I. Parameters of the force field for the atoms

Table S1. Bond potential $U_{bond} = \varepsilon_b (l - l_0)^2$

Bond type	ε_b, kJ·mol^{-1}nm^{-2}	l_0, nm
CH_2–CH_2	135110	0.1526
CH_2–CH_3	135110	0.1526
Si–CH_2	99650	0.1809
Si–CH_3	99650	0.1809

Table S2. Valence angle potential $U_{angle} = \varepsilon_{angle} (\theta - \theta_0)^2$

Atom type	ε_{angle}, kJ·mol^{-1}rad^{-2}	θ_0, grad
X–Si–X	186	113.5
X–CH_2–X	251	109.5

Table S3. Torsion angle potential $U_{tors} = \varepsilon_{tors} (1 + \cos 3\varphi)$

Atom type	ε_{tors}, kJ·mol^{-1}
X–Si–CH_2–X	1.394
X– CH_2–CH_2–X	5.954

Table S4. Lennard-Jones potential $U_{ij} = \varepsilon_{ij} \left[\left(\frac{R_{min,ij}}{r_{ij}} \right)^{12} - 2 \left(\frac{R_{min,ij}}{r_{ij}} \right)^{6} \right]$,

$$\varepsilon_{ij} = \left(\varepsilon_i \varepsilon_j \right)^{1/2}, R_{min,ij} = 0.5 (R_{min,i} + R_{min,j})$$

Atom type i	ε_i, kJ·mol^{-1}	$R_{min,i}$, nm
Si	0.7955	0.4450
CH_2	0.4580	0.4116
CH_3	0.6255	0.4116

Table S5. Atomic masses and partial charges of the atoms

Atom type	m, a.e.	q, e
Si	28	0.540
(Si)–**CH_2**	14	-0.135
(Si)–**CH_3**	15	-0.135
(CH_2)–**CH_2**–(CH_2) or (CH_2)–**CH_2**–(CH_3)	14	0
(CH_2)–**CH_3**	15	0

II. Gyration radius and half shafts of an effective ellipsoid

Table S6. The average values of $R=(5/3)^{0.5}\cdot Rg$, $a=5^{0.5}\cdot Rg_1$, $b=5^{0.5}\cdot Rg_2$, $c=5^{0.5}\cdot Rg_3$ for the iGj systems (i=1,8,27 and j=3-8) at various temperatures, nm, errors do not exceed 2%

	T=300 K	T=350 K	T=400 K	T=500 K	T=600 K
01G3					
<R>	1.20	1.23	1.26	1.31	1.35
<a>	1.41	1.44	1.49	1.55	1.59
<b>	1.18	1.20	1.23	1.29	1.33
<c>	0.98	1.01	1.01	1.04	1.07
01G4					
<R>	1.52	1.55	1.58	1.64	1.69
<a>	1.74	1.76	1.81	1.88	1.93
<b>	1.50	1.52	1.55	1.62	1.67
<c>	1.30	1.32	1.33	1.37	1.41
01G5					
<R>	1.69	1.94	1.98	2.04	2.10
<a>	1.93	2.14	2.22	2.27	2.33
<b>	1.67	1.93	1.96	2.03	2.09
<c>	1.41	1.73	1.72	1.78	1.84
01G6					
<R>	2.42	2.44	2.47	2.54	2.60
<a>	2.63	2.61	2.67	2.74	2.78
<b>	2.42	2.43	2.47	2.54	2.60
<c>	2.19	2.26	2.27	2.33	2.41
01G7					
<R>	3.04	3.06	3.10	3.17	3.22
<a>	3.19	3.20	3.22	3.31	3.35
<b>	3.04	3.06	3.10	3.16	3.22
<c>	2.88	2.93	2.97	3.02	3.09
01G8					
<R>	3.82	3.84	3.86	3.92	3.97
<a>	3.91	3.93	3.94	4.00	4.04
<b>	3.83	3.85	3.87	3.92	3.96
<c>	3.70	3.73	3.78	3.84	3.89

	T=300 K	T=350 K	T=400 K	T=500 K	T=600 K
08G3					
<R>	1.35	1.38	1.37	1.38	1.38
<a>	1.60	1.62	1.62	1.62	1.62
<b>	1.33	1.36	1.35	1.36	1.36
<c>	1.07	1.08	1.09	1.09	1.10
08G4					
<R>	1.66	1.69	1.70	1.70	1.71
<a>	1.92	1.95	1.96	1.94	1.95
<b>	1.64	1.67	1.68	1.69	1.70
<c>	1.38	1.40	1.40	1.43	1.45
08G5					
<R>	2.06	2.07	2.08	2.10	2.12

<a>	2.31	2.32	2.32	2.33	2.34
<b>	2.04	2.06	2.07	2.09	2.11
<c>	1.78	1.80	1.81	1.85	1.88
08G6					
<R>	2.51	2.52	2.57	2.59	2.62
<a>	2.71	2.72	2.76	2.79	2.82
<b>	2.51	2.52	2.57	2.59	2.63
<c>	2.31	2.31	2.36	2.37	2.40
08G7					
<R>	3.11	3.12	3.14	3.19	3.23
<a>	3.29	3.28	3.30	3.34	3.39
<b>	3.11	3.13	3.17	3.20	3.26
<c>	2.90	2.94	2.96	3.02	3.04
08G8					
<R>	3.85	3.87	3.89	3.94	3.97
<a>	4.01	4.02	4.04	4.07	4.11
<b>	3.88	3.91	3.93	3.99	4.02
<c>	3.65	3.66	3.68	3.74	3.78

	T=300 K	T=350 K	T=400 K	T=500 K	T=600 K
27G3					
<R>	1.36	1.38	1.38	1.38	1.38
<a>	1.62	1.63	1.63	1.63	1.63
<b>	1.34	1.36	1.36	1.36	1.37
<c>	1.06	1.08	1.08	1.09	1.10
27G4					
<R>	1.68	1.69	1.70	1.71	1.72
<a>	1.94	1.94	1.95	1.95	1.96
<b>	1.65	1.68	1.68	1.69	1.71
<c>	1.38	1.40	1.41	1.42	1.45
27G5					
<R>	2.06	2.07	2.08	2.10	2.12
<a>	2.31	2.32	2.32	2.33	2.35
<b>	2.03	2.06	2.07	2.09	2.12
<c>	1.79	1.80	1.81	1.84	1.87
27G6					
<R>	2.52	2.55	2.57	2.59	2.62
<a>	2.70	2.73	2.74	2.79	2.82
<b>	2.53	2.55	2.57	2.59	2.63
<c>	2.33	2.35	2.37	2.37	2.40
27G7					
<R>	3.12	3.14	3.16	3.20	3.23
<a>	3.28	3.31	3.33	3.37	3.40
<b>	3.13	3.15	3.17	3.21	3.24
<c>	2.94	2.96	2.97	3.00	3.05
27G8					
<R>	3.85	3.87	3.89	3.93	3.97
<a>	3.93	3.96	3.98	4.01	4.05
<b>	3.85	3.87	3.89	3.93	3.97
<c>	3.76	3.78	3.80	3.84	3.88

I. Time evolution of the density for 8G5 and 27G5 melts at fixed temperature of 400 K and varying pressure.

To test the effect of pressure on the density of dendrimer melts we have performed modelling of G5 dendrimer melts at T = 400 K while changing external pressure P_{ref} from 0.0001 GPa to 0.1 GPa, and back down to 0.0001 GPa. Results for 8G5 and 27G5 melts are shown in Fig. S1. The blue curve and the left axis show the pressure applied with time while the density evolution is depicted by the black curve and the right axis. The horizontal dashed pastel blue line corresponds to the equilibrium density of the melt at the given temperature. Barostat pressure is changed at the rate of 0.0001 GPa / ps for the system 8G5 and at the rate of 0.00025 GPa / ps for 27G5 system.

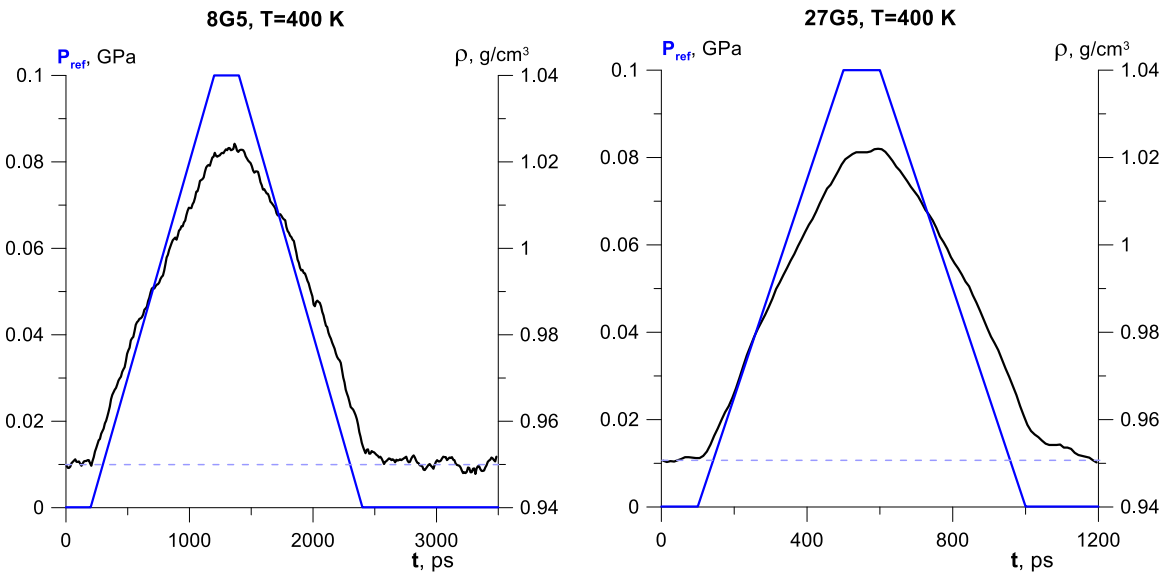


Fig. S1. Time dependences of melt density (black curve) under change of the pressure (shown by blue) for 8G5 and 27G5 systems.

