Influence of the surroundings and conformerisation of *n*-dodecane molecules on evaporation/condensation processes analysed by DFT method

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Aim

This work is aimed on the analysis of evaporation/condensation coefficient (ECC) as a function of temperature, pressure, gas and liquid density, and surface surroundings effects. The analysis is based on calculations using quantum chemical DFT methods applied to *n*-dodecane, as a representative of *n*-alkanes in Diesel fuel, taking into account conformerisation and cross-conformerisation of n-dodecane molecules (CDM) in the gas and liquid phases, and comparison of the conformation-dependent ECC values to those calculated previously by the MD FF methods.

Analysis of several effects caused by variations in

(i) structure and population of different *n*-dodecane conformers in the gas and liquid phases (conformerisation and cross-conformerisation, CMD);

(ii) surroundings, especially in the liquid phase, related also to orientation of evaporating (or condensing) molecules and a number of neighbouring molecules for each evaporated molecule at a surface of liquid droplets;

(iii) temperature, total and partial pressures, and liquid and gas density *vs*. temperature and pressure can influence the evaporation/condensation processes of dodecane.

Conformation-dependent Gibbs free energy of evaporation

$$\left\langle \Delta G_{\mathrm{l}\to\mathrm{g}} \right\rangle = \sum_{i \le j = 1}^{N} (G_{\mathrm{g},i} - G_{\mathrm{l},j}) P_{\mathrm{g},i}(T) P_{\mathrm{l},j}(T)$$

where $P_{\mathrm{g},i}$ and $P_{\mathrm{l},j}$ are the populations of conformer states in the gas (vapour) and liquid phases, respectively, i, j = 1, 2, 3, …N, N is the number of conformers (here $N \le 95$ for different sets of conformers)

$$P_{\mathrm{x},i} = \frac{\exp[-(G_{\mathrm{x},i} - G_{\mathrm{x,min}})/RT]}{\sum_{j} \exp[-(G_{\mathrm{x},j} - G_{\mathrm{x,min}})/RT]}$$

where x = g or l, R is the universal gas constant.

ECC vs. CDM

$$\frac{1-\beta_{\mathrm{g}}}{\beta_{\mathrm{g}}}=\exp\left(\frac{\Delta G_{\mathrm{g}\to\mathrm{l}}}{RT}\right) \xrightarrow{\text{CDM}} \frac{1-\langle\beta_{\mathrm{g}}\rangle}{\langle\beta_{\mathrm{g}}\rangle}=\sum_{i\le j=1}^{N}\exp\left(\frac{G_{\mathrm{g},i}-G_{\mathrm{l},j}}{RT}\right)P_{\mathrm{g},i}(T)P_{\mathrm{l},j}(T)$$

CDM – conformerisation/cross-conformerisation of *n*-dodecane molecules

$$\beta_{\mathrm{V}}=[1-(V_{\mathrm{l}}/V_{\mathrm{g}})^{1/3}]\exp\{-0.5/[(V_g/V_l)^{1/3}-1]\}$$

where V_{l} and V_{g} are the specific volumes of the liquid and gas phases, respectively

$$\beta_{\mathrm{V,g}}=[1-(V_{\mathrm{l}}/V_{\mathrm{g}})^{1/3}]\exp(-\Delta G_{\mathrm{ev}}/\mathrm{RT})$$

$$\frac{V_{\mathrm{l}}}{V_{\mathrm{g}}}=\frac{\rho_{\mathrm{g}}}{\rho_{\mathrm{l}}}\sum_{i\le j=1}^{N}\exp\left(\frac{G_{\mathrm{g},i}-G_{\mathrm{l},j}}{RT}\right)P_{\mathrm{g},i}(T)P_{\mathrm{l},j}(T)$$

