Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information of "Thermal transport in amorphous small organic materials: A mechanistic study"

1. Molecular structure

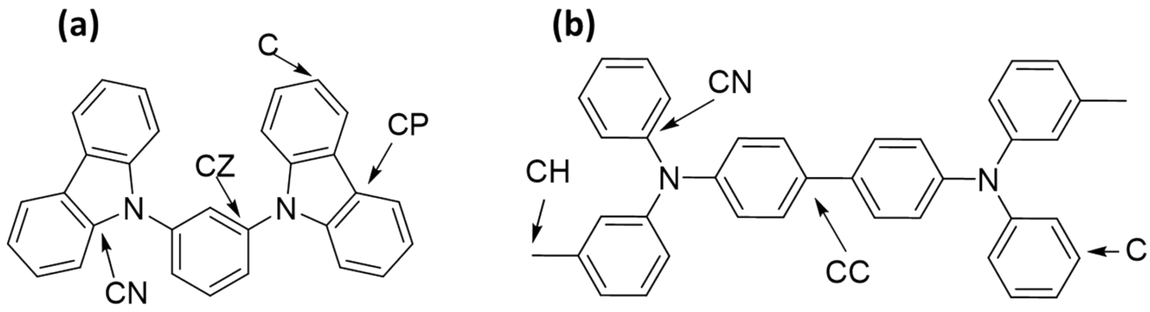

Fig. S1. Molecular formula of mCP (left) and TPD (right).

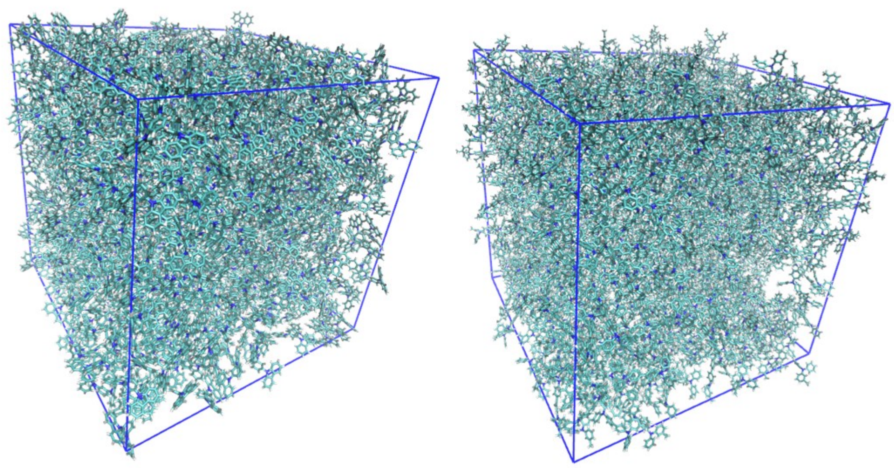

Fig. S2. Morphology of amorphous mCP (left) and TPD (right).

2. Force Field

In this work, we apply the OPLS force field to describe the interatomic interactions. In OPLS force field, there are four terms to describe the full force field, i.e., bond, angle, dihedral and improper. For bond, angle and improper, the potential energy is described by the harmonic potential with the following expression:

$$E^i(\xi) = \frac{1}{2}k^i(\xi - \xi_0)^2$$

Where k^i is force constant corresponding to bond/angle/improper, and ξ_0 is the equilibrium bond length or angle. The dihedral potential is described by the Ryckaert-Bellemans function:

$$E^d(\varphi) = \sum_{n=0}^{N} C_n[\cos(\varphi - 180°)]^n$$

Where n corresponds to n minimum points from 0 to 360 degrees, C_n is the dihedral constant.

We adopted the force field parameters of rigid fragments from literatures while the soft bonds such as dihedral, angle and improper connecting two rigid fragments are parametrized based on quantum chemistry calculations.