It is clearly seen that the density changes simultaneously with changes in pressure and it returns to its initial level after restoration of the initial pressure value of 0.0001 GPa.

II. Autocorrelation functions for the gyration radius and dendrimer asphericity.

The autocorrelation functions were calculated according to the following expression:

$$A(t) = \frac{\langle \delta X(t) \cdot \delta X(0) \rangle}{\langle \delta X^2 \rangle}$$

with

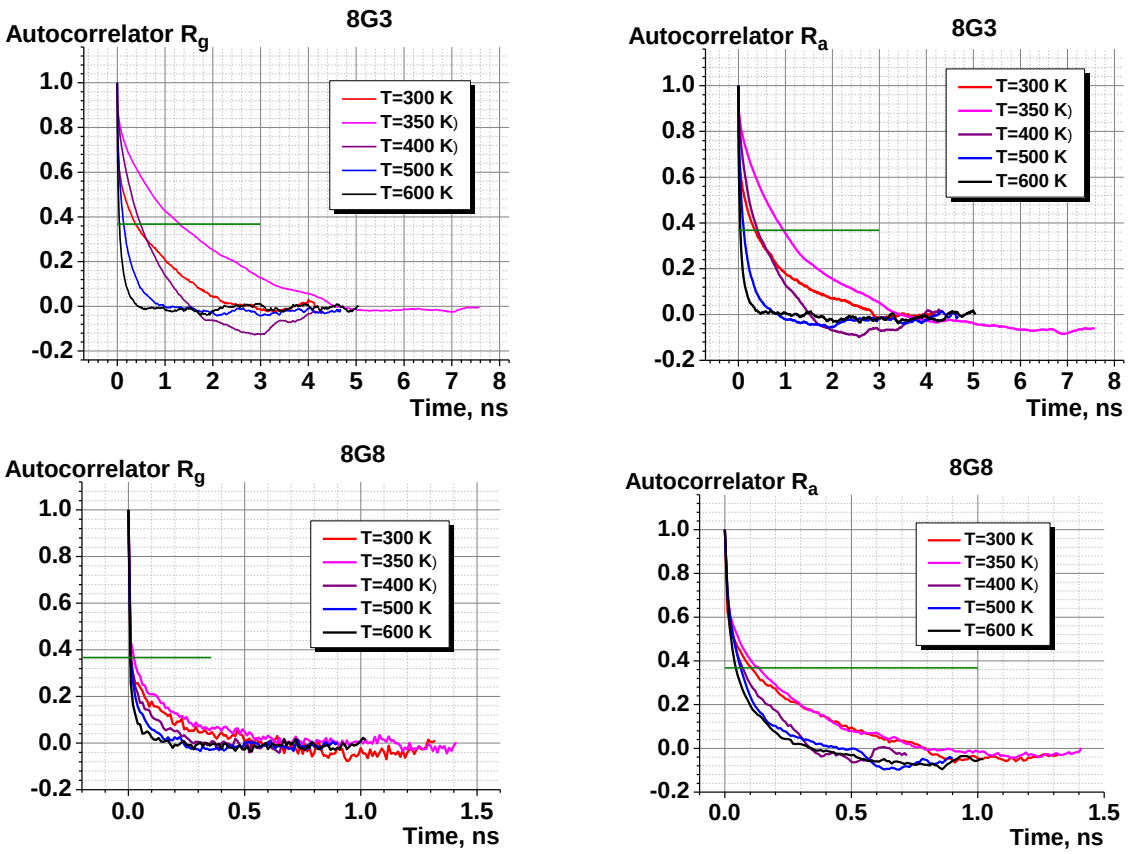
$$\delta X(t) = X(t) - \langle X \rangle$$

where X is either gyration radius or asphericity defined as

$$R_a = \frac{(R_1 + R_2 + R_3)^2 - 3(R_1R_2 + R_2R_3 + R_3R_1)}{(R_1 + R_2 + R_3)^2}$$

The relaxation time is defined as the time at which $A(t)$ reaches the value of $1/e$.

In Fig. S2 the autocorrelation functions for the gyration radius and asphericity calculated over the production runs are shown for the 8G3, 8G8 and 27G8 dendrimer melts at various temperatures. The green line indicates the value of $1/e$. One can see that the largest relaxation time is observed for 8G3 system at 350 K, it is equal to 1.3 ns. The relaxation times for other systems and other temperatures do not exceed this value varying between 0.008 and 1 ns.



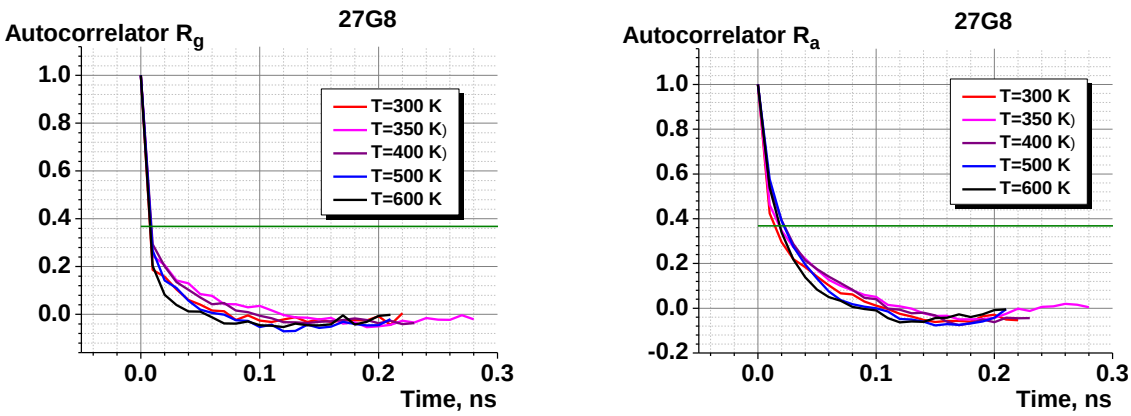
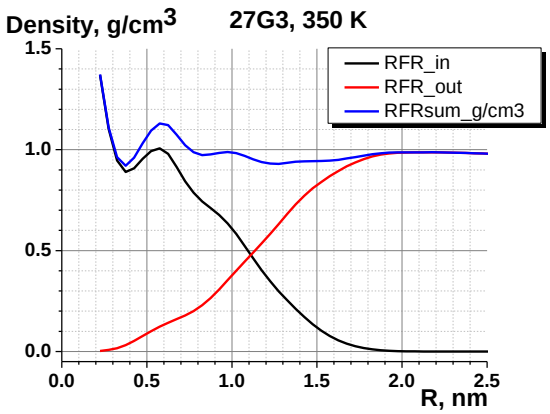
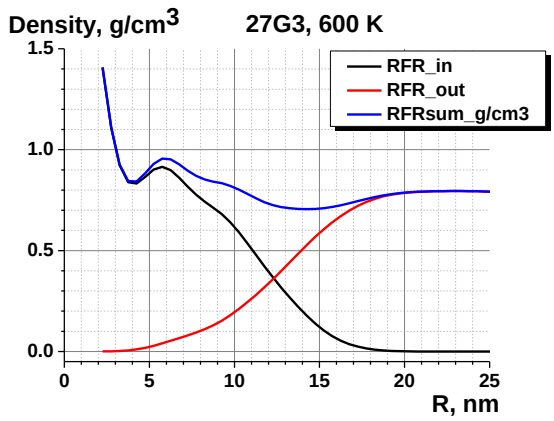
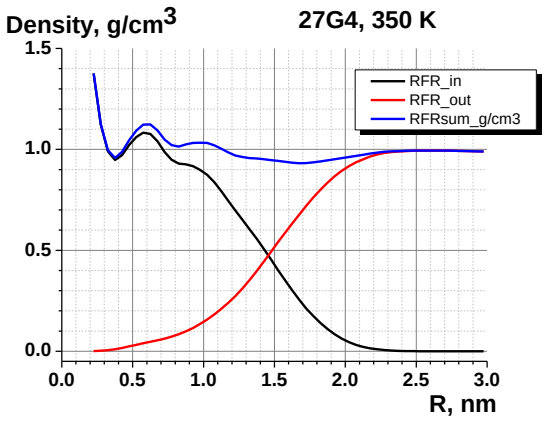


