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Dynamic odd-even effect in n-alkane systems: A molecular dynamics study

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Molecule	**Unit cell dimensions**	**Unit cell multiplicity**
Propane	a = 4.14800 b = 12.61200 c = 6.97700; α = 90.0000 β = 91.2800 γ = 90.0000	7 × 3 × 5
Butane	a = 5.70270 b = 5.52470 c = 8.38900; α = 90.0000 β = 115.2200 γ = 90.0000	6 × 6 × 4
Pentane	a = 4.13570 b = 9.02500 c = 14.81600; α = 90.0000 β = 90.0000 γ = 90.0000	8 × 4 × 2
Hexane	a = 4.13090 b = 4.69630 c = 8.53900; α = 83.4000 β = 87.2650 γ = 75.1720	8 × 8 × 4
Heptane	a = 4.11600 b = 4.68600 c = 20.34800; α = 78.1100 β = 81.7900 γ = 74.2500	8 × 8 × 2
Octane	a = 4.12300 b = 4.68600 c = 10.97400; α = 85.0600 β = 83.7200 γ = 75.100	8 × 8 × 3

Table S1: Structural details with unit cell dimensions and the related multiplicity values for n - alkanes.

Temperature dependence of Density

Density as a function of temperature is obtained by performing simulations using NPT ensemble for 1.2 ns.

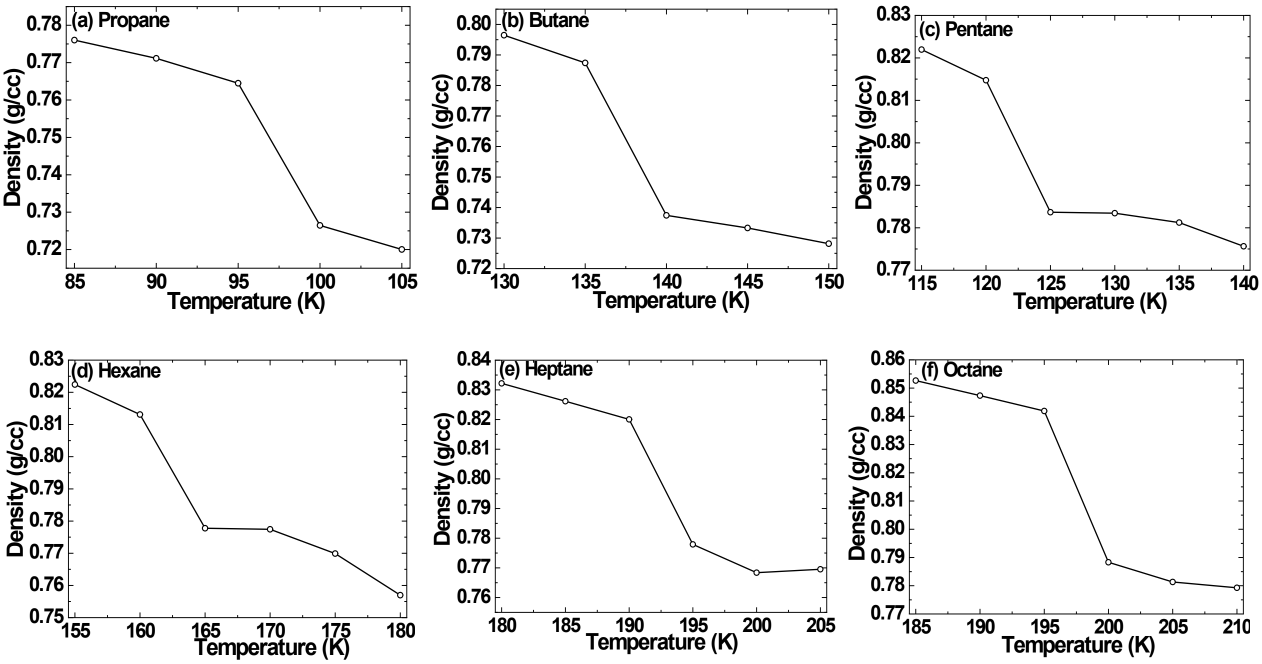
(a) Propane
Density (g/cc)
0.72
0.73
0.74
0.75
0.76
0.77
0.78
85
90
95
100
105
Temperature (K)
(b) Butane
Density (g/cc)
0.72
0.73
0.74
0.75
0.76
0.77
0.78
0.79
0.80
130
135
140
145
150
Temperature (K)
(c) Pentane
Density (g/cc)
0.77
0.78
0.79
0.80
0.81
0.82
0.83
115
120
125
130
135
140
Temperature (K)
(d) Hexane
Density (g/cc)
0.75
0.76
0.77
0.78
0.79
0.80
0.81
0.82
0.83
155
160
165
170
175
180
Temperature (K)
(e) Heptane
Density (g/cc)
0.76
0.77
0.78
0.79
0.80
0.81
0.82
0.83
0.84
180
185
190
195
200
205
Temperature (K)
(f) Octane
Density (g/cc)
0.77
0.78
0.79
0.80
0.81
0.82
0.83
0.84
0.85
0.86
185
190
195
200
205
210
Temperature (K)