Table S1 OPLS Parameters Used in the Simulations

TPD						
Bond length	Force constant (kcal/mol Å^2)			Equilibrium (Å)		
C-C	392.4			1.40		
C-CC	392.4			1.40		
C-CN	392.4			1.40		
C-CH	392.4			1.50		
CC-CC	392.4			1.50		
CN-N	392.4			1.42		
C-H	307.1			1.09		
CH-H	307.1			1.09		
Bond angle	Force constant (kcal/mol rad^2)			Equilibrium (deg)		
C-C-C	527.0			120.0		
C-CN-C	527.0			118.0		
CN-C-C	527.0			120.0		
C-CN-N	286.0			120.0		
CN-N-CN	400.0			120.0		
CC-C-C	527.0			121.0		
C-CC-C	527.0			118.1		
CC-C-CN	527.0			121.0		
C-CC-CH	385.0			120.0		
C-C-H	292.9			120.0		
CC-C-H	292.9			120.0		
CN-C-H	292.9			120.0		
CC-CH-H	292.9			111.0		
H-CH-H	292.9			107.0		
Improper angle	Force constant (kcal/mol)			Phase angle (deg)		
X-C-C-X	167.4			180.0		
X-C-CN-X	167.4			180.0		
X-C-CC-X	167.4			180.0		
N-CN-CN-CN	25.0			180.0		
CN-C-C-N	740.0			180.0		
CC-C-C-CH	515.0			180.0		
CC-C-C-C	477.0			180.0		
Dihedral angle	Ryckaert-Bellemans constant (kcal/mol)					
	C_0	C_1	C_2	C_3	C_4	C_5
C-CC-CC-C	8.9636	0.0313	-29.6793	-0.2072	19.9632	0.1656
C-CN-N-CN	50.6415	1.5540	-28.6706	1.1613	-21.7435	-2.7452
Van der waals	ε (eV)			σ (nm)		

