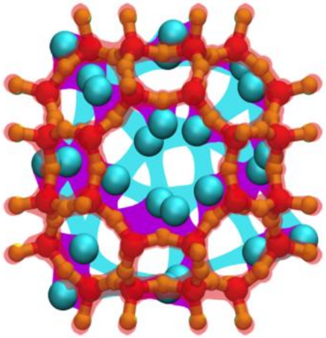
New thermodynamic and transport phenomena

Adsorption/transport interplay
Complex hydrodynamics

e.g. slippage, interfacial transport, and non-viscous effects

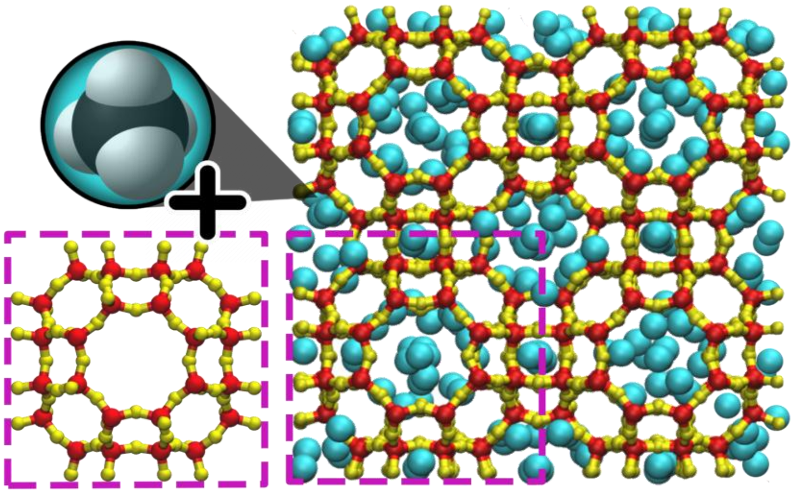
Theory/molecular modeling of adsorption and transport in nanoporous media

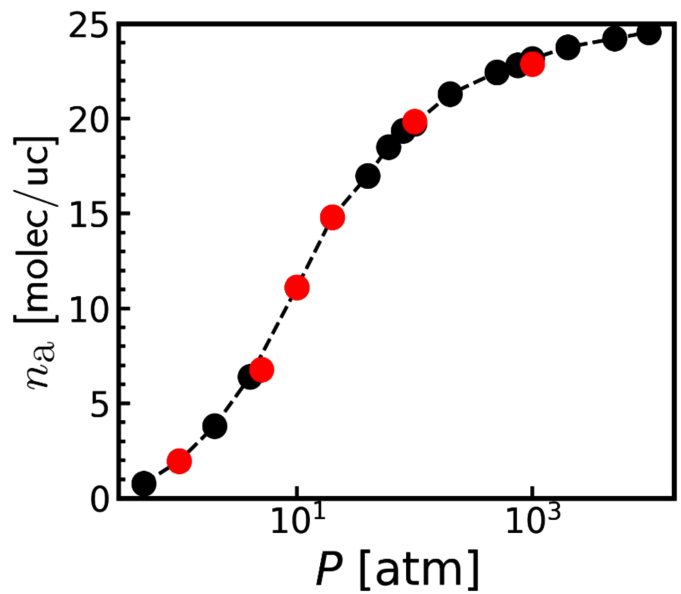
Thermal conductivity and sound propagation in nanopores



Ferreira de Souza et al., *J. Phys. Chem B* **2024**
Didier et al., *Phys. Rev. Mat.* **2025**