Figure S1: Density as a function of temperature obtained from NPT simulations for all the alkane (a) propane (b) butane (c) pentane (d) hexane (e) heptane and (f) octane molecules.

Structural Details

The orientation order parameter, s(t), is a calculation characterizing the alignment of a system, suitable for intrinsically anisotropic materials, such as liquid crystals. S is given by the equation below,

$$s(t) = \left\langle \frac{3}{2}\cos\theta(t) - \frac{1}{2} \right\rangle$$

where θ(t) denote the angle made by the molecular axis with respect to the reference direction and ⟨⟩ denotes an average ensemble. For all alkanes, except butane, order parameter value increases from - 0.5 to - 0.2. This implies the change in orientation from anti-parallel / parallel to completely random alignment with respect to the reference direction, indicating that system changes from crystalline to liquid state. For butane, initial crystalline state is in a partially alignment with s = 0.25 and with increasing temperature goes to completely random alignment at s = 0. The calculations are plotted in Figure S1.

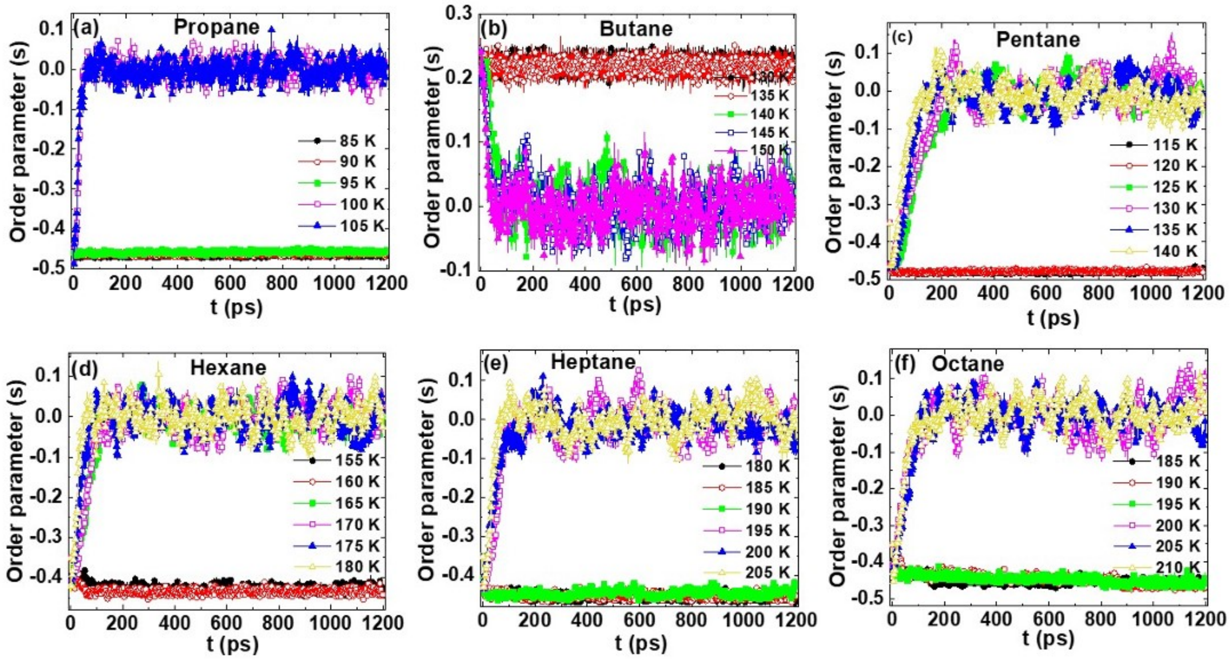

Figure S2: Orientational order parameter (s) calculated for all the alkane as a function of temperature for (a) propane (b) butane (c) pentane (d) hexane (e) heptane and (f) octane molecules.