<table>
<tr><td>C</td><td colspan="3">0.293</td><td colspan="3">0.355</td></tr>
<tr><td>CC</td><td colspan="3">0.293</td><td colspan="3">0.355</td></tr>
<tr><td>CN</td><td colspan="3">0.293</td><td colspan="3">0.355</td></tr>
<tr><td>N</td><td colspan="3">0.711</td><td colspan="3">0.325</td></tr>
<tr><td>H</td><td colspan="3">0.126</td><td colspan="3">0.242</td></tr>
<tr><th colspan="7">mCP</th></tr>
<tr><th>Bond length</th><th colspan="3">Force constant (kcal/mol Å^2)</th><th colspan="3">Equilibrium (Å)</th></tr>
<tr><td>C-C</td><td colspan="3">392.4</td><td colspan="3">1.40</td></tr>
<tr><td>C-CZ</td><td colspan="3">322.2</td><td colspan="3">1.40</td></tr>
<tr><td>C-CP</td><td colspan="3">392.4</td><td colspan="3">1.40</td></tr>
<tr><td>C-CN</td><td colspan="3">392.4</td><td colspan="3">1.40</td></tr>
<tr><td>CZ-N</td><td colspan="3">392.4</td><td colspan="3">1.42</td></tr>
<tr><td>CN-N</td><td colspan="3">349.8</td><td colspan="3">1.42</td></tr>
<tr><td>C-H</td><td colspan="3">307.1</td><td colspan="3">1.08</td></tr>
<tr><th>Bond angle</th><th colspan="3">Force constant (kcal/mol rad^2)</th><th colspan="3">Equilibrium (deg)</th></tr>
<tr><td>C-C-CZ</td><td colspan="3">527.0</td><td colspan="3">120.0</td></tr>
<tr><td>C-CZ-C</td><td colspan="3">527.0</td><td colspan="3">120.0</td></tr>
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<tr><td>C-C-CP</td><td colspan="3">527.0</td><td colspan="3">120.0</td></tr>
<tr><td>C-CN-CP</td><td colspan="3">527.0</td><td colspan="3">120.0</td></tr>
<tr><td>C-CP-CN</td><td colspan="3">527.0</td><td colspan="3">120.0</td></tr>
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<tr><td>CN-N-CN</td><td colspan="3">585.8</td><td colspan="3">108.4</td></tr>
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<tr><td>C-CN-N</td><td colspan="3">585.8</td><td colspan="3">131.0</td></tr>
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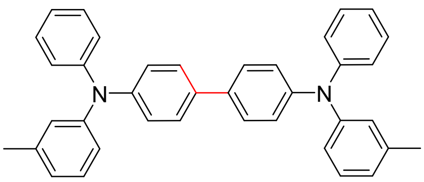
<tr><td>C-C-H</td><td colspan="3">292.0</td><td colspan="3">120.0</td></tr>
<tr><th>Improper angle</th><th colspan="3">Force constant (kcal/mol)</th><th colspan="3">Phase angle (deg)</th></tr>
<tr><td>X-C-C-X</td><td colspan="3">167.0</td><td colspan="3">180.0</td></tr>
<tr><td>X-C-CZ-X</td><td colspan="3">167.0</td><td colspan="3">180.0</td></tr>
<tr><td>X-C-CP-X</td><td colspan="3">167.0</td><td colspan="3">180.0</td></tr>
<tr><td>X-C-CN-X</td><td colspan="3">167.0</td><td colspan="3">180.0</td></tr>
<tr><td>CN-CP-N-C</td><td colspan="3">516.5</td><td colspan="3">180.0</td></tr>
<tr><td>N-CN-CN-CZ</td><td colspan="3">235.0</td><td colspan="3">180.0</td></tr>
<tr><th rowspan="2">Dihedral angle</th><th colspan="6">Ryckaert-Bellemans constant (kcal/mol)</th></tr>
<tr><th>C_0</th><th>C_1</th><th>C_2</th><th>C_3</th><th>C_4</th><th>C_5</th></tr>
<tr><td>CN-N-CZ-C</td><td>14.5527</td><td>0.6824</td><td>-14.7613</td><td>-3.6577</td><td>-6.0691</td><td>4.0042</td></tr>
<tr><th>Van der waals</th><th colspan="3">ε (eV)</th><th colspan="3">σ (nm)</th></tr>
<tr><td>C</td><td colspan="3">0.293</td><td colspan="3">0.355</td></tr>
<tr><td>CZ</td><td colspan="3">0.293</td><td colspan="3">0.355</td></tr>
</table>

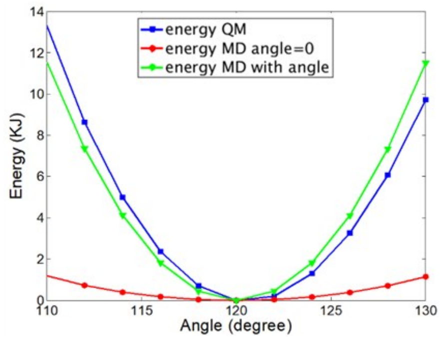
CN	0.293	0.355
CP	0.293	0.355
N	0.711	0.325
H	0.126	0.242

To fit the parameters of soft "bonds", we first use the Gaussian 09 package[1] to perform a scan with different dihedral, angle or improper. The DFT energy calculation is done in the level of B3LYP/6-311(d,p). The energy at each angle is then obtained and illustrated by the curve "energy QM". After that, we use the Gromacs package to do the scan again by setting the parameters of corresponding "bonds" to be zero, which means that the energy of the corresponding "bond" is not considered. The obtained energy is demonstrated by the curve "energy MD dihedral=0". As a result, the energy difference between the two curves is regarded as the potential energy of the corresponding "bond" and this difference can be fitted by the functional types of the corresponding "bond".