Methane in Zeolite



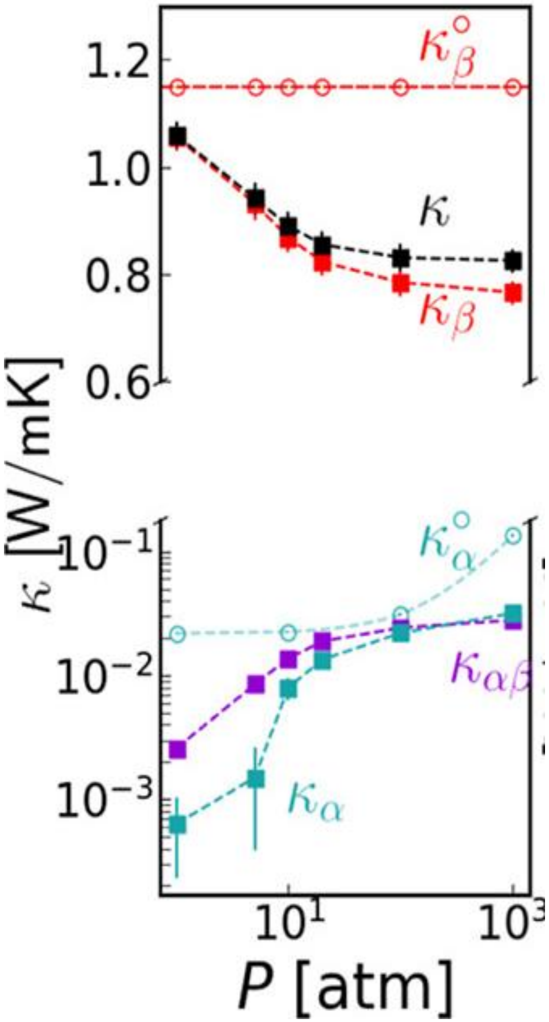


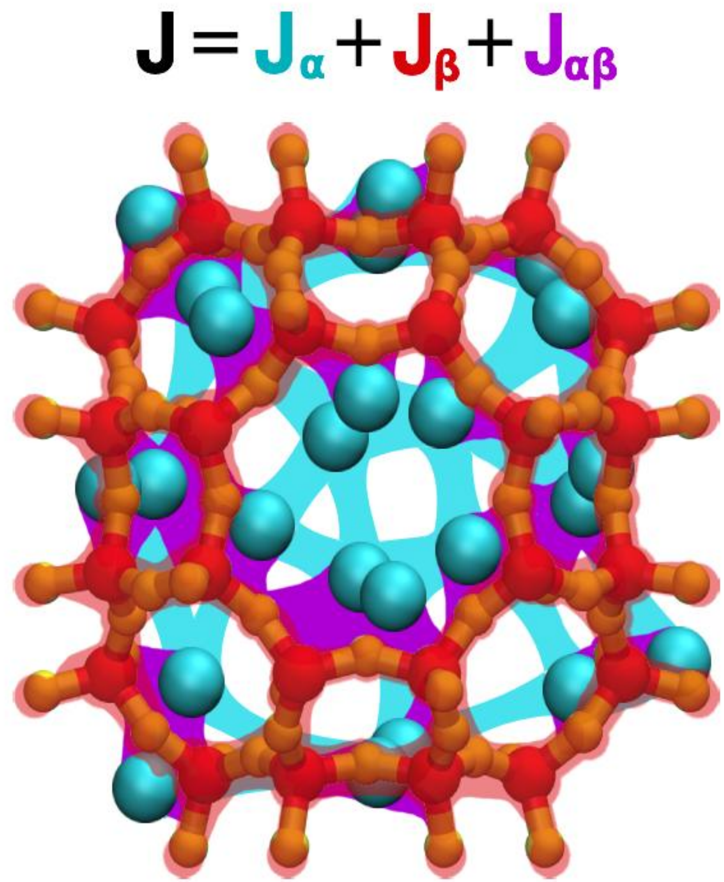
$$J = \frac{1}{V}\left[\sum_i E_i \mathbf{v}_i + \frac{dE_i}{dt}\mathbf{r}_i\right]$$

$$\kappa = \frac{V}{k_B T}\int_0^{\infty} \langle \mathbf{J}(t)\cdot\mathbf{J}(0)\rangle dt$$