The orientation distribution function (ODF) is a measure of molecular orientation aligned at an angle (θ) with Cartesian directions (x, y, z). In the crystalline state, molecules depict preferred orientation with respect the Cartesian directions (x, y, z) and therefore the ODF exhibits sharp distinct peaks. In liquid state the orientation is isotropic along all directions, which is represented by shallow and uniform overlapping peaks (for all x, y, and z directions) with a smooth maximum at 90 degrees.

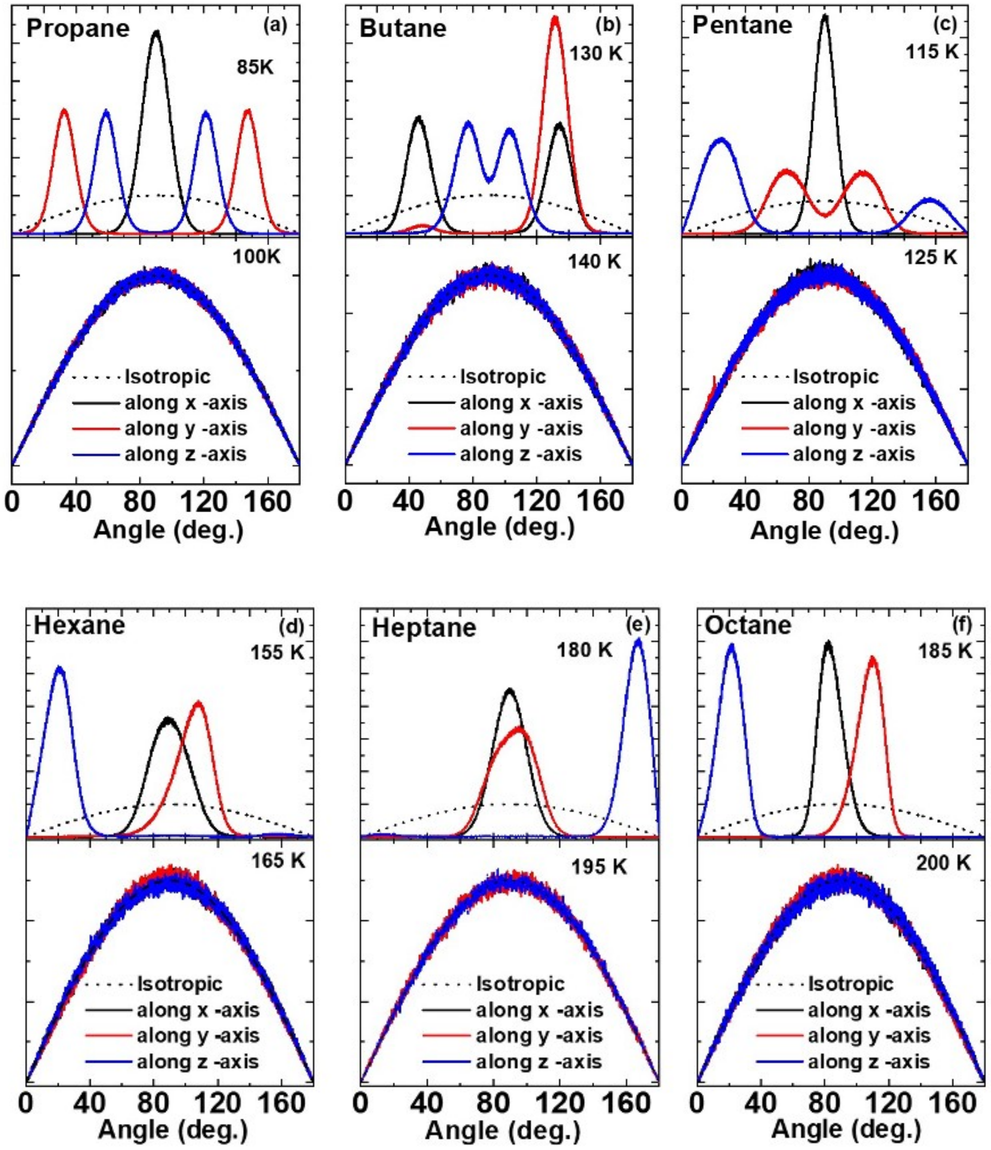

Figure S3: Orientational distribution function for (a) propane (b) butane (c) pentane and (d) hexane (e) heptane and (f) octane molecules along X - (black line), Y - (red line), and Z - (blue line) axis, above and below the respective melting points. The expected orientational distribution for an ideal isotropic behavior for comparison is shown with black dashed lines.

