Quasi Normal Modes in Liquids

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Complex atomic motion is frequently represented as collective excitations that delineate the dynamical modes of a system. Although liquids lack long-range order, they demonstrate surprisingly coherent vibrational dynamics, especially over short timescales and intermediate length scales. X-ray and neutron scattering experiments reveal dispersion phenomena in liquids often marked by quasi-Brillouin zones (QBZs). The diffuse nature of this dispersion often renders further modal analysis, particularly challenging. In this study, a dynamical framework grounded in the generalized Langevin equation (GLE) is established, using species-dependent momentum correlations. The ensuing dynamical matrix, which captures the oscillatory dynamics of the system, is defined independently of any reference configuration. We show that the dynamical matrix decomposes into three contributions that reflect distinct aspects of microscopic dynamics. The first is a harmonic term associated with the ensemble-averaged curvature of the potential energy surface, which governs the coherent restoring forces. The second is a tangential-coupling term that mixes longitudinal and transverse motion through non-affine, shear-like interactions; the third is a kinetic term that captures inertial transport of momentum.

Within the GLE framework, the collective excitations can be characterized as quasi-normal modes (QNMs) that capture both the characteristic frequencies and the temporal decays encoded in the GLE's memory kernel. This coupling naturally accommodates dissipation while simultaneously renormalizing the oscillatory response. As a result, each QNM is characterized by a frequency and a finite lifetime, reflecting the persistence of collective motion in the presence of a dissipative dynamical environment. QNMs, therefore, represent a direct generalization of phonons to liquid systems and offer a robust basis for probing the emergence and attenuation of coherence in fluctuating, disordered systems.

The proposed formalism is validated through atomistic simulations of two liquids systems – argon and molten potassium chloride. These simulations reveal the emergence of quasi-Brillouin zones, from which mode-dependent wave speeds are determined. By utilizing the decay times associated with the QNMs, the isotropic kinetic theory is applied to compute thermal conductivity of the aforementioned liquid systems by integrating over various wavevectors. Notably, the calculated thermal conductivities exhibit excellent agreement with available experimental data and independent evaluations performed using non-equilibrium molecular dynamics. Intriguingly, the QNMs that contribute most to liquid thermal conductivity lie in the intermediate wavevector band, particularly between the first and second peaks of the structure factor. We further show that the thermal conductivity converges to the correct value when the QNM propagation length, which is analogous to the mean free path of phononic systems, becomes smaller than the excitation distance.