

Supplementary Material

Boson peak, elasticity, and glass transition temperature in polymer glasses: Effects of the rigidity of chain bending

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S.1. FORMALISM OF THE HESSIAN MATRIX

The Hessian matrix of the interaction potential $U(\mathbf{r})$ is generally expressed as follows:

$$H_{nm}^{ab} = \frac{\partial^2 U(\mathbf{r})}{\partial r_n^a \partial r_m^b} \quad (a, b = x, y, z) \quad (\text{S.1})$$

where n and m denote the particle number index ($n, m=1, 2, \dots, N_p$). As given in Ref. [S1], the following expressions are useful using a generic argument z for the first and second derivatives of $U(z)$:

$$\frac{\partial U(z)}{\partial x} = \frac{\partial U(z)}{\partial z} \frac{\partial z}{\partial x}, \quad (\text{S.2})$$

$$\frac{\partial^2 U(z)}{\partial x \partial y} = \frac{\partial^2 U(z)}{\partial^2 z} \frac{\partial z}{\partial x} \frac{\partial z}{\partial y} + \frac{\partial U(z)}{\partial z} \frac{\partial^2 z}{\partial x \partial y} = c \frac{\partial z}{\partial x} \frac{\partial z}{\partial y} + t \frac{\partial^2 z}{\partial x \partial y}. \quad (\text{S.3})$$

S.1 (a). Two-body interaction

For two-body interactions (FENE and LJ potentials), the distance between particles i and j , $z = |\mathbf{r}_j - \mathbf{r}_i| = r_{ij}$ is used and the following relationships are obtained:

$$H_{nm}^{ab} = \frac{\partial^2 U(r_{ij})}{\partial r_n^a \partial r_m^b} = c_{ij} \frac{\partial r_{ij}}{\partial r_n^a} \frac{\partial r_{ij}}{\partial r_m^b} + t_{ij} \frac{\partial^2 r_{ij}}{\partial r_n^a \partial r_m^b}, \quad (\text{S.4})$$

with

$$c_{ij} = \frac{\partial^2 U(r_{ij})}{\partial r_{ij}^2}, \quad t_{ij} = \frac{\partial U(r_{ij})}{\partial r_{ij}}, \quad (\text{S.5})$$

and

$$\frac{\partial r_{ij}}{\partial r_n^a} = (\delta_{nj} - \delta_{ni}) \hat{n}_{ij}^a, \quad (\text{S.6})$$

$$\frac{\partial^2 r_{ij}}{\partial r_n^a \partial r_m^b} = \frac{1}{r_{ij}} (\delta_{nj} - \delta_{ni}) (\delta_{mj} - \delta_{mi}) (\delta_{ab} - \hat{n}_{ij}^a \hat{n}_{ij}^b), \quad (\text{S.7})$$

where, $\hat{n}_{ij} = \mathbf{r}_{ij}/r_{ij}$ is the unit vector between the particles i and j . These expressions are same as those presented in Ref. [S1].

S.1 (b). Three-body interaction

For three-body interactions (bending potential), the bond angle of particles i , j , and k is used as follows:

$$z = \theta_{ijk} = \arccos \frac{(\mathbf{r}_j - \mathbf{r}_i) \cdot (\mathbf{r}_k - \mathbf{r}_i)}{r_{ij} r_{ki}} = \arccos A_{ijk}, \quad (\text{S.8})$$

hence,

$$H_{nm}^{ab} = \frac{\partial^2 U(\theta_{ijk})}{\partial r_n^a \partial r_m^b} = \tilde{c}_{ijk} \frac{\partial \theta_{ijk}}{\partial r_n^a} \frac{\partial \theta_{ijk}}{\partial r_m^b} + \tilde{t}_{ijk} \frac{\partial^2 \theta_{ijk}}{\partial r_n^a \partial r_m^b} \quad (\text{S.9})$$

with

$$\tilde{c}_{ijk} = \frac{\partial^2 U(\theta_{ijk})}{\partial \theta_{ijk}^2}, \quad \tilde{t}_{ijk} = \frac{\partial U(\theta_{ijk})}{\partial \theta_{ijk}}. \quad (\text{S.10})$$