The radial distribution function (RDF) describes the probability distribution of molecules at a given distance, hence providing the local structural information. The temperature dependence of RDF for CH_3 – CH_2 and CH_2 - CH_2 (CH_3 - CH_3 is shown in the main manuscript) pairs for all molecules are shown in Figure S3 and S4, respectively. Similar for all alkanes, we observe a temperature dependent transition from an ordered crystalline state represented by the presence of sharp peaks to a disordered liquid state shown by shallower and broader peaks. The slight broadening of RDF peaks in the ordered state, i. e. below their respective melting points for all the molecules, can be attributed to the presence of rotational disorder, angular and dihederal vibrations in the system.

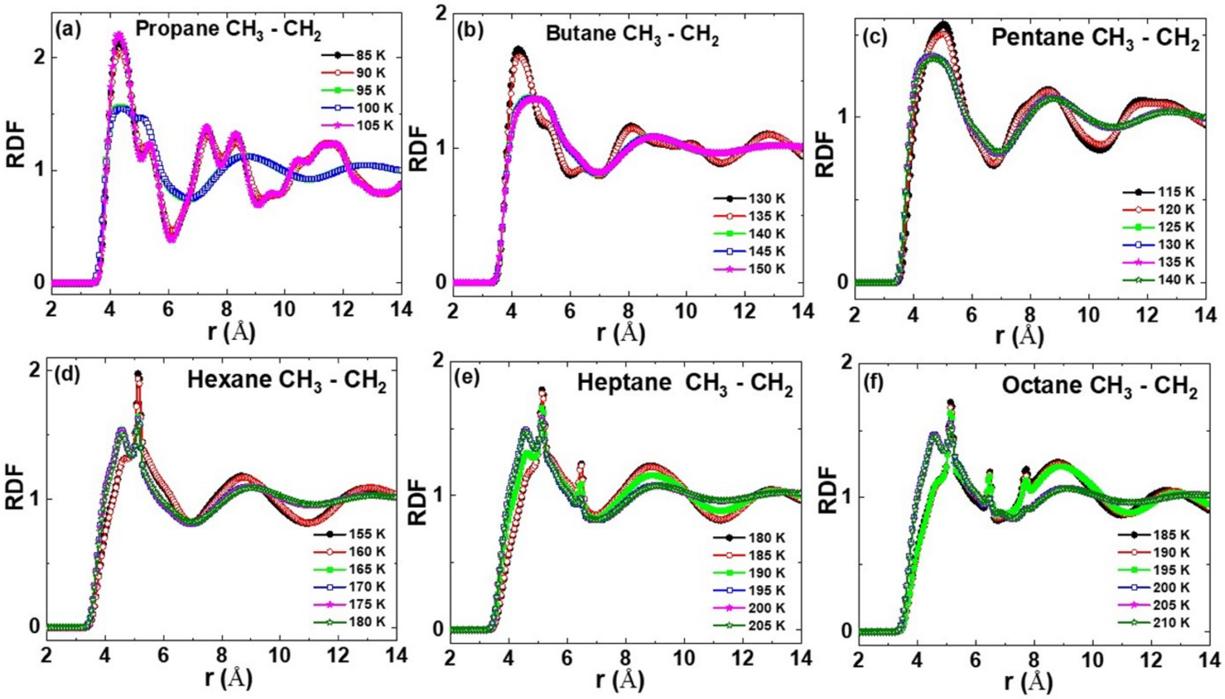

Figure S4: Radial distribution function (RDF) as a function of temperature of $C(H_3)$ - $C(H_2)$ pairs belonging to two different molecules (a) propane (b) butane (c) pentane (d) hexane (e) heptane and (f) octane molecules.

