

# Vibrational Properties Beyond Debye Model

Dehong Yu

*Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW 2234, Australia.*

The vibrational density of states (VDOS, denoted  $g(\omega)$ ) is a fundamental property of solid materials, determining their specific heat and thermal transport. For over 100 years, the Debye model has served the fundamental law for our understanding of the vibrational properties of bulk solid materials which show a low energy relationship of  $g(\omega) \propto \omega^2$ , where  $\omega$  is the frequency and  $g(\omega)$  is the number of modes within an energy/frequency interval. In this presentation, I will report the recent discoveries on systems where the Debye model failed.

Upon the transition from solid to liquid phase, the conventional stable phonon vibration modes in solid phase are replaced by more complex instable vibrational modes, called instantaneous normal modes (INM) at the liquid state. The INMs are consequences of the intrinsic anharmonic interaction potentials among the atoms in liquid phase. Due to the complicated potential landscape, it has been very difficult to analytically describe the vibrational phonon density of states (VDOS) of liquids until very recently. Zaccone and Baggioli [1] have recently developed a theoretic model based on overdamped Langevin liquid dynamics. Distinct from the Debye law,  $g(\omega) \propto \omega^2$ , for solids, the model for liquids reveals a linear relationship,  $g(\omega) \propto \omega$ , in the low-energy region. With inelastic neutron scattering, we confirmed this model on real liquid systems including water, liquid metal, and polymer liquids. We have applied this model and extracted the effective relaxation rate for the short time dynamics for these liquids [2].

Contrastingly, when the crystalline materials are confined in nanometre scale with reduced degrees of freedom, a crossover from the Debye  $\omega^2$  scaling to an  $\omega^3$  behaviour is discovered through measurement of the VDOS of amorphous ice confined inside graphene oxide membranes using inelastic neutron scattering. The experimental observation is well reproduced by molecular dynamics simulations. Theoretically, it is shown that the  $\omega^3$  behaviour results from the geometric constraints on the momentum phase space induced by confinement along one spatial direction [3].

[1] A. Zaccone and M. Baggioli, *Proc. Natl. Acad. Sci, USA* **118**, e2022303118 (2021).

[2] C. Stamper, D. Cortie, Z. Yue, X. L. Wang and D. H. Yu, *J. Phys. Chem. Lett.* **13**, 3105 (2022).

[3] Y. Yu, C. Yang, M. Baggioli, A. E. Philips, A. Zaccone, L. Zhang, R. Kajimoto, M. Nakamura, D H. Yu and L. Hong, *Nature Communications*, **13**, 3649, (2022).

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