TPD

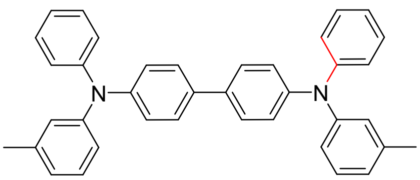
Angles

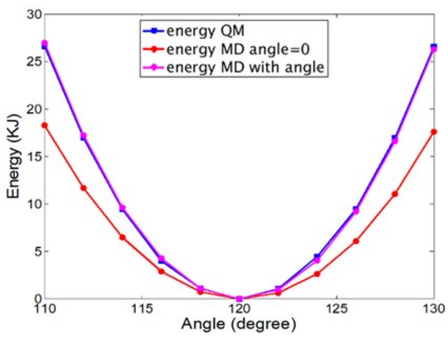




C-CC-CC

$k_{ij} = 422.0$ $\theta_0 = 120°$

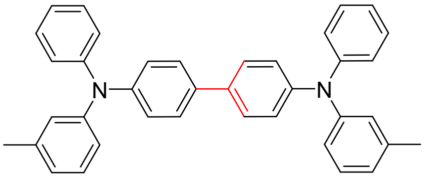


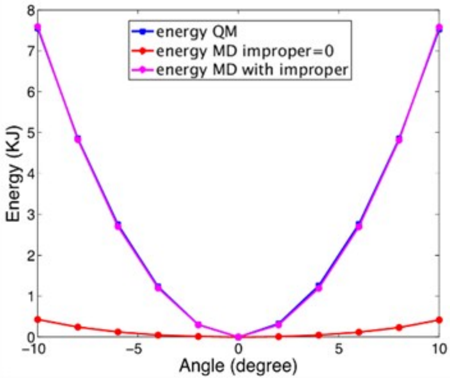


C-CN-N

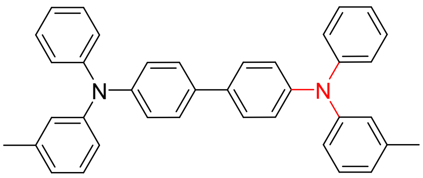
$k_{ij} = 286.0$ $\theta_0 = 120°$

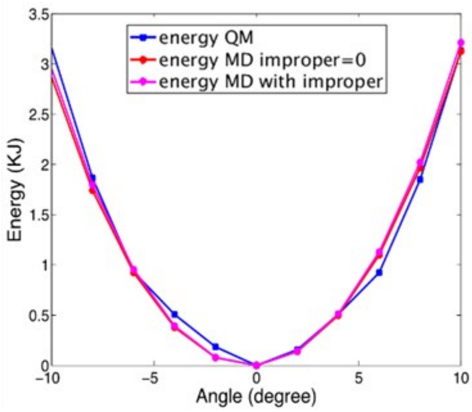
Impropers



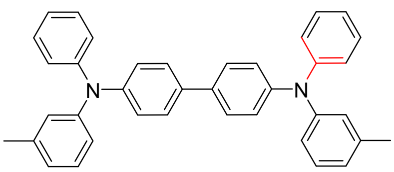


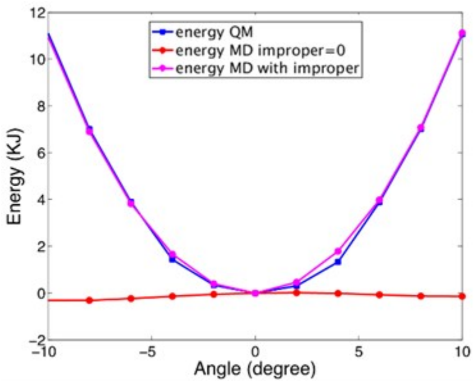
CC-C-C-C
k_{ijk}= 477.0 theta0= 0



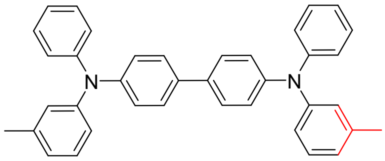


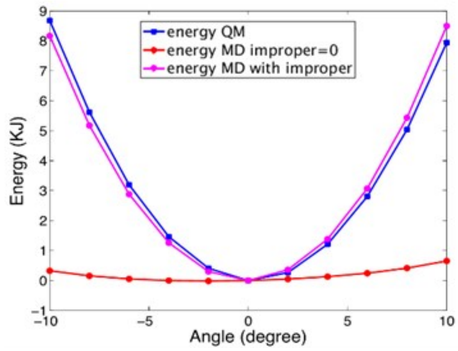
N-CN-CN-CN
k_{ijk}= 25 theta0 = 0





CN-C-C-N
k_{ijk} = 740 theta0 = 0

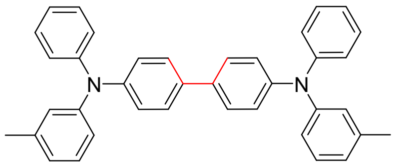


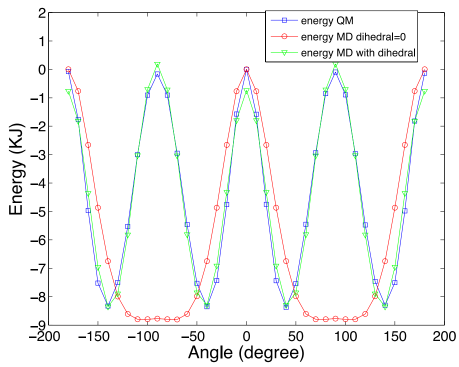


CC-C-C-CH