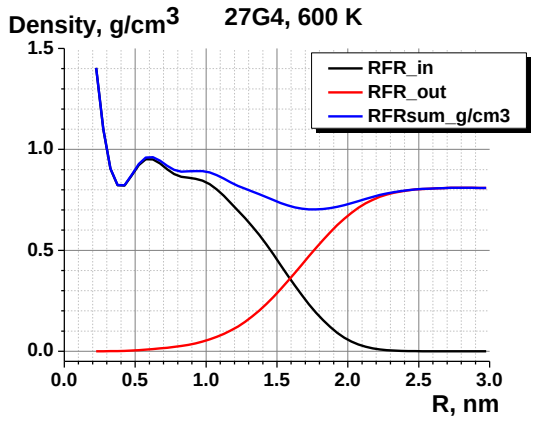
Fig. S2. Autocorrelation functions for the gyration radius and dendrimer asphericity

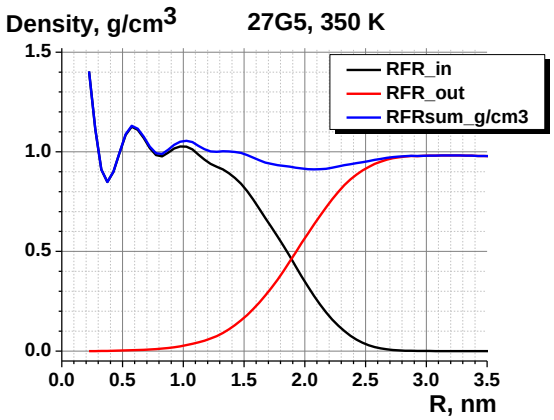
III. Radial density distributions for all systems under study at T=350 K and T=600 K

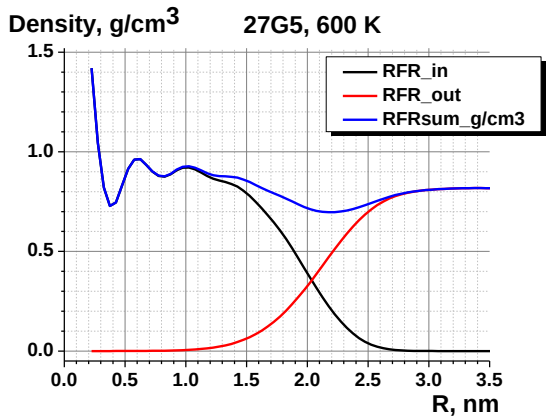


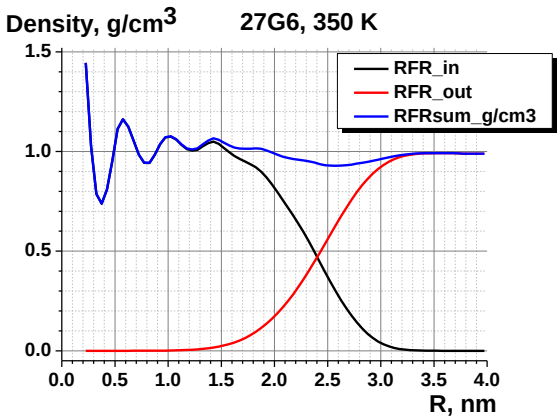


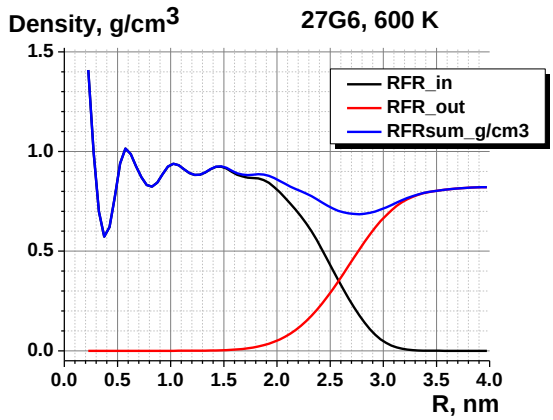












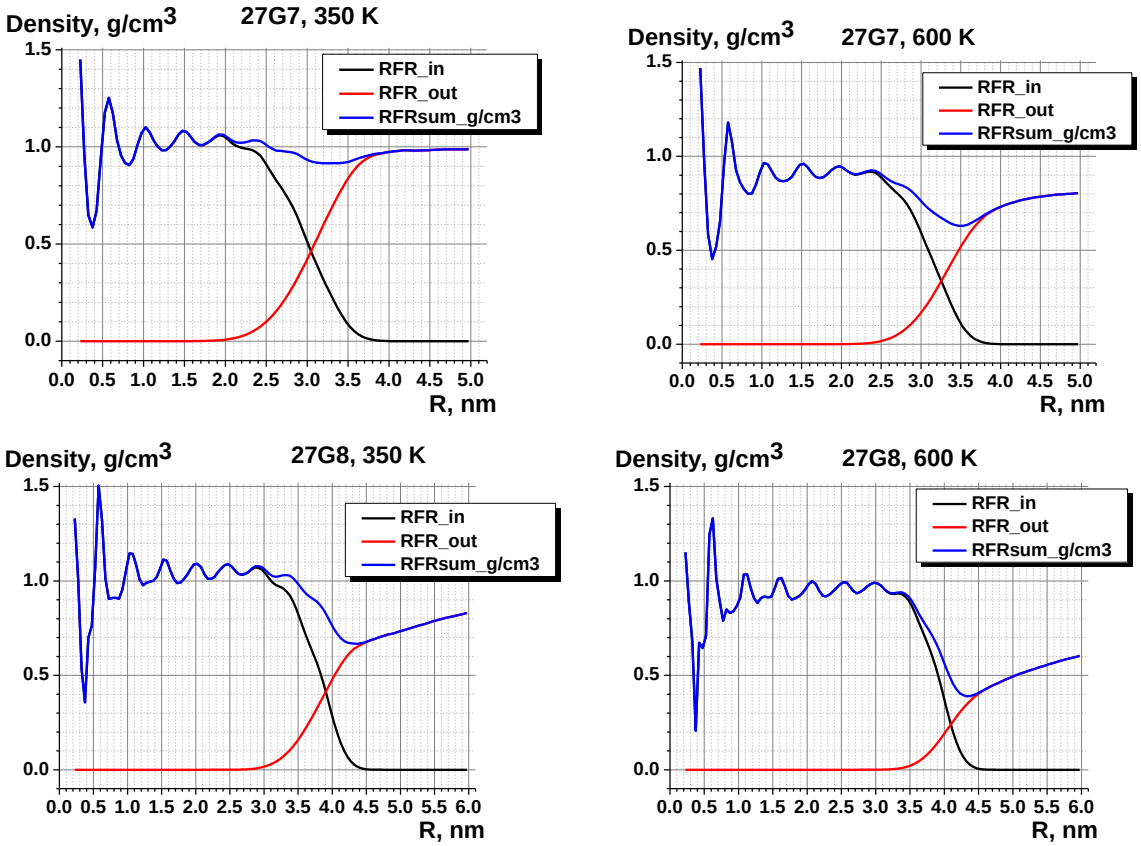
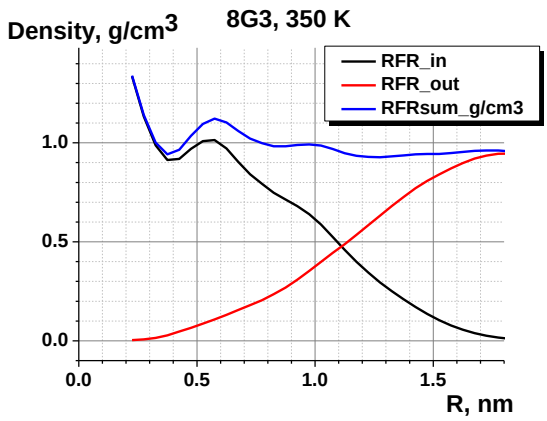
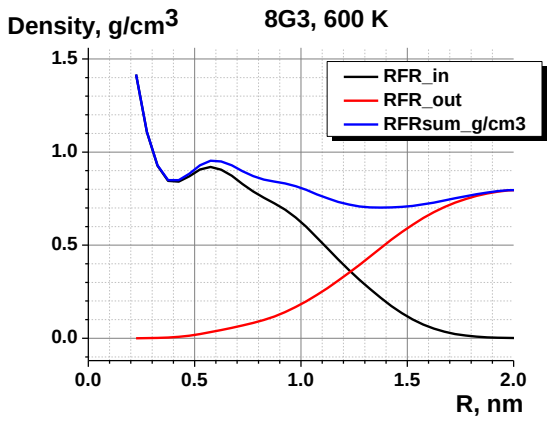
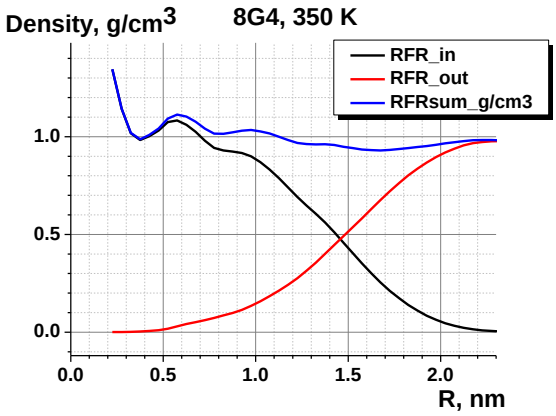
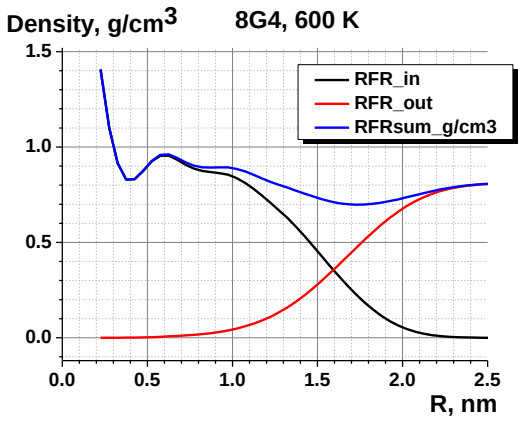


