Velocity Autocorrelation Function

Velocity autocorrelation function (VAC)

For a system of N atoms, the velocity autocorrelation function is defined as

$$Z(t) = \frac{\langle \vec{v}_i(t+t_0) \bullet \vec{v}_i(t_0) \rangle}{\langle \vec{v}_i(t_0) \bullet \vec{v}_i(t_0) \rangle} = \frac{\displaystyle\sum_{t_0} \sum_{i=0}^{N-1} \vec{v}_i(t+t_0) \bullet \vec{v}_i(t_0)}{\displaystyle\sum_{t_0} \sum_{i=0}^{N-1} \vec{v}_i(t_0) \bullet \vec{v}_i(t_0)} , \tag{1}$$

where $\vec{v}_i(t)$ is the velocity of the i-th atom at time t. The bracket denotes averages over atoms, i, and the time origin, t_0. We have omitted the division by the number of atoms and that of time origins for the averaging, since they cancel out between the numerator and denominator.

Note that $Z(t) = 1$ at time $t = 0$ by definition. For sufficiently large t, there will be no correlation between velocities and thus

$$Z(t) \xrightarrow[t\to\infty]{} \frac{\langle \vec{v}_i(t+t_0) \rangle \bullet \langle \vec{v}_i(t_0) \rangle}{\langle \vec{v}_i \bullet \vec{v}_i \rangle} = 0 , \tag{2}$$

since the average velocity is zero in thermal equilibrium without flow. In gas phase, ballistic motions of atoms are interrupted by collisions with other atoms. These collisions change the velocity of each atom and cause the loss of memory about its initial velocity. Accordingly, $Z(t)$ exhibits an exponential decay characterized by the collision time τ:

$$Z(t) = \exp(-t/\tau) . \tag{3}$$

Figure 1 shows $Z(t)$ for density $\rho = 0.1$ and temperature $T = 1.0$ in the Lennard-Jones unit. The red curve is a molecular-dynamics (MD) simulation result, whereas the blue dashed curve is the best exponential fit with the estimated collision time of $\tau = 1.3985$.
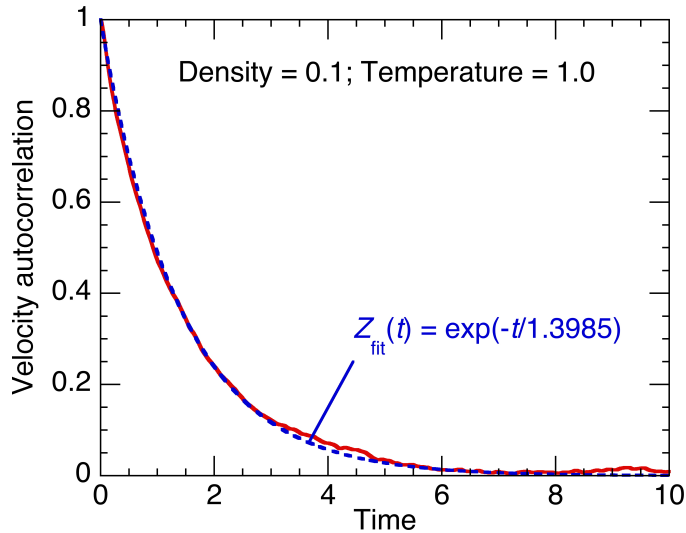

Figure 1: Gas-phase velocity autocorrelation function for Lennard-Jones atoms with density $\rho = 0.1$ and temperature $T = 1.0$.

In solid phase, atoms are vibrating around an equilibrium position, and atomic vibrations are described by the dynamical matrix, which is the second derivative of the potential energy with

respect to the atomic positions. Namely, atomic trajectories can be represented as a superposition of the eigenmodes (*i.e.*, phonons) of the dynamical matrix. As a result, $Z(t)$ is a superposition of sinusoidal curves with the eigenfrequencies. Figure 2 shows $Z(t)$ for density $\rho = 1.0$ and temperature $T = 0.1$ in the Lennard-Jones unit.
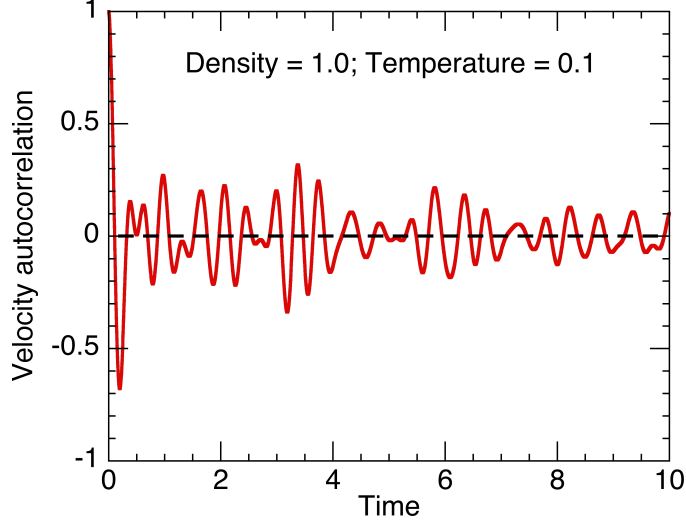