k_{ijk} = 515.0 theta0=0

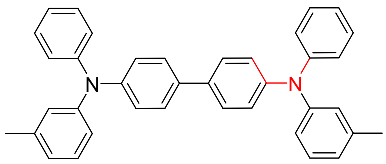
Dihedrals

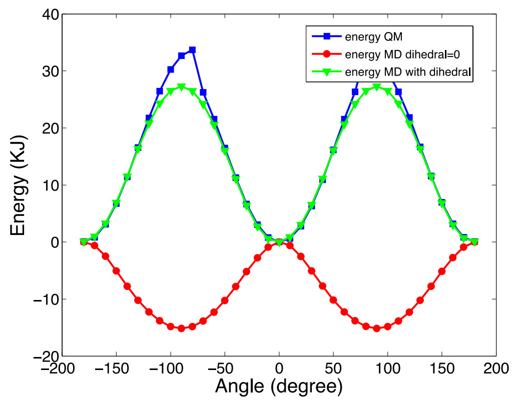




C-CC-CC-C

$a_0 \sim a_5$= 8.9636 0.0313 -29.6793 -0.2072 19.9632 0.1656



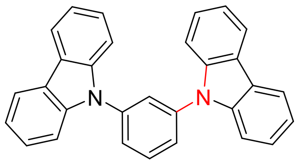


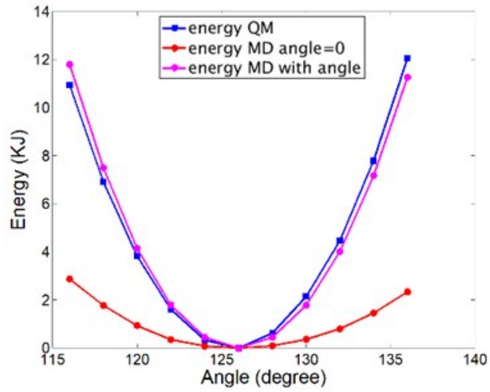
C-CN-N-CN

$a_0 \sim a_5$ = 50.6415 1.5540 -28.6706 1.1613 -21.7435 -2.4752

mCP

Angles

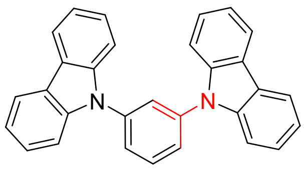


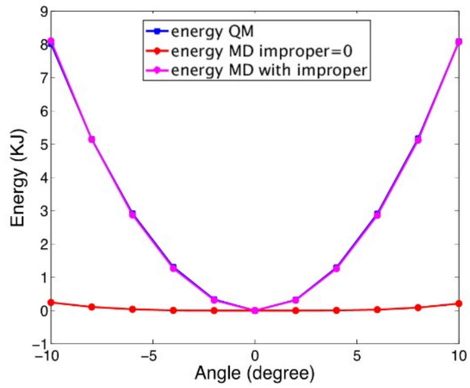


CN-N-CZ

k_{ij} = 332.0 theta0 = 125.80

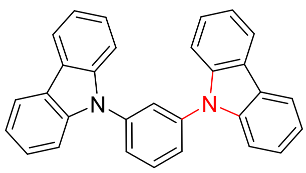
Improper

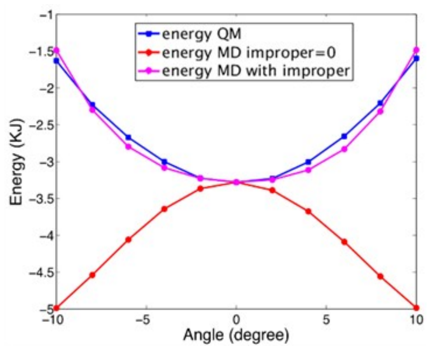




CN-CP-N-C

k_{ijk} = 516.50 theta0 = 0

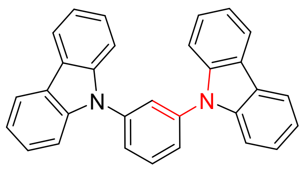


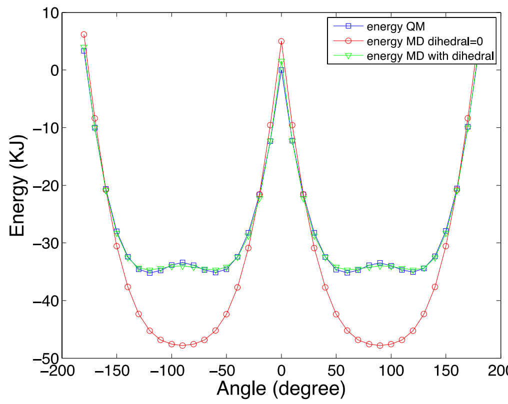


C-CN-CN-CZ

k_{ijk} = 235.00 theta0 = 0