$$\langle\beta_{\mathrm{V}}\rangle=\left\{1-\left[\frac{\rho_{\mathrm{g}}}{\rho_{\mathrm{l}}}\sum_{i\le j=1}^{N}\exp\left(\frac{G_{\mathrm{g},i}-G_{\mathrm{l},j}}{RT}\right)P_{\mathrm{g},i}(T)P_{\mathrm{l},j}(T)\right]^{1/3}\right\}\exp\left\{-0.5\left[\left[\frac{\rho_{\mathrm{g}}}{\rho_{\mathrm{l}}}\sum_{i\le j=1}^{N}\exp\left(\frac{G_{\mathrm{g},i}-G_{\mathrm{l},j}}{RT}\right)P_{\mathrm{g},i}(T)P_{\mathrm{l},j}(T)\right]^{-1/3}-1\right]^{-1}\right\}$$

$$\langle\beta_{\mathrm{V,g}}\rangle=\left\{1-\left[\frac{\rho_{\mathrm{g}}}{\rho_{\mathrm{l}}}\sum_{i\le j=1}^{N}\exp\left(\frac{G_{\mathrm{g},i}-G_{\mathrm{l},j}}{RT}\right)P_{\mathrm{g},i}(T)P_{\mathrm{l},j}(T)\right]^{1/3}\right\}\sum_{i\le j=1}^{N}\exp\left(\frac{G_{\mathrm{g},i}-G_{\mathrm{l},j}}{RT}\right)P_{\mathrm{g},i}(T)P_{\mathrm{l},j}(T)$$

Gas density for dodecane

The V_l/V_g ratio can be computed from the corrected ratio (*vide infra*) of the liquid density and the gas density determined with equation of state (for real gas) for *n*-dodecane

$$p = \rho RT\left[1+\delta\left(\frac{\partial A}{\partial \delta}\right)_{\tau}\right]$$

where p is the pressure, $\tau = T_c/T$, $\delta = \rho/\rho_c$, ρ and ρ_c = 1.33 mol/dm^3 are the density and critical density of *n*-decane, respectively, and A is the Helmholtz free energy

$$A(\delta,\tau) = \delta(n_1\tau^{0.32} + n_2\tau^{1.23} + n_3\tau^{1.5}) + \delta^2[n_4\tau^{1.4} + n_5\delta\tau^{0.07} + n_6\delta^5\tau^{0.8} + n_7\tau^{2.16}\exp(-\delta)] + n_8\delta^5\tau^{1.1}\exp(-\delta) + \delta\exp(-\delta^2)(n_9\tau^{4.1} + n_{10}\delta^3\tau^{5.6}) + \delta^3\exp(-\delta^3)(n_{11}\tau^{14.5} + n_{12}\delta\tau^{12})$$

with the equation constants n_1, n_2,…n_{12}

Parameter	Value
n_1	1.38031
n_2	–2.85352
n_3	0.288897
n_4	–0.165993
n_5	0.0923993
n_6	0.000282772
n_7	0.956627
n_8	0.0353076
n_9	–0.445008
n_{10}	–0.118911
n_{11}	–0.0366475
n_{12}	0.0184223

Evaporation rate vs. CDM

$$\left\langle \gamma_{i(i+j)} \right\rangle = b_{ij} \frac{p}{k_{\mathrm{B}} T n_0} \sum_{k \le m \le n = 1}^{N} \exp\left(\frac{\Delta G_{i+j,k} - \Delta G_{i,m} - \Delta G_{j,n}}{k_{\mathrm{B}} T} \right) P_{i+j,k}(T) P_{i,m}(T) P_{j,n}(T)$$

where $\left\langle \gamma_{i(i+j)} \right\rangle$ is the average evaporation rate of the *i*th-molecule (averaged by states of *N* conformers) from a cluster (or nanodroplet) *i+j* calculated taking into account the CMD, b_{ij} is the collision rate of the *i*th molecule with the *j*th molecule (conformer/cluster/nanodroplet) calculated using the kinetic gas theory, n_0 is the initial number of molecules in a cluster or nanodroplet, $\Delta G_{i+j,k}$, $\Delta G_{i,m}$, and $\Delta G_{j,n}$ are the Gibbs free energies of formation of the molecules (conformers/clusters/nanodroplets) from monomers (molecules/conformers) averaged by conformer states (*k, n, m* = 1, 2,…*N* at $k \le m \le n$) at the reference pressure *p*.

