form:

$$U(\mathbf{r}) = U(\mathbf{r_0}) - \mathbf{F} \bullet \mathbf{z} + \frac{1}{2}\mathbf{r^T} \bullet \mathbf{H} \bullet \mathbf{z} \tag{6}$$

where $\mathbf{z_i} = \sqrt{m_i}(\mathbf{r_i} - \mathbf{r_0})$ are the mass-scaled position coordinates of a particle i. The first and second derivatives of $U(\mathbf{r})$ with respect to the vector $\mathbf{z}$ are the force and the Hessian matrix, denoted by $\mathbf{F}$ and $\mathbf{H}$ respectively. The eigenvalues of the Hessian $\mathbf{H}$ are $(\{\omega_i^2\}, i = 1, 3N)$ representing the squares of normal mode frequencies, and $\mathbf{W}(\mathbf{r})$ are the corresponding eigenvectors. In a stable solid, $\mathbf{r_0}$ can be conveniently taken as the global minimum of the potential energy surface $U(R)$, which implies that $\mathbf{F} = 0$ and $\mathbf{H}$ has only positive eigenvalues corresponding to oscillatory modes. The INM approach for liquids interprets $\mathbf{r}$ as the configuration at time t relative to the configuration $\mathbf{r_0}$ at time t_0. Since typical configurations, $\mathbf{r_0}$ are extremely unlikely to be local minima, therefore $\mathbf{F} \neq 0$ and $\mathbf{H}$ will have negative eigenvalues. The negative eigenvalue modes are those which sample negative curvature regions of the PES, including barrier crossing modes. The ensemble-averaged INM spectrum, $\langle f(\omega) \rangle$, is defined as

$$f(\omega) = \langle \frac{1}{3N} \sum_{i=1}^{3N} \delta(\omega - \omega_i) \rangle. \tag{7}$$

Quantities that are convenient for characterizing the instantaneous normal mode spectrum are: (i) the fraction of imaginary frequencies, namely

$$F_{im} = \int_{im} f(\omega) d\omega \tag{8}$$

where the subscript in means that the integral is performed only in the imaginary branch; (ii) the fraction of real frequencies, that is

$$F_r = \int_r f(\omega) d\omega \tag{9}$$

where the subscript r indicates that the integral is performed only in the real branch and (ii) the mean square or Einstein frequency, ω_E, given by

$$\begin{aligned} \omega_E^2 &= \int \omega^2 f(\omega) d\omega \\ &= \frac{\langle Tr\mathbf{H} \rangle}{m(3N-3)} \end{aligned} \tag{10}$$

where the last equality comes from using Eq. (7) and $\langle Tr\mathbf{H} \rangle$ is the ensemble-averaged value of the trace of the Hessian.