Ferreira de Souza, Coasne, et al.
J. Phys. Chem. B. 2024

Thermal Conductivity





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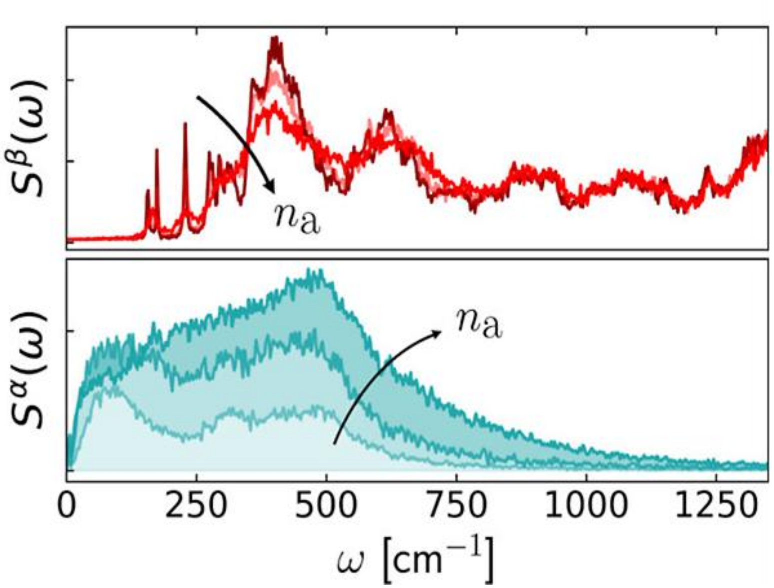
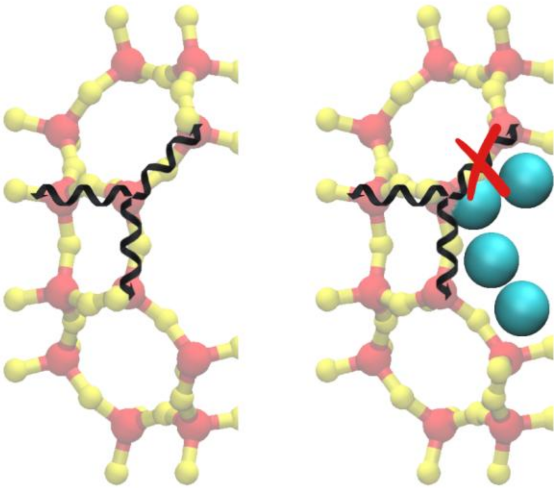
Solid/Fluid Coupling





- Solid/fluid coupling in the energy range where both DoS overlap
- Such coupling leads to a broadening of the phonon modes in the zeolite (peak width ~ inverse phonon life time)

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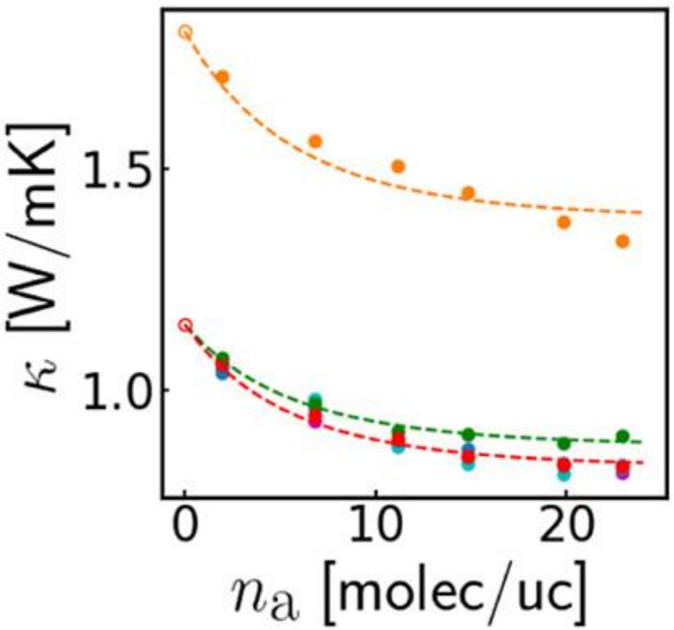
Phonon Scattering (Rattle Effect)