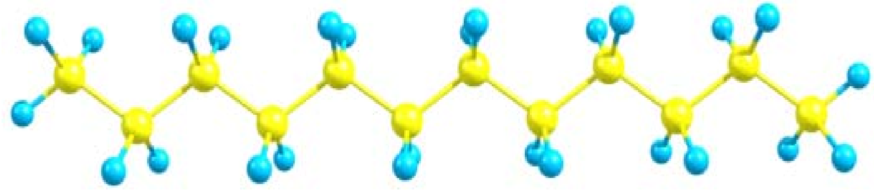
Quantum chemical (QC) methods

Density functional theory (DFT) calculations were carried out with hybrid functional ωB97X-D and two cc-pVTZ (larger - 724 basis functions for dodecane molecule) and cc-pVDZ (smaller - 298 basis functions).

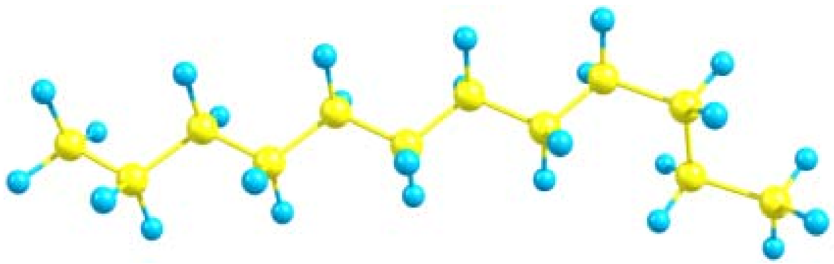
The solvation effects for *n*-dodecane conformers in dodecane medium were analysed applying the solvation method SMD with ωB97X-D (cc-pVTZ or cc-pVDZ).

All the calculations were performed with consideration of zero-point and thermal corrections to the Gibbs free energy in both phases and also adding the solvation terms for molecules in the liquid phase with the geometry of *n*-dodecane conformers optimised by ωB97X-D/cc-pVTZ.