This following expression is obtained:

$$H_{nm}^{ab} = \frac{\tilde{c}_{ijk}}{\sin^2 \theta_{ijk}} \frac{\partial A_{ijk}}{\partial r_n^a} \frac{\partial A_{ijk}}{\partial r_m^b} - \frac{\tilde{t}_{ijk}}{\sin \theta_{ijk}} \left[\frac{\cos \theta_{ijk}}{\sin^2 \theta_{ijk}} \frac{\partial A_{ijk}}{\partial r_n^a} \frac{\partial A_{ijk}}{\partial r_m^b} + \frac{\partial^2 A_{ijk}}{\partial r_n^a \partial r_m^b} \right], \quad (\text{S.11})$$

with

$$\begin{aligned} \frac{\partial A_{ijk}}{\partial r_n^a} &= \frac{1}{r_{ij}} (\delta_{nj} - \delta_{ni}) (\hat{n}_{ik}^a - \hat{n}_{ij}^a \cos \theta_{ijk}) + \frac{1}{r_{ik}} (\delta_{nk} - \delta_{ni}) (\hat{n}_{ij}^a - \hat{n}_{ik}^a \cos \theta_{ijk}), \\ \frac{\partial^2 A_{ijk}}{\partial r_n^a \partial r_m^b} &= \frac{\delta_{ji}^n \delta_{ji}^m}{r_{ij}^2} \left[(3\hat{n}_{ij}^a \hat{n}_{ij}^b - \delta_{ab}) \cos \theta_{ijk} - (\hat{n}_{ik}^a \hat{n}_{ij}^b + \hat{n}_{ij}^a \hat{n}_{ik}^b) \right] \\ &\quad + \frac{\delta_{ji}^n \delta_{ki}^m}{r_{ij} r_{ik}} \left[\delta_{ab} + \hat{n}_{ij}^a \hat{n}_{ik}^b \cos \theta_{ijk} - (\hat{n}_{ik}^a \hat{n}_{ik}^b + \hat{n}_{ij}^a \hat{n}_{ij}^b) \right] \\ &\quad + \frac{\delta_{ki}^n \delta_{ji}^m}{r_{ij} r_{ik}} \left[\delta_{ab} + \hat{n}_{ik}^a \hat{n}_{ij}^b \cos \theta_{ijk} - (\hat{n}_{ik}^a \hat{n}_{ik}^b + \hat{n}_{ij}^a \hat{n}_{ij}^b) \right] \\ &\quad + \frac{\delta_{ki}^n \delta_{ki}^m}{r_{ik}^2} \left[(3\hat{n}_{ik}^a \hat{n}_{ik}^b - \delta_{ab}) \cos \theta_{ijk} - (\hat{n}_{ij}^a \hat{n}_{ik}^b + \hat{n}_{ik}^a \hat{n}_{ij}^b) \right]. \end{aligned} \quad (\text{S.12})$$

The differences between the proposed calculation and the expression defined in Ref. [S1] arise from Eq. (S.7) and the second term in the r.h.s. of Eq. (S.11). The overall profile of the vDOS $g(\omega)$ is not affected by implementing the diagonalization of the Hessian matrix using the expressions in Ref. [S1]. A certain number of negative frequency eigenmodes that have been reported in Ref. [S1] have also been observed. On the contrary, the presented results of $g(\omega)$ using Eqs. (S.7) and (S.11) do not exhibit any negative eigenfrequency modes (see Fig. 4 in the main text).

[S1] R. Milkus, C. Ness, V. V. Palyulin, J. Weber, A. Lapkin, and A. Zaccone, *Macromolecules* **51**, 1559 (2018).