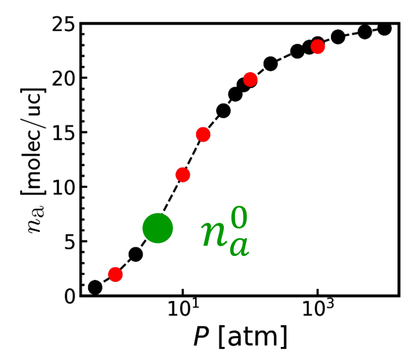


$$\kappa = \frac{1}{3} v^2 \tau C_p$$

$$N(t + \mathrm{d}t) = N(\mathrm{t}) \left[1 - \frac{1}{\tau_0} - \frac{f(n_\mathrm{a})}{\tau_a} \right] \mathrm{d}t$$

$$f(n_\mathrm{a}) = n_a^0 [1 - \exp(-n_a / n_a^0)]$$

$$\tau(n_\mathrm{a}) = \left[\frac{1}{\tau_0} + \frac{n_a^0 [1 - \exp(-n_a / n_a^0)]}{\tau_a} \right]^{-1}$$



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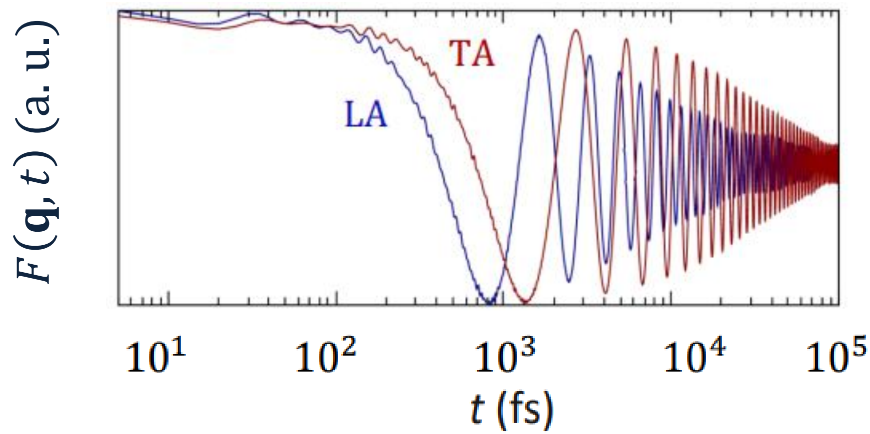
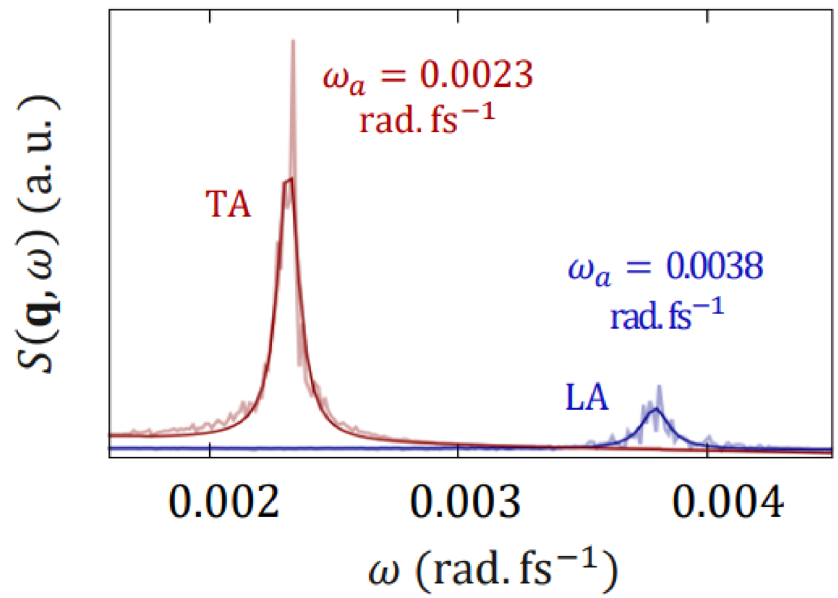
Sound Propagation