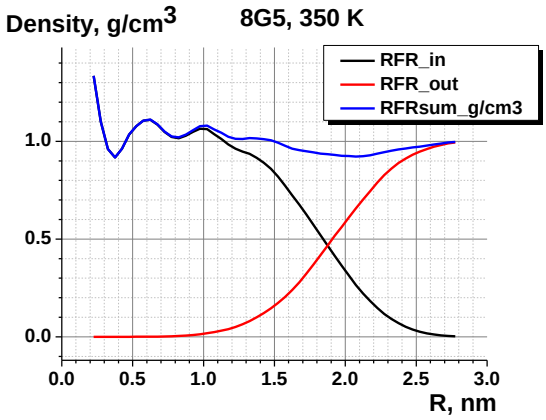
Fig. S3. Radial density distributions of single dendrimer atoms (black), atoms of other dendrimers (red) and the total density distribution (blue) around the center of mass of a dendrimer molecule calculated for the system of 27 molecules of various generations at T=350 and 600 K.

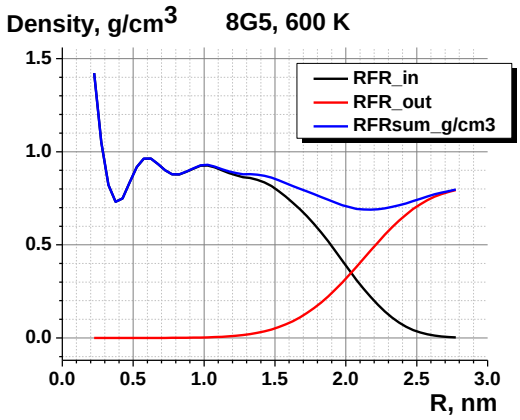

Density, g/cm3
8G3, 350 K
RFR_in
RFR_out
RFRsum_g/cm3
R, nm

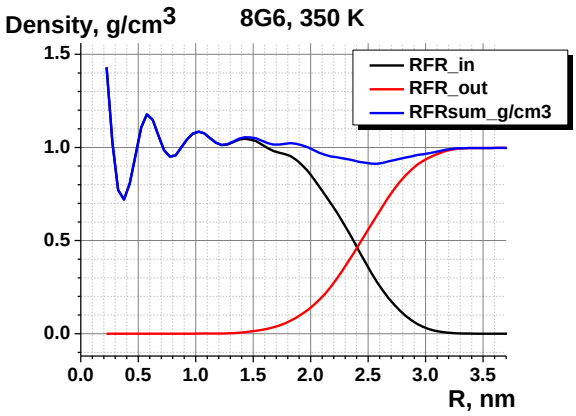

Density, g/cm3
8G3, 600 K
RFR_in
RFR_out
RFRsum_g/cm3
R, nm

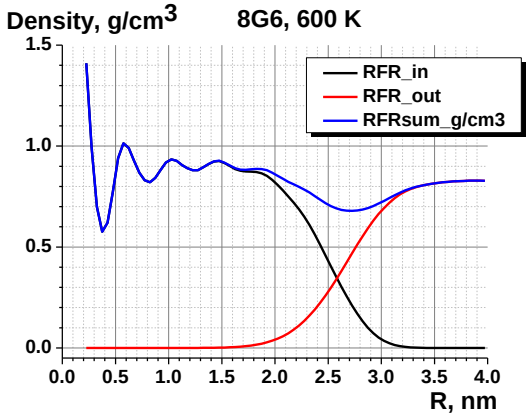

Density, g/cm3
8G4, 350 K
RFR_in
RFR_out
RFRsum_g/cm3
R, nm


Density, g/cm3
8G4, 600 K
RFR_in
RFR_out
RFRsum_g/cm3
R, nm


Density, g/cm3
8G5, 350 K
RFR_in
RFR_out
RFRsum_g/cm3
R, nm


Density, g/cm3
8G5, 600 K
RFR_in
RFR_out
RFRsum_g/cm3
R, nm


Density, g/cm3
8G6, 350 K
RFR_in
RFR_out
RFRsum_g/cm3
R, nm


Density, g/cm3
8G6, 600 K
RFR_in
RFR_out
RFRsum_g/cm3
R, nm

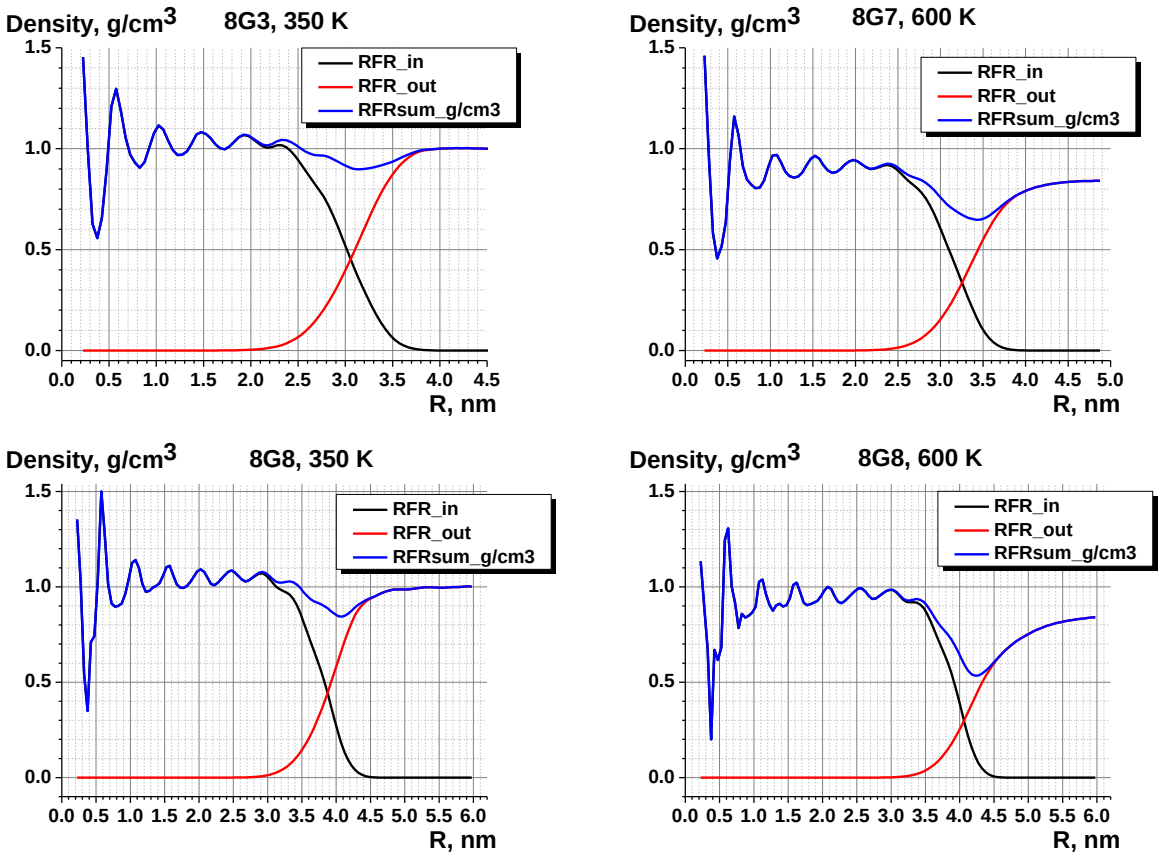
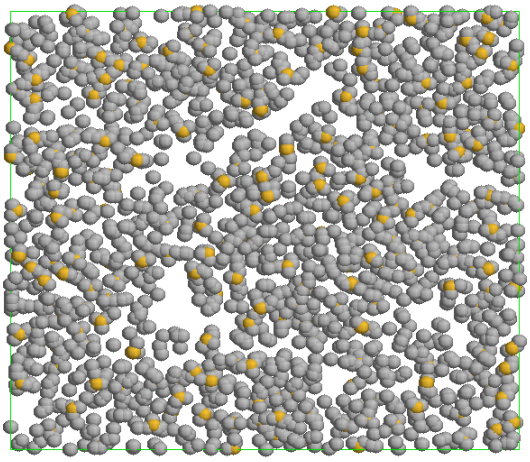


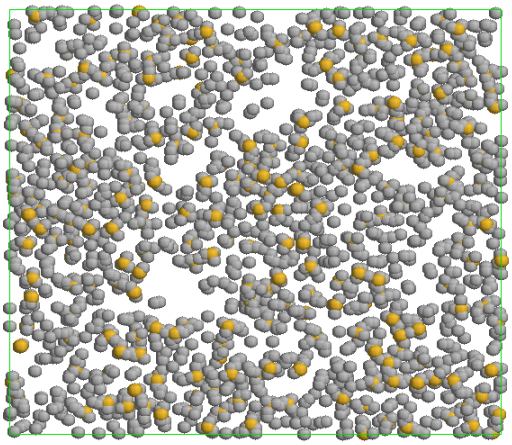
Fig. S3. Radial density distributions of single dendrimer atoms (black), atoms of other dendrimers (red) and the total density distribution (blue) around the center of mass of a dendrimer molecule calculated for the system of 8 molecules of various generations at T=350 and 600 K.