Some conformers



Initial

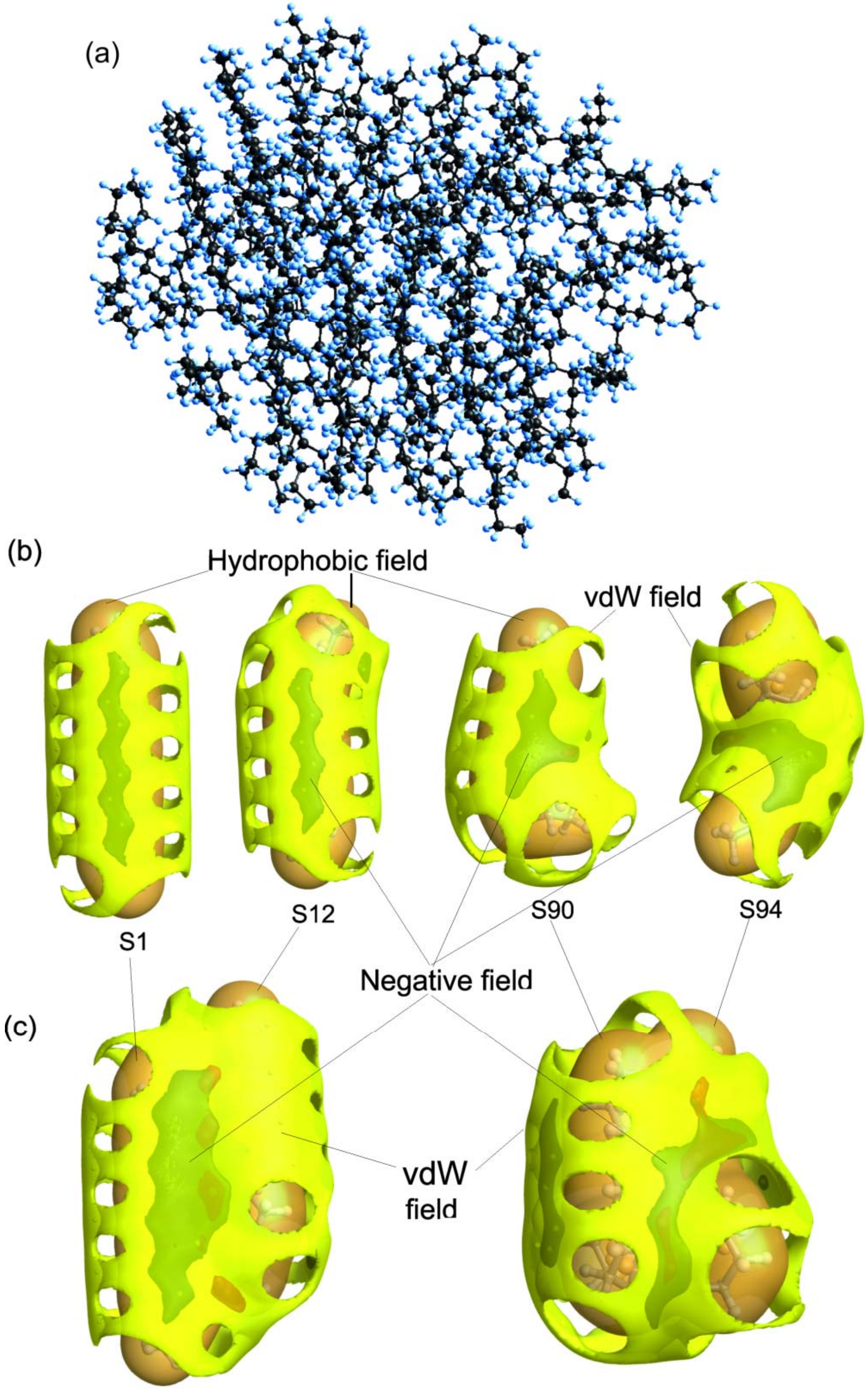


Maximum stable

Minimum stable

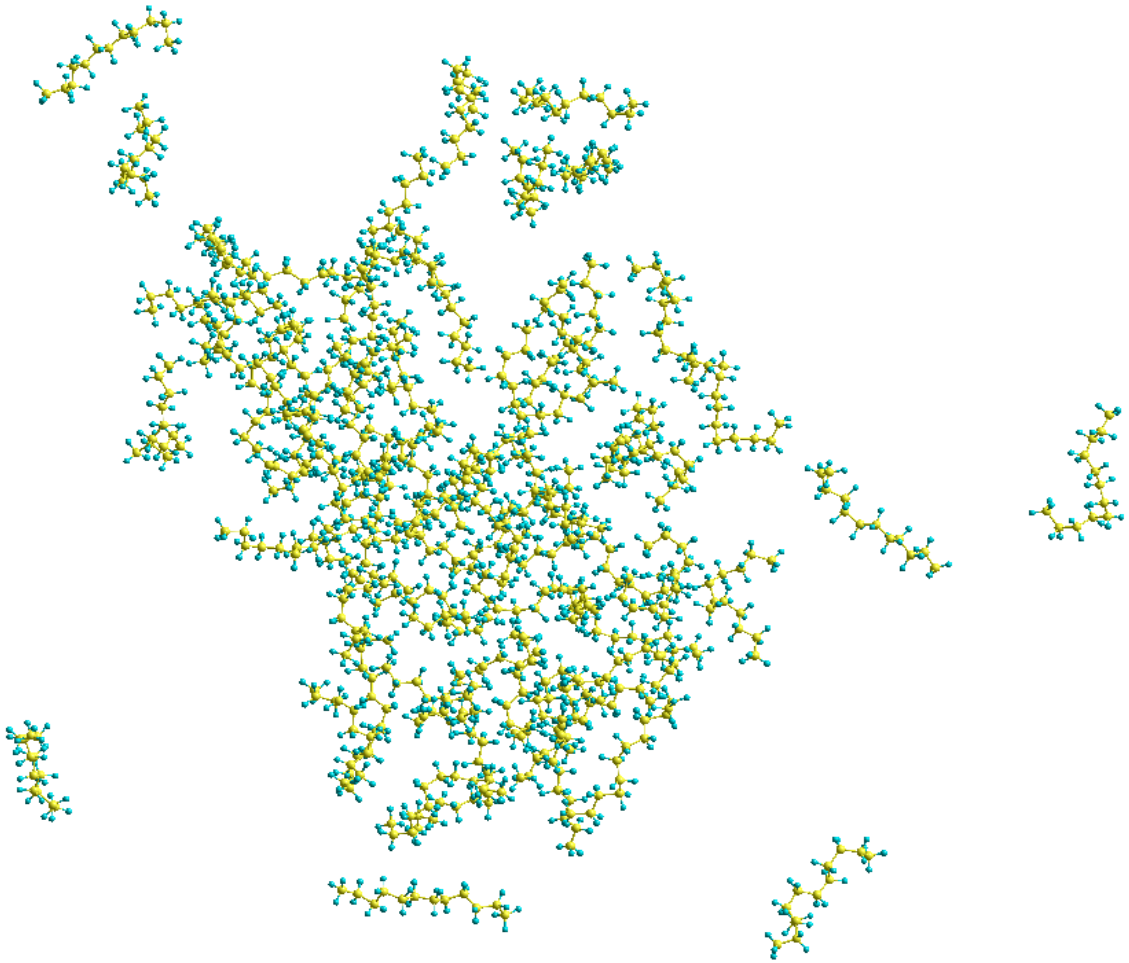
among used 95 conformers

Models



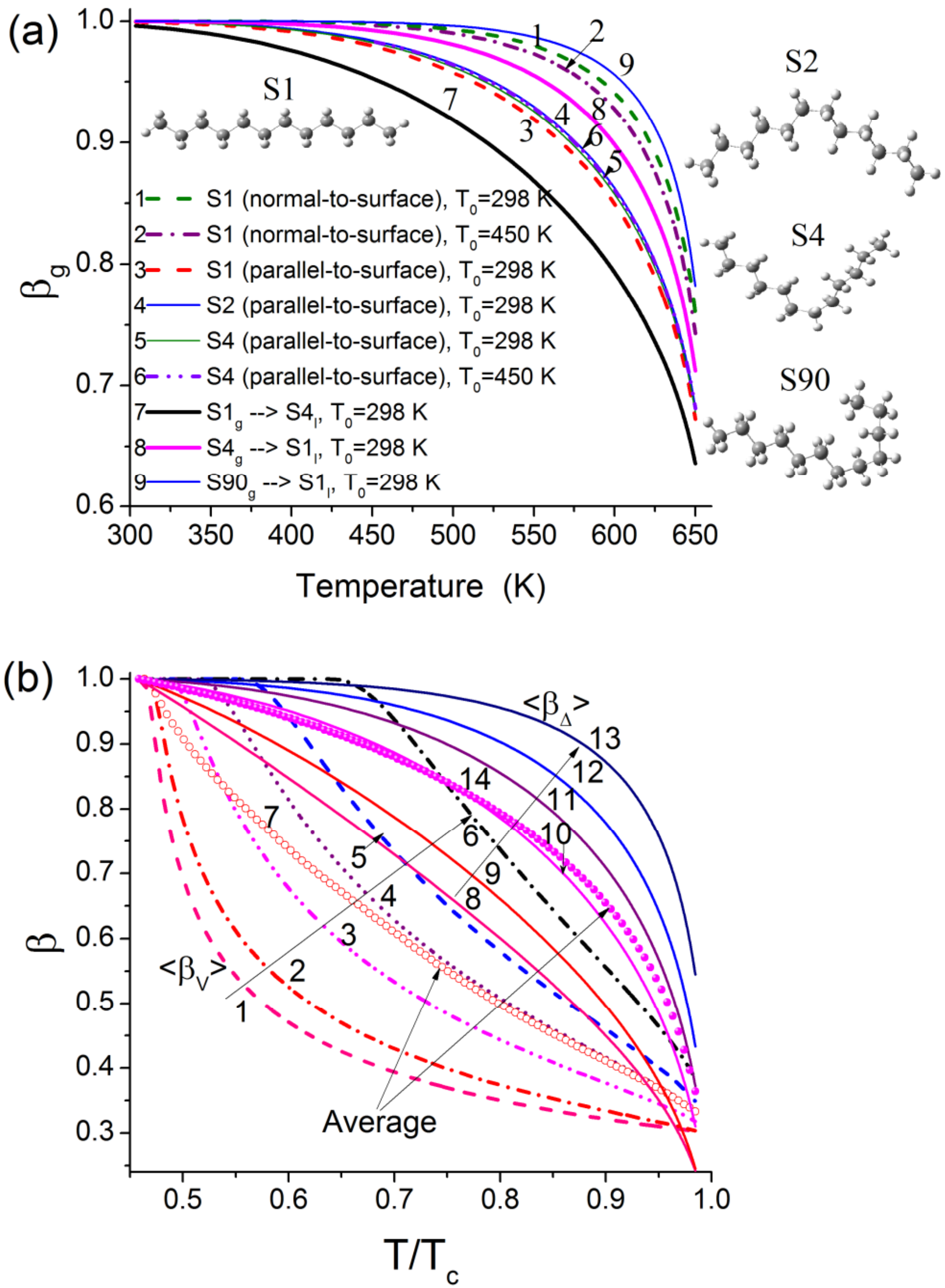
(a) A nanodroplet (cluster) with 64 *n*-dodecane molecules upon MD modelling of heating at 293 K for 20 ps and then at 400 K for 20 ps using MM+ FF; and
visualisation of the vdW, hydrophobic (describing regions with high hydrophobicity), and negative (due to positive charges on the H atoms) fields around the molecules for
(b) individual conformers (S1, S12, S90, and S94)
and (c) conformers interacting in dimers
S1 & S12 and S90 & S94.