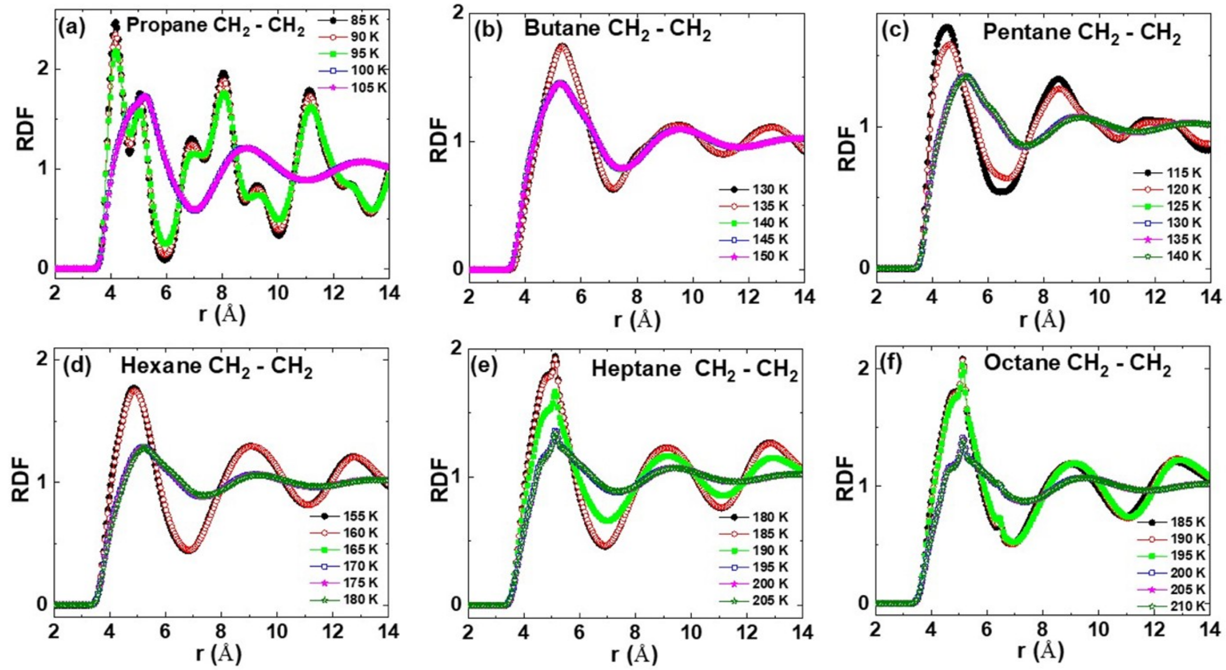

Figure S5: Radial distribution function (RDF) as a function of temperature of C(H_2) - C(H_2) pairs belonging to two different molecules (a) propane (b) butane (c) pentane (d) hexane (e) heptane and (f) octane molecules.

Dynamical Details

The mean squared displacement (MSD) is a measure of the deviation of a molecule position with respect to its starting position over time. Therefore, the time dependent MSD from the center of mass of the molecules can be used to understand the translational diffusive behavior of alkanes. The overall MSD for n = 3 - 8 as a function of temperature at shorter and longer (inset) timescales is shown in the Figure S5.