IV. Snapshots of the dendrimer melt layers

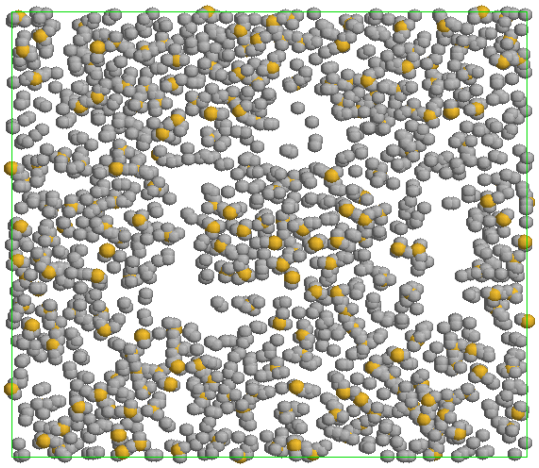
The following snapshots show dendrimer melt layers for 8G8 at T=600 K.



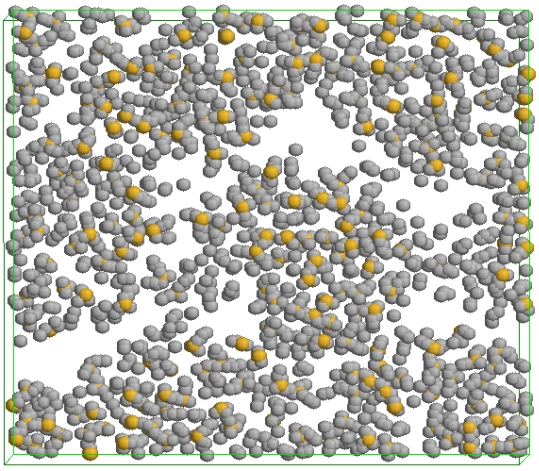
0 – 0.35 nm



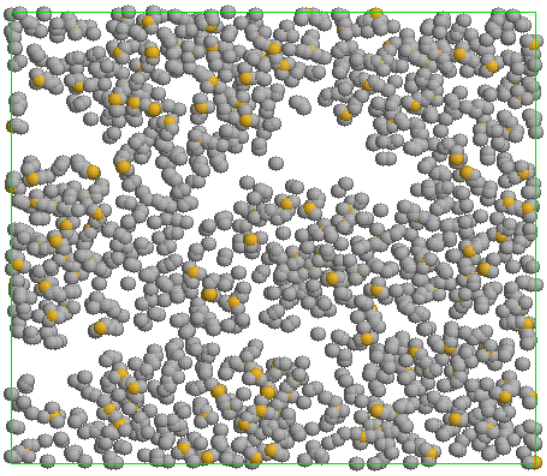
0.35 – 0.70 nm



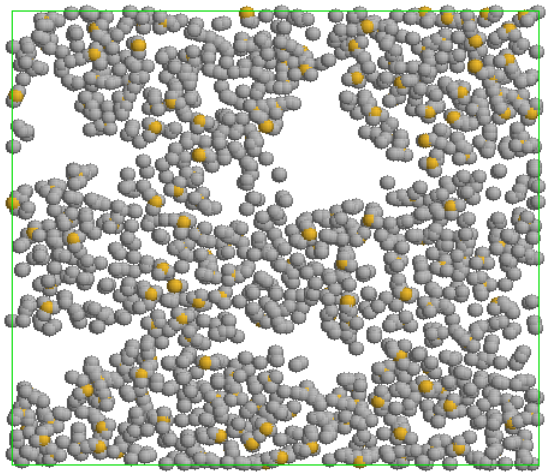
0.70 – 1.05 nm



1.05 – 1.40 nm



1.40 – 1.75 nm



1.75 – 2.10 nm

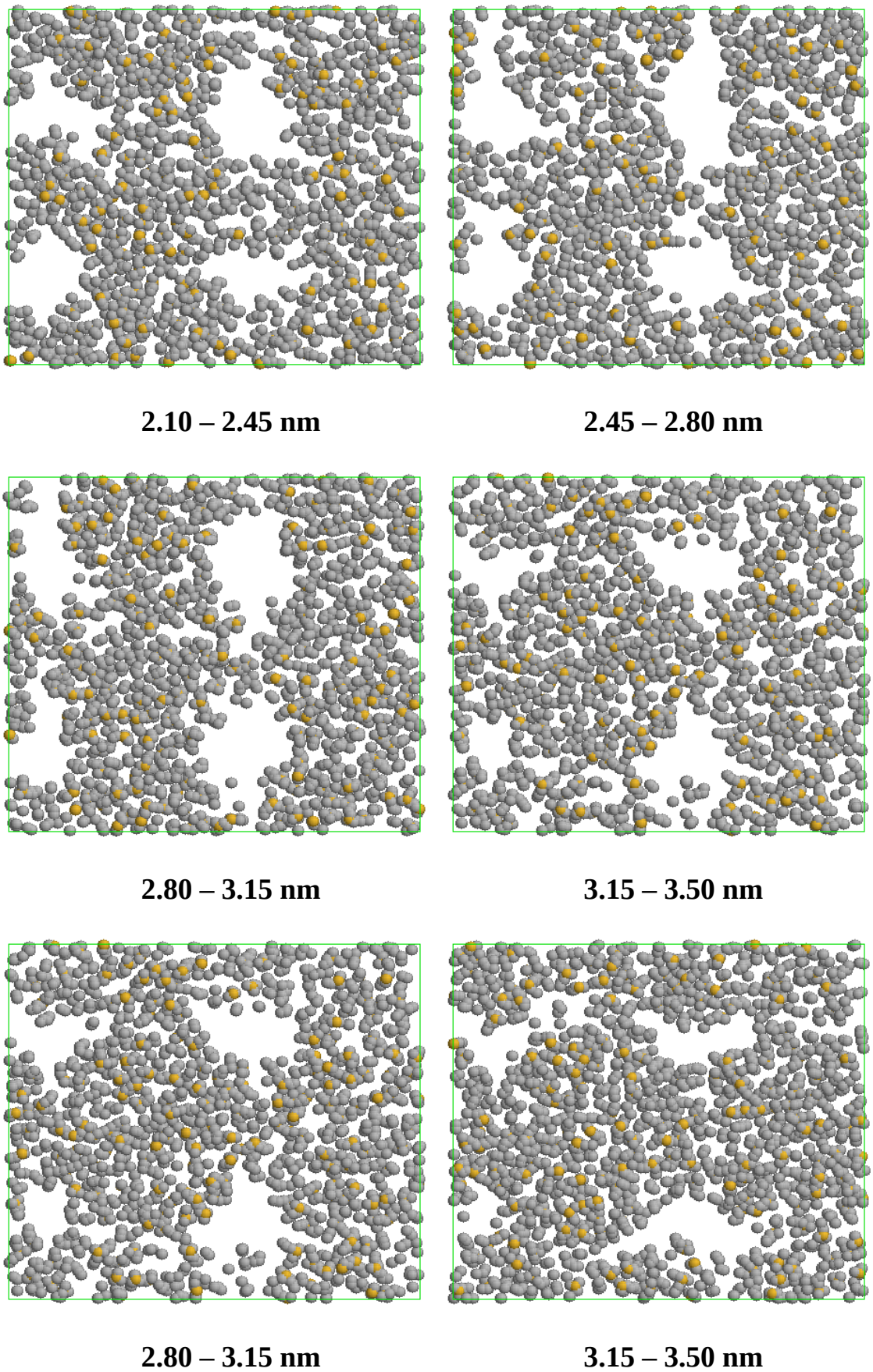


Fig. S4. Snapshots of the dendrimer melt layers for 8G8 at T=600 K. The atoms are shown with their van der Waals radii.