Heated nanodroplet with different conformers



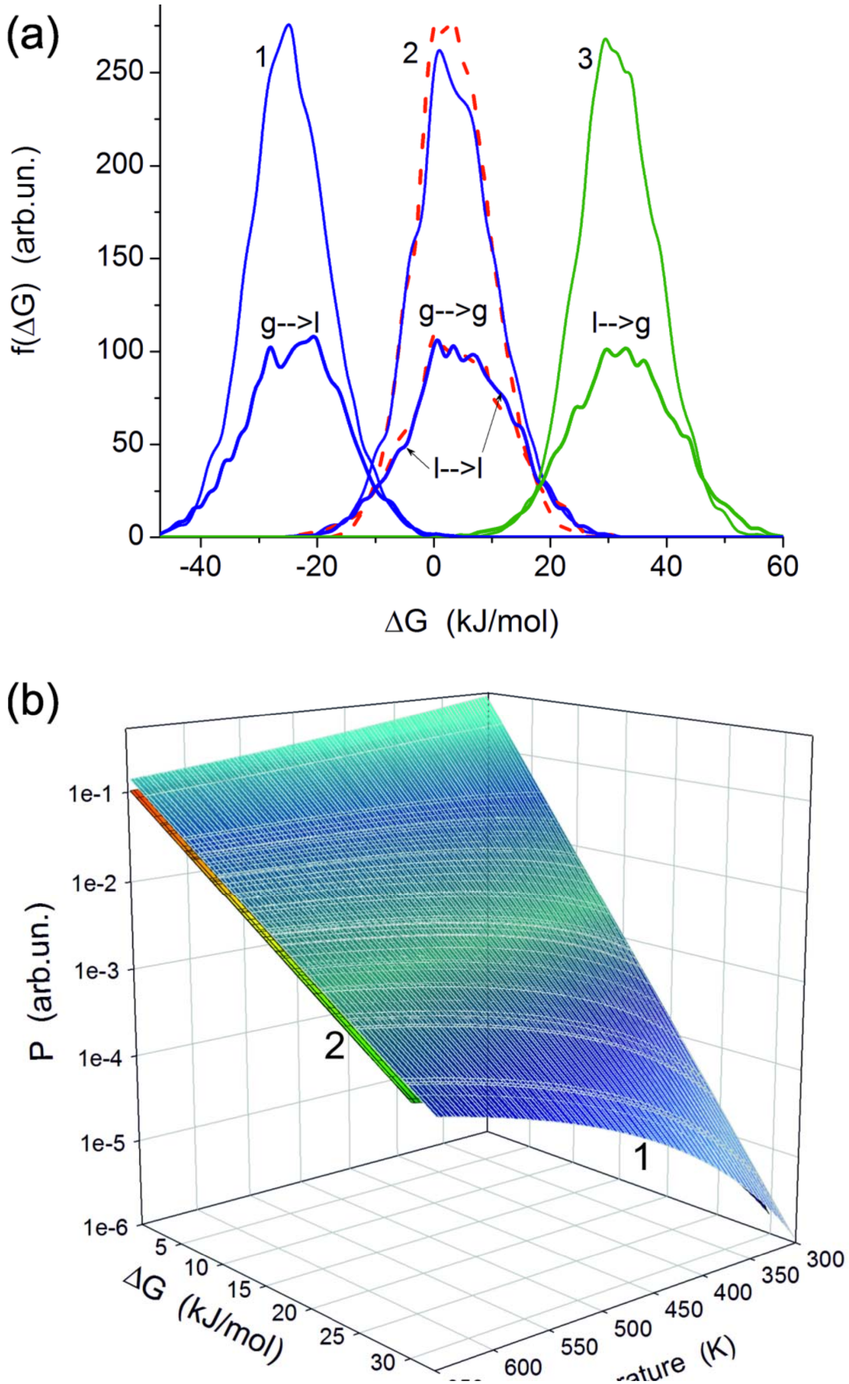
Heating at 293 K for 27 ps, subsequent heating at 400 K for 20 ps, at 489 K for 40 ps, and at 650 K for 20 ps

Surroundings effects



Condensation coefficient *vs*. temperature *(a)* β_g with two orientations of a molecule at a surface of liquid *n*-dodecane as normal to surface (w = 1) and parallel to a surface (w = 5/8) for conformers S1, S2, S4, and S90; and (b) (solid lines) and (dashed and dot-dashed lines) with CDM at w = (curves 1 and 8) 1/4, (2, 9) 1/3, (3, 10) 1/2, (4, 11) 5/8, (5, 12) 3/4, and (6, 13) 1; and average curves (7 and 14). T_0 is temperature in QC calculations using ωB97X-D/cc-pVTZ and SMD/ωB97X-D/cc-pVTZ for (a) selected conformers and (b) a collection of 67 conformers (see Table S2) at pressure of 0.35 MPa.