Dihedrals





CN-N-CZ-C

$a_0 \sim a_5$ = 14.5527   0.6824

-14.7613   -3.6577   -6.0691

4.0042

Figure S3. Quantum mechanics and molecular dynamics energy scan for the soft bonds.

3. EMD results

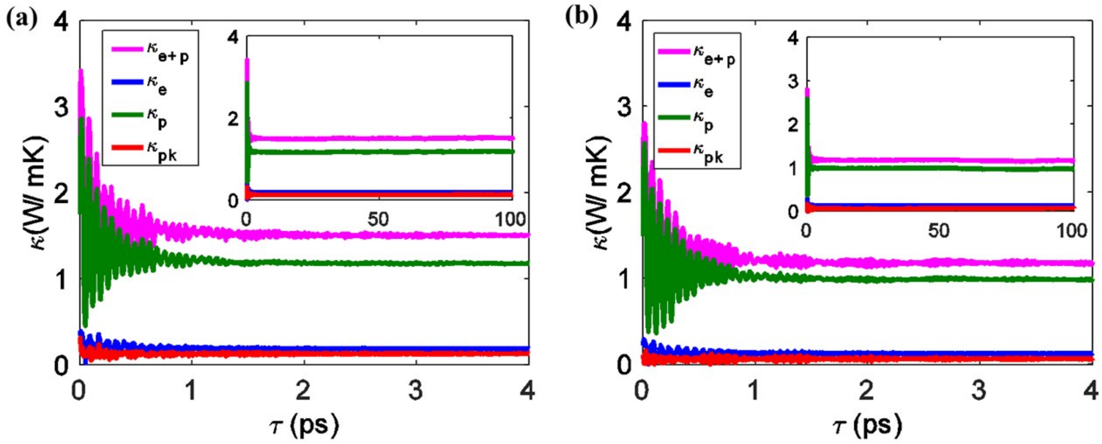


Figure S4. Thermal conductivities from the kinetic heat flux (κ_e), the potential heat flux (κ_p) and the total heat flux (κ_{e+p}) versus the correlation time for TPD (a), mCP (b) with correlation time τ. κ_{e+p}, κ_p, κ_e and κ_{pk} represent the TC calculated based on the autocorrelation of the total heat flux (pink line), the Virial heat flux (green line), the convective heat flux (blue line), and based on the cross-correlation between convective and Virial heat flux (red line), respectively.