V. Intermolecular interaction energy including Coulomb and van-der-Waals

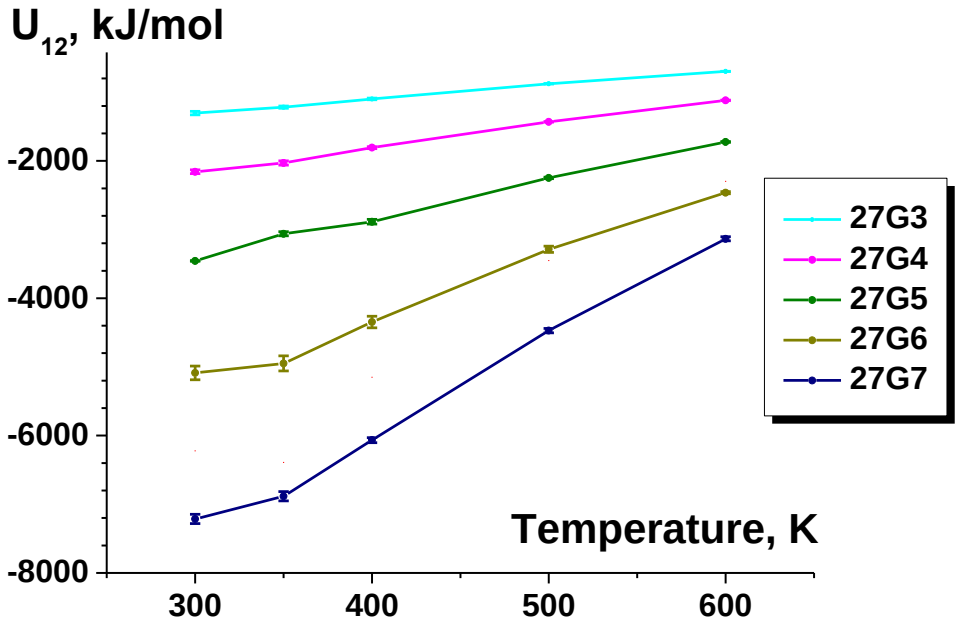
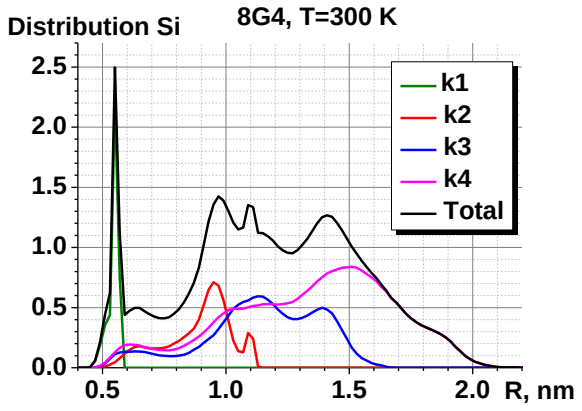
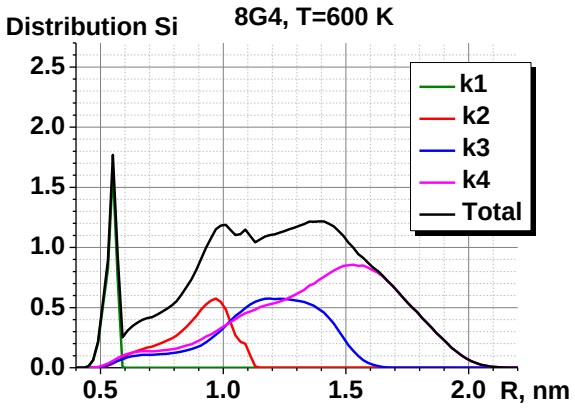
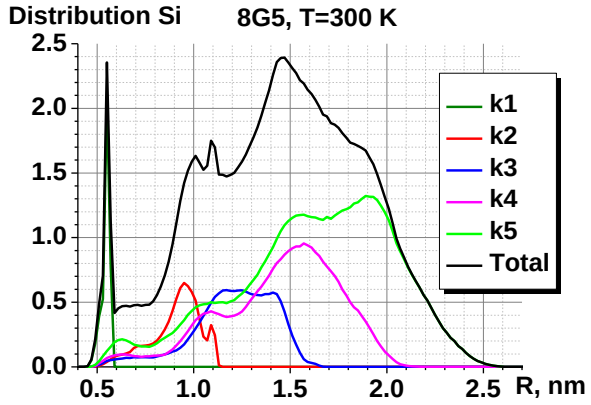


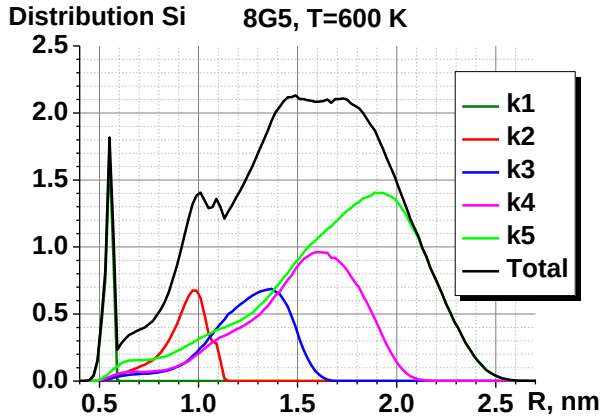
Fig.S5. Dependence of intermolecular interaction energy, U_{12}, on dendrimer generation for the system of 27 molecules in the simulation box.

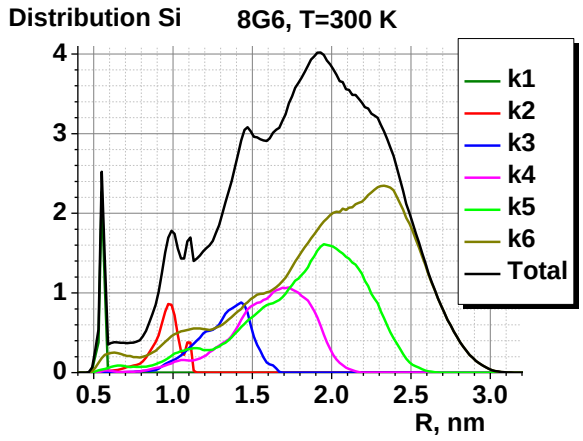
VI. Distributions of Si atoms

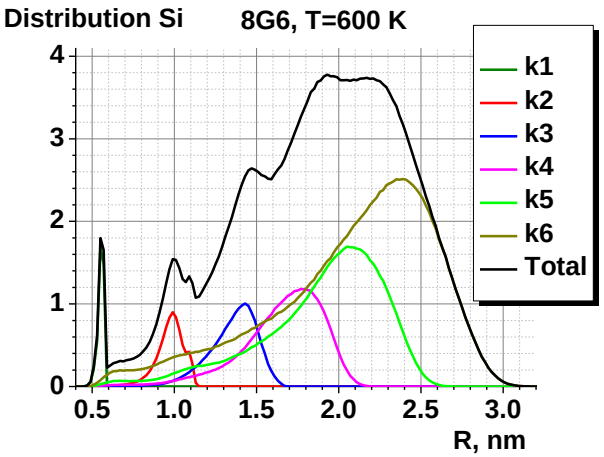


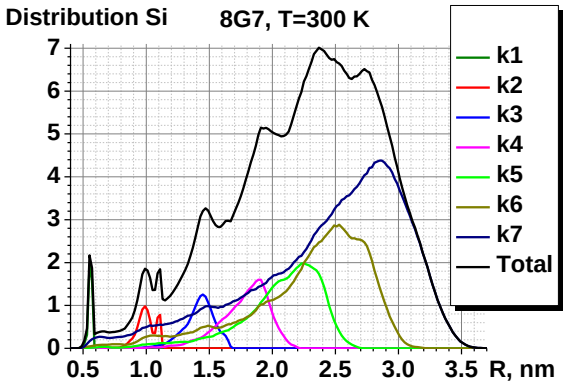


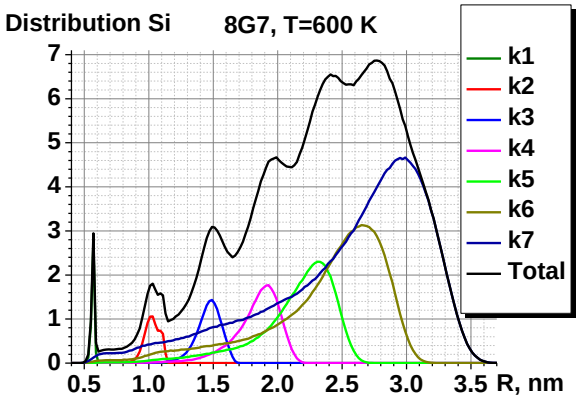












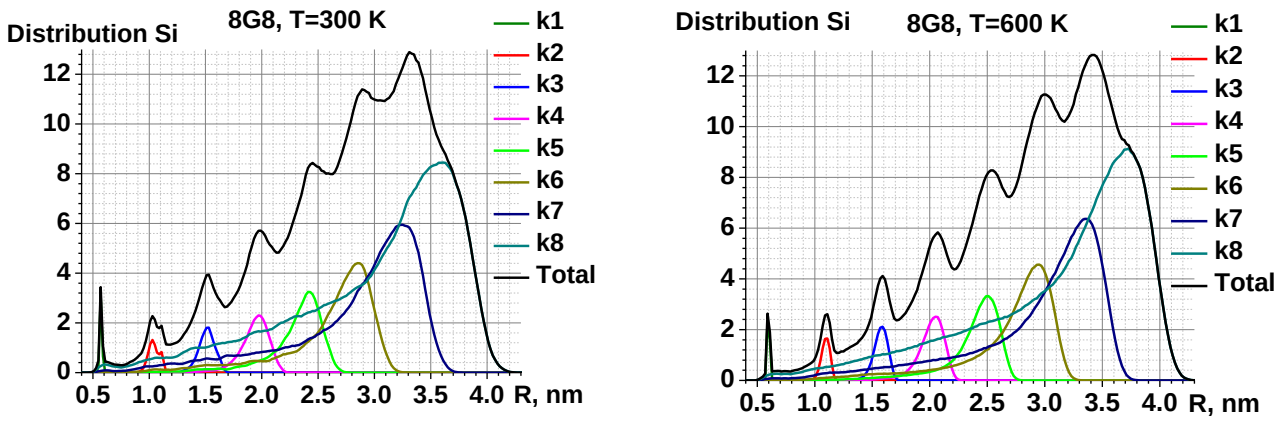


Fig. S6. Distance distributions of Si atoms belonging to various layers **k** from a central Si atom in dendrimers of various generations.