Dynamic structure factor

$$F(\boldsymbol{q},t) = \int G(r,t)\exp(-i\boldsymbol{q}.\boldsymbol{r})dr$$

$$S(\boldsymbol{q},\omega) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} F(\boldsymbol{q},t)e^{i\omega t}dt$$

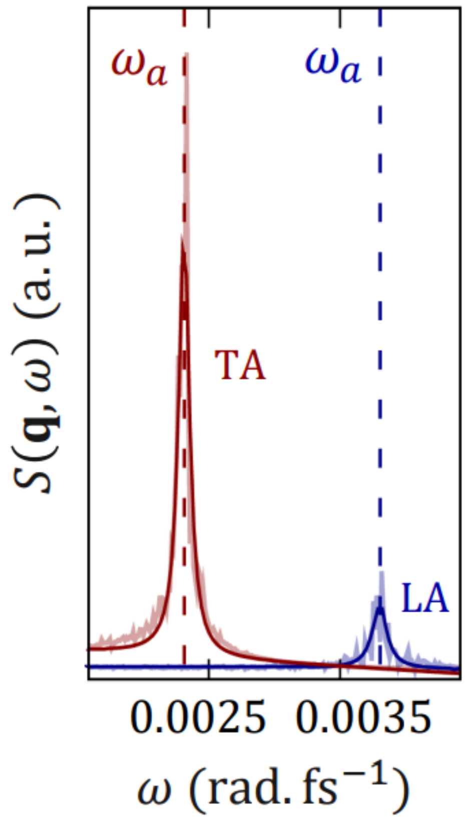




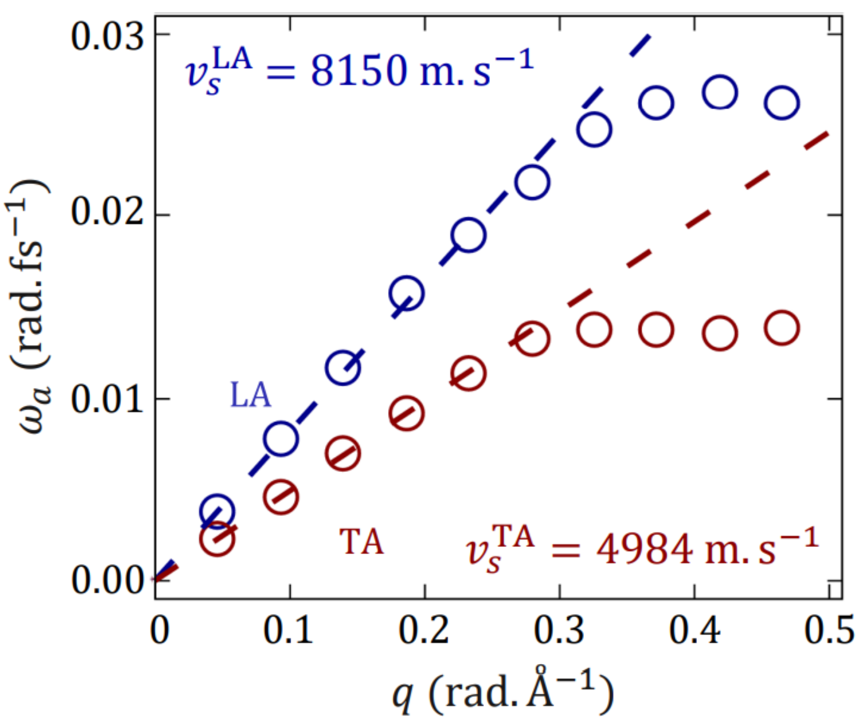
Sound Velocity

Damped harmonic oscillator approximation

In region of small wavevector $\boldsymbol{q}$: $S_a(\boldsymbol{q},\omega) \sim \frac{\Gamma_a(\boldsymbol{q})\omega_a^2(\boldsymbol{q})}{\left[\omega_a^2(\boldsymbol{q})-\omega^2\right]^2+\omega^2\Gamma_a^2(\boldsymbol{q})}$



$$\omega_{\mathrm{LA,TA}}(q) = v_{\mathrm{LA,TA}} \times q$$



Sound Velocity

Sound velocity from mechanical properties:

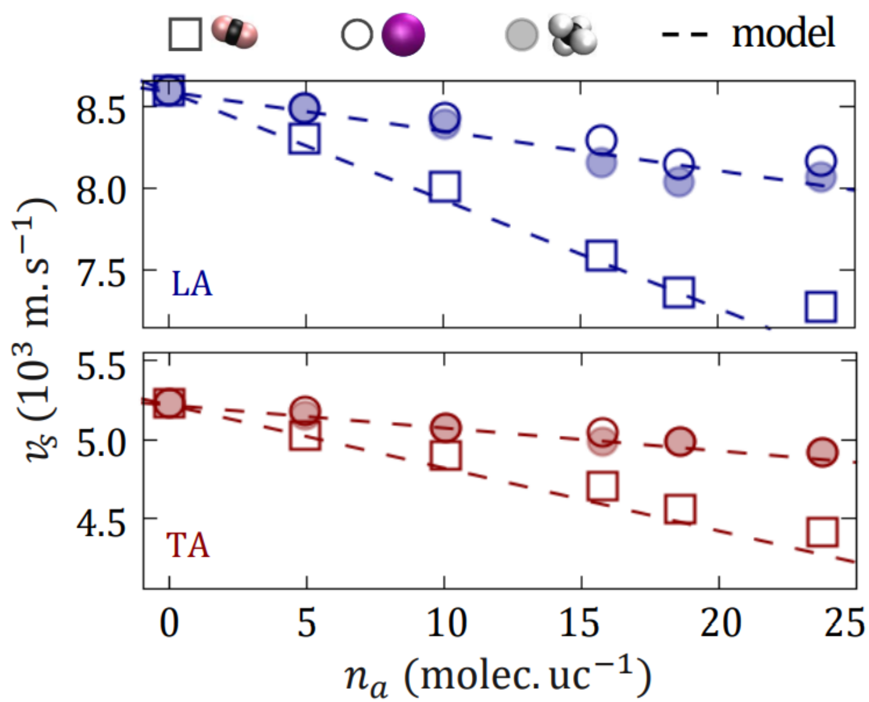
$$v_s(n_a) = \sqrt{\frac{C(n_a)}{\rho(n_a)}} \quad \text{with} \quad \rho(n_a) = \frac{m_s + m_a(n_a)}{V(n_a)}$$

Approximations: $C(n_a) \sim C_0$ and $V(n_a) \sim V_0$

Taylor development with $m_s \gg m_a$:

$$v_s = v_0(T)\left(1 - \frac{1}{2}\frac{m_a(n_a)}{m_s}\right)$$

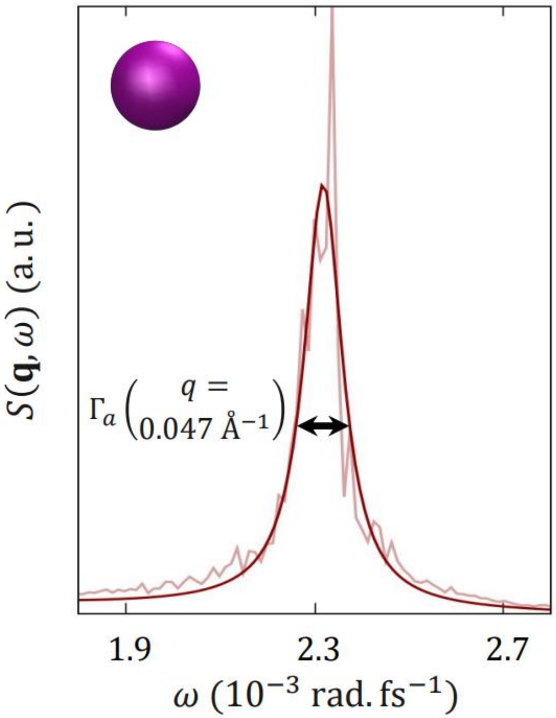
with $v_0(T) = \sqrt{\frac{C_0 V_0}{m_s}}$