Figure 2: Solid-phase velocity autocorrelation function for Lennard-Jones atoms with density $\rho = 1.0$ and temperature $T = 0.1$.

Phonon Density of States (DOS) and Fourier transform

We can find the phonon frequencies that constitute $Z(t)$ by decomposing it into a sum of sinusoidal curves, namely by performing Fourier transform. To do so, first note that

$$Z(t) \propto \langle \vec{v}(t) \bullet \vec{v} \rangle = \langle \vec{v} \bullet \vec{v}(-t) \rangle = \langle \vec{v}(-t) \bullet \vec{v} \rangle = Z(-t). \tag{4}$$

Here, the first equality arises from the time invariance (*i.e.*, the statistical quantity should not change by shifting the time origin by t), and the second equality is obtained by the commutative property of the inner product. Using Eq. (4), the Fourier transform is calculated as

$$
\begin{aligned}
\tilde{Z}(\omega) &\equiv \int_{-\infty}^{\infty} dt Z(t) e^{i\omega t} \\
&= \int_{-\infty}^{0} dt Z(t) e^{i\omega t} + \int_{0}^{\infty} dt Z(t) e^{i\omega t} \\
&= \int_{0}^{\infty} dt' \underbrace{Z(-t')}_{=Z(t')} e^{-i\omega t'} + \int_{0}^{\infty} dt Z(t) e^{i\omega t} \quad (t' = -t) \\
&= 2 \int_{0}^{\infty} dt Z(t) \cos(\omega t)
\end{aligned}
\tag{5}
$$

In practice, we only sample $Z(t)$ for a finite time interval, $[0, t_{\max}]$ during MD simulation. We then calculate the spectral function as

$$\tilde{Z}(\omega) = 2 \int_{0}^{t_{\max}} dt Z(t) \exp\left(-(t / \tau_{\text{damping}})^2\right) \cos(\omega t). \tag{6}$$

2

Here, τ_{damping} is a damping time to smoothen out the numerical artifact due to the finite-time truncation at $t = t_{\mathrm{max}}$. Here, we use $\tau_{\mathrm{damping}} = t_{\mathrm{max}}/\sqrt{3}$. Figure 3 shows $\tilde{Z}(\omega)$ calculated from the solid-phase $Z(t)$ in Fig. 2.
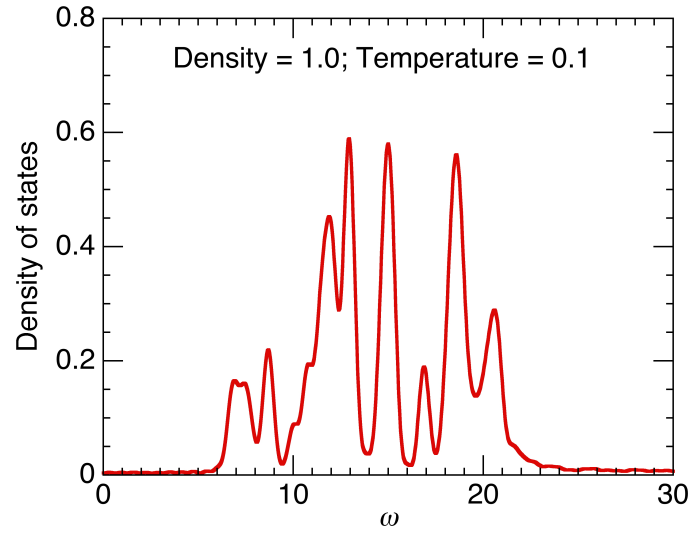

Figure 3: Solid-phase phonon density of states for Lennard-Jones atoms with density $\rho = 1.0$ and temperature $T = 0.1$.