VII. Shape factors and gyration radii

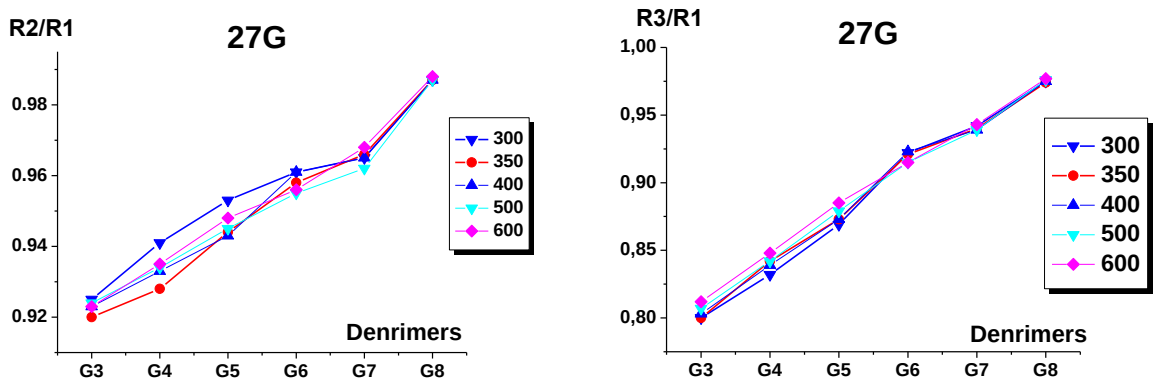


Fig. S7. Dendrimer shape factors for the 27 molecule melt at various temperatures

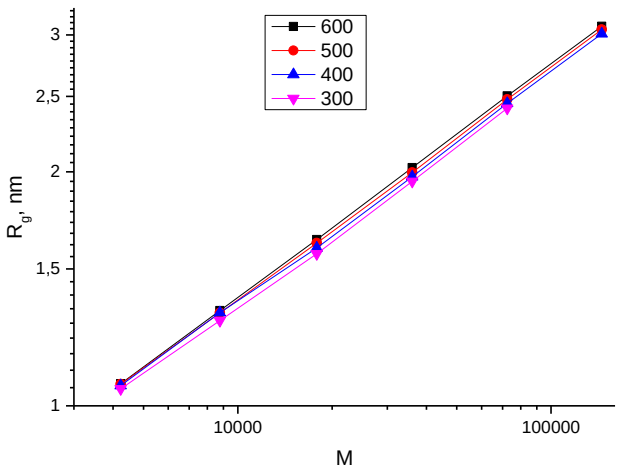
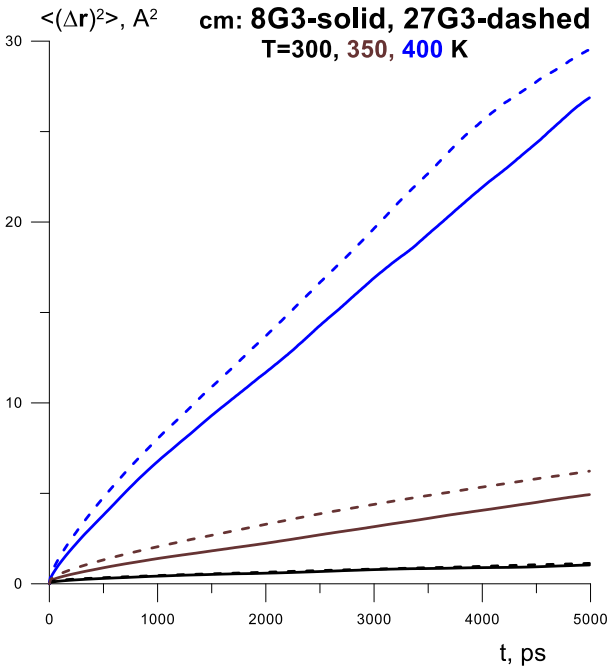
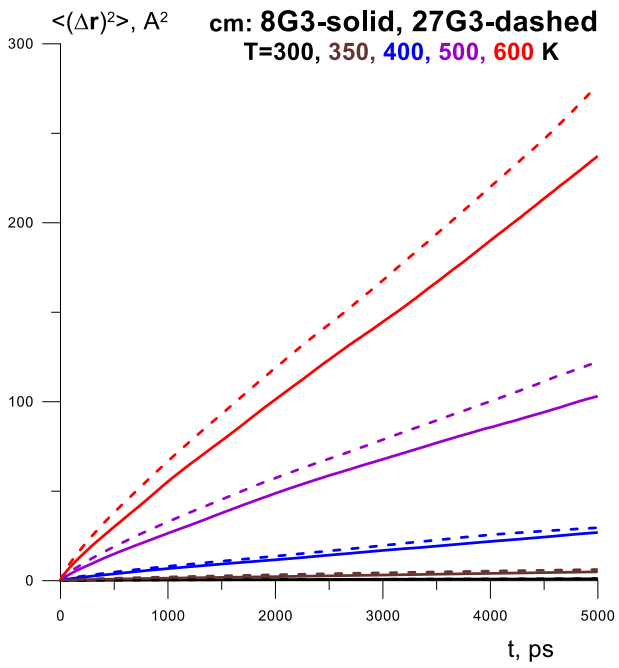
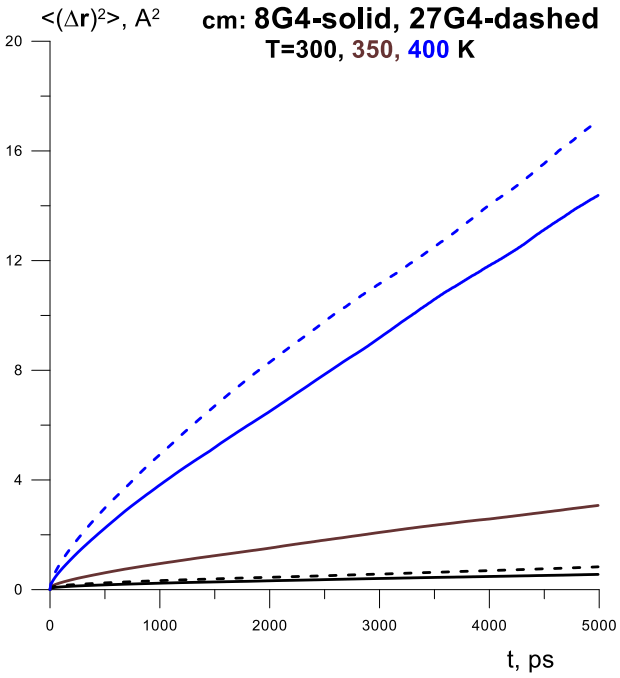


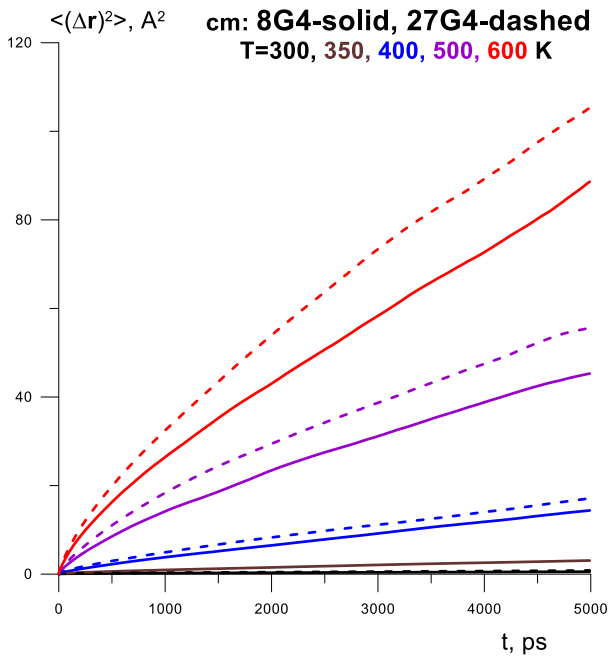
Fig. S8. Gyration radius of isolated dendrimers vs molecular mass at various temperatures