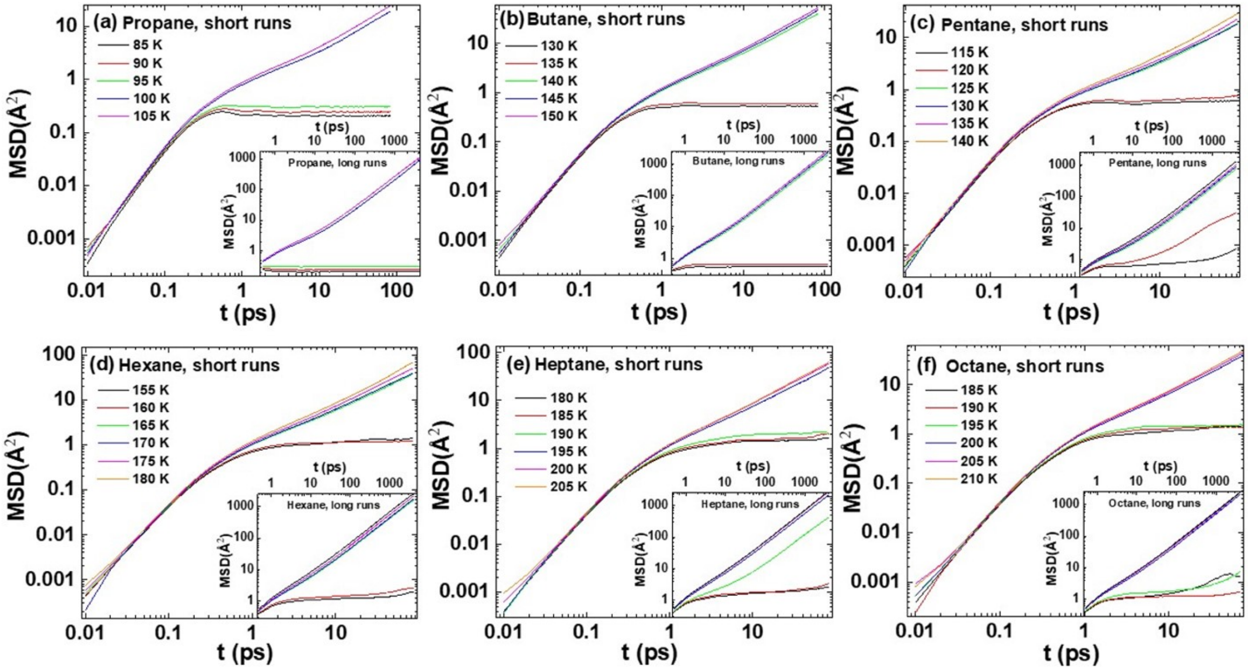

Figure S6: Mean square displacement (MSD) at various temperature for (a) propane (b) butane (c) pentane and (d) hexane (e) heptane and (f) octane molecules. The inset shows the MSD for the respective alkanes at longer timescales (10 ns). Lines between the point serve as guide to the eye.

To investigate rotational motion, the orientational correlation function (OCF) as a function of temperature was used. For all the alkane the time dependent first order (l = 1) OCF behavior is shown in Figure S6.

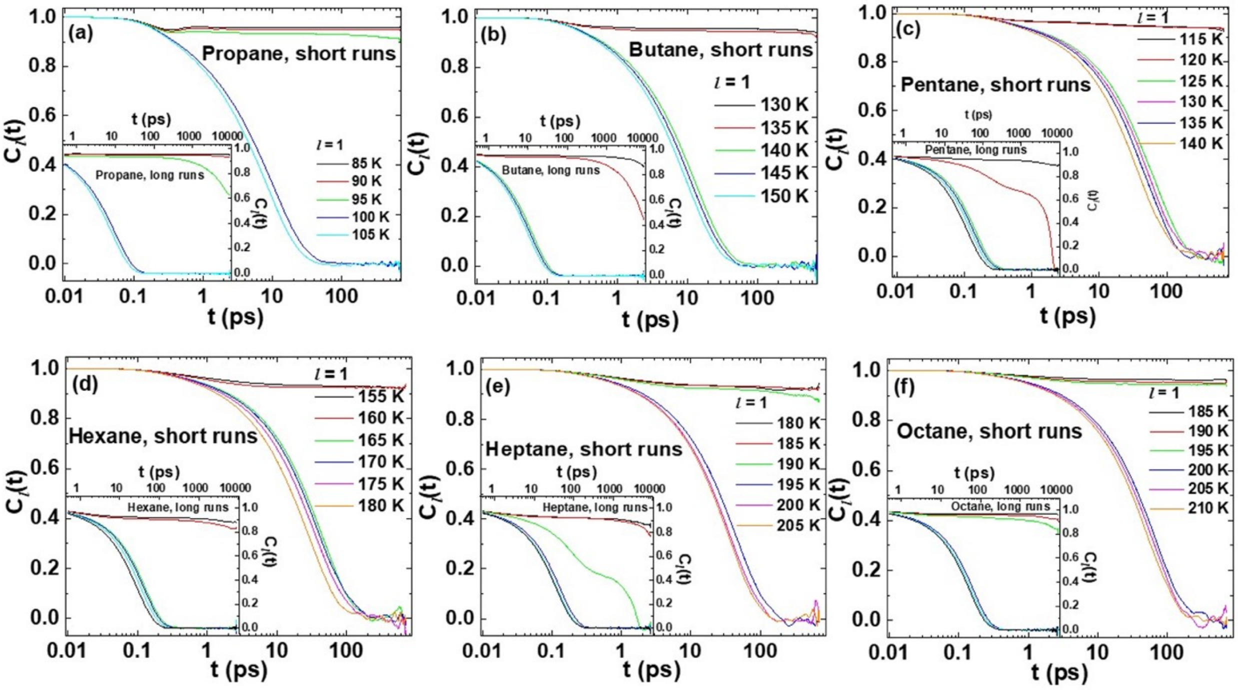

Figure S7: Orientational correlation function (OCF) as a function of temperature for (a) propane (b) butane (c) pentane (d) hexane (e) heptane and (f) octane molecules.