Table S2. The converged TCs based on the autocorrelation of the total heat flux (κ_{e+p}), the Virial heat flux (κ_p), the convective heat flux (κ_e), and based on the cross-correlation between convective and Virial heat flux (κ_{pk}) at 300 K, respectively

	κ_{e+p}	κ_e	κ_p	κ_{pk}
TPD	1.497	0.193	1.176	0.133
mCP	1.183	0.127	0.999	0.060

Table S3. Longitudinal (vp) and shear (vs) velocities of mCP and TPD under 0 and 3 GPa.

	mCP		TPD	
Pressure	0 GPa	3 GPa	0 GPa	3 GPa
v_p (km/s)	3.18	4.45	3.4	5.43
v_s (km/s)	1.77	1.94	1.75	2.11

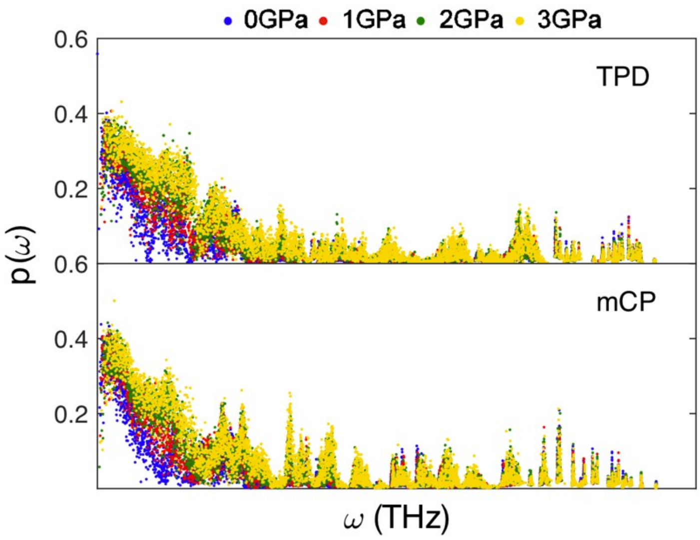


Figure S5. Mode participation ratio under different pressures.

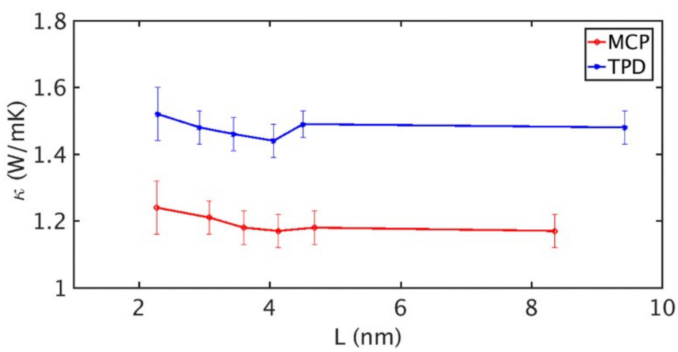


Figure S6. Convergence test of thermal conductivity calculations.

References:

1. Frisch, M.; Trucks, G.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G., Gaussian 09, revision D. 01. Gaussian, Inc., Wallingford CT: 2009.

2. Hess, B.; Kutzner, C.; Van Der Spoel, D.; Lindahl, E., GROMACS 4: algorithms for highly efficient, load-balanced, and scalable molecular simulation. *Journal of chemical theory and computation* **2008,** *4* (3), 435-447.