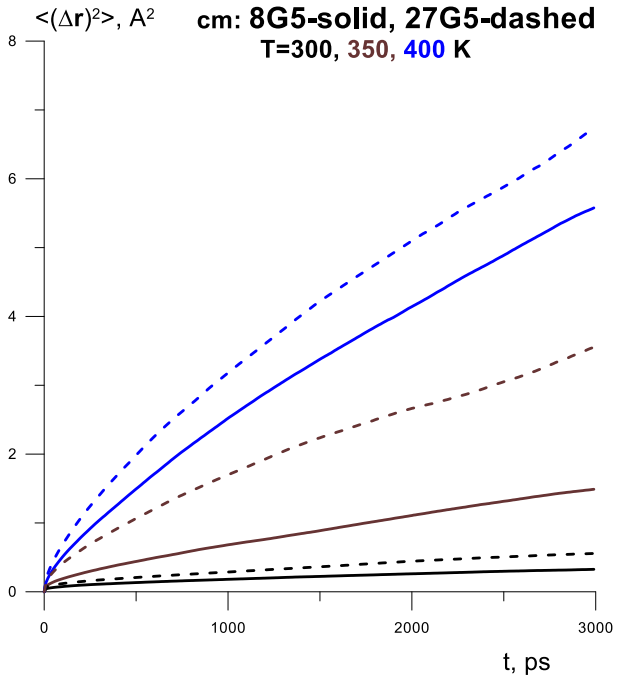
VIII. Center-of-mass displacements







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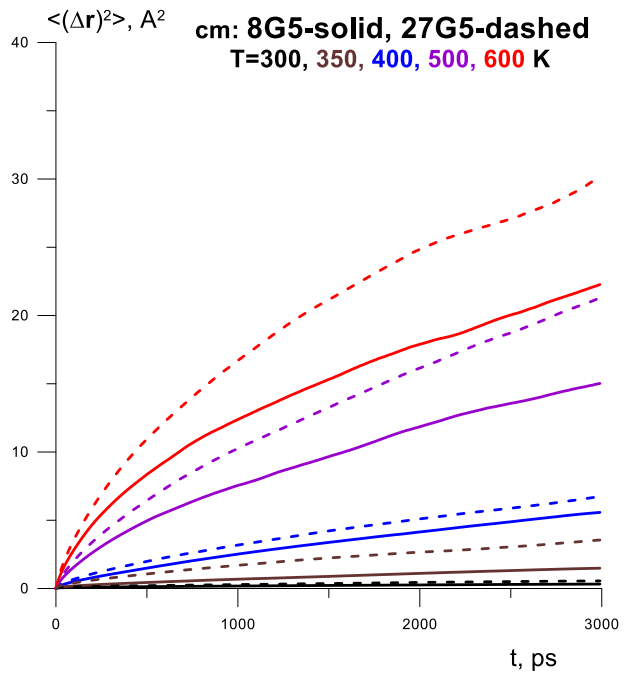
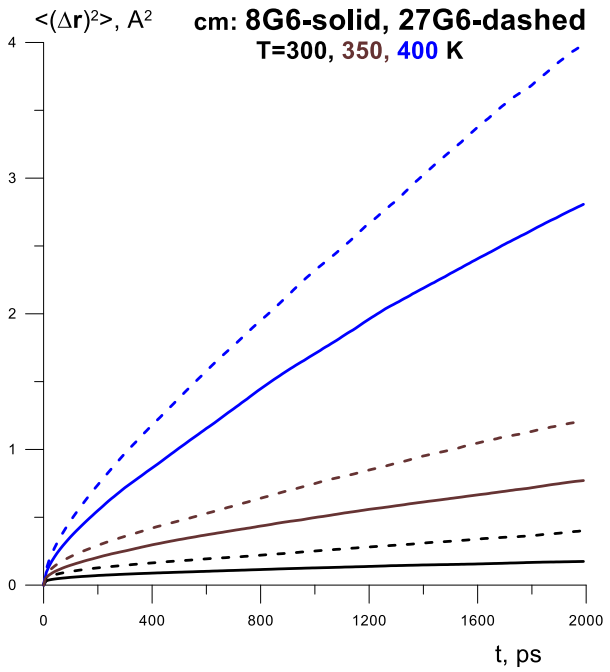
cm: 8G5-solid, 27G5-dashed
T=300, 350, 400 K
0
2
4
6
8
0
1000
2000
3000
t, ps


<(Δr)²>, A²
cm: 8G5-solid, 27G5-dashed
T=300, 350, 400, 500, 600 K
0
10
20
30
40
0
1000
2000
3000
t, ps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cm: 8G6-solid, 27G6-dashed
T=300, 350, 400 K
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1
2
3
4
0
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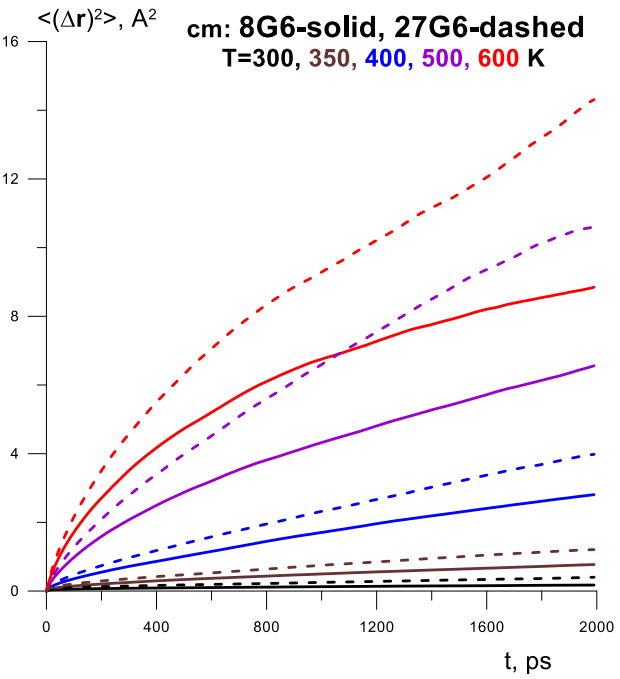
800
1200
1600
2000
t, ps


<(Δr)²>, A²
cm: 8G6-solid, 27G6-dashed
T=300, 350, 400, 500, 600 K
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4
8
12
16
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1200
1600
2000
t, ps

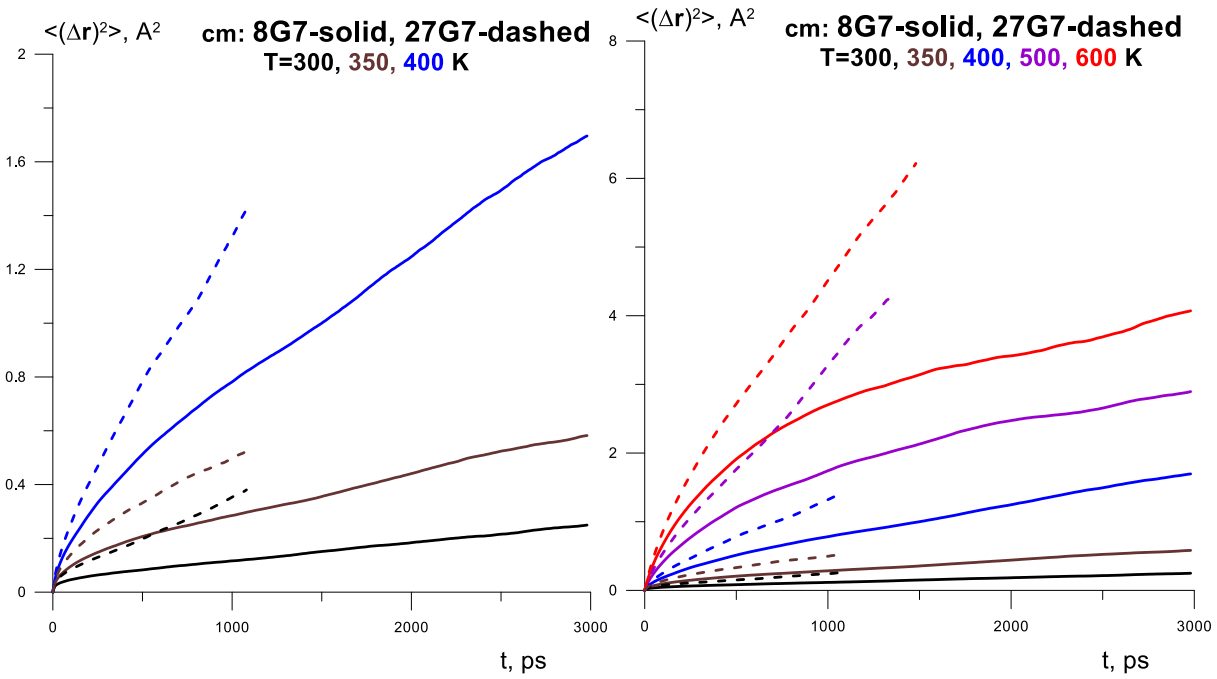

Fig. S9. Time dependences of dendrimer center-of-mass displacements melts containing 8 and 27 dendrimers in the simulation box calculated at different temperatures