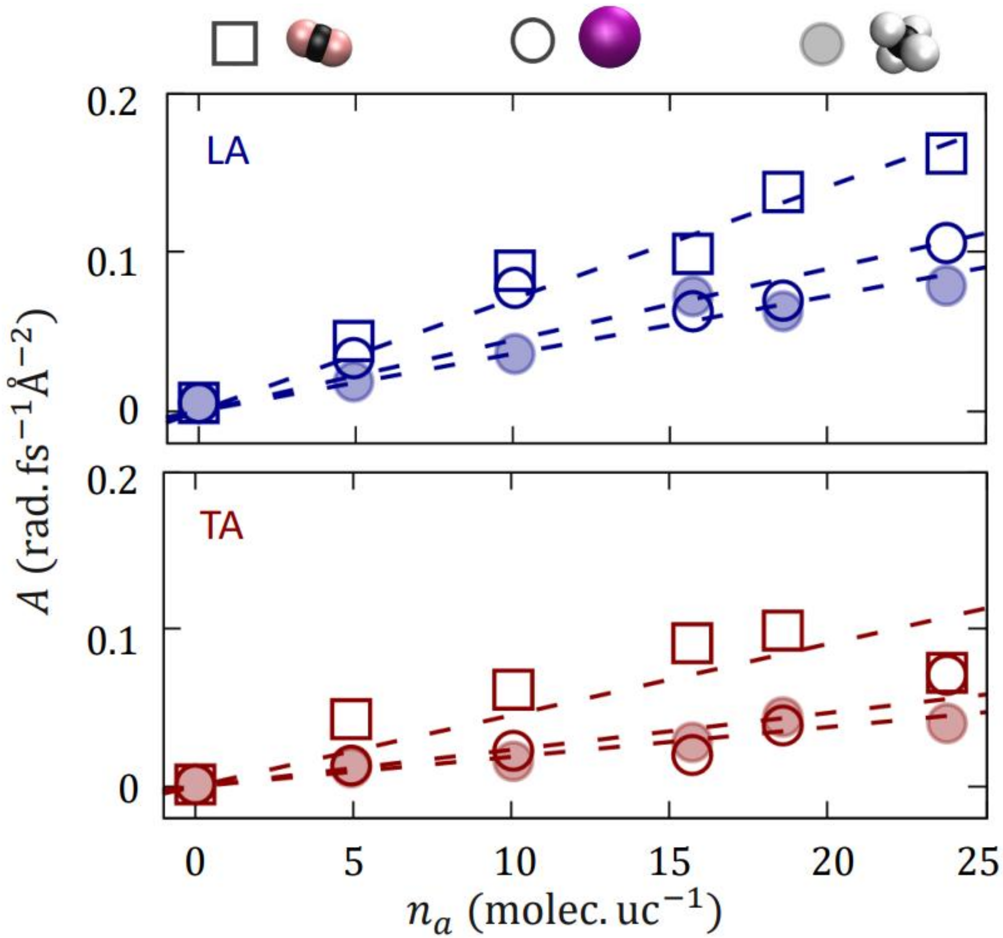


Sound Attenuation

$$S_a(n_a, \boldsymbol{q}, \omega) \xrightarrow[q\to 0]{} \frac{\Gamma_a(n_a,\boldsymbol{q})\,\omega_a^2(n_a,\boldsymbol{q})}{\left[\omega_a^2(n_a,\boldsymbol{q})-\omega^2\right]^2+\omega\Gamma_a^2(n_a,\boldsymbol{q})}$$

Sound attenuation: $\Gamma_a(n_a, q) \xrightarrow[q\to 0]{} A(n_a)\, q^2$





Conclusion

- Simple physical models – relying on available parameters – are available to describe thermal conductivity and sound propagation in fluid-filled nanoporous media

- Thermal conductivity shows an interesting rattle effect as phonon scattering occurs due to fluid/solid collisions

- Both sound propagation and attenuation – which are involved in thermal conductivity in fluid-filled nanoporous media – can be rationalized using a simple picture