Population of different conformer states

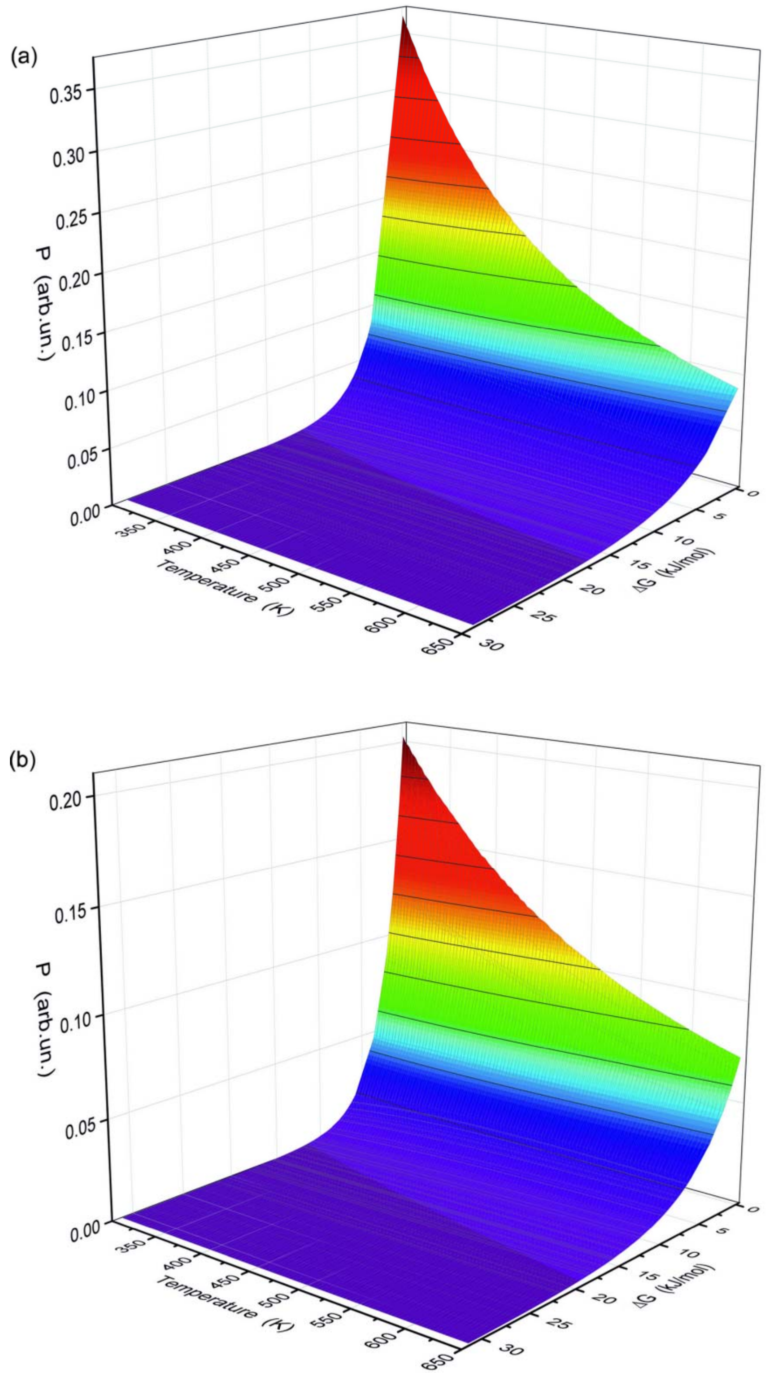


(a) Gibbs free energy distribution functions $f(\Delta G)$ Corresponding to changes in the conformer structure in the same phase (2) or upon transfer between phases (1, 3)
$\Delta G_{g\to l}$ (1), $\Delta G_{g\to g}$ and $\Delta G_{l\to l}$ (2) and $\Delta G_{l\to g}$ (3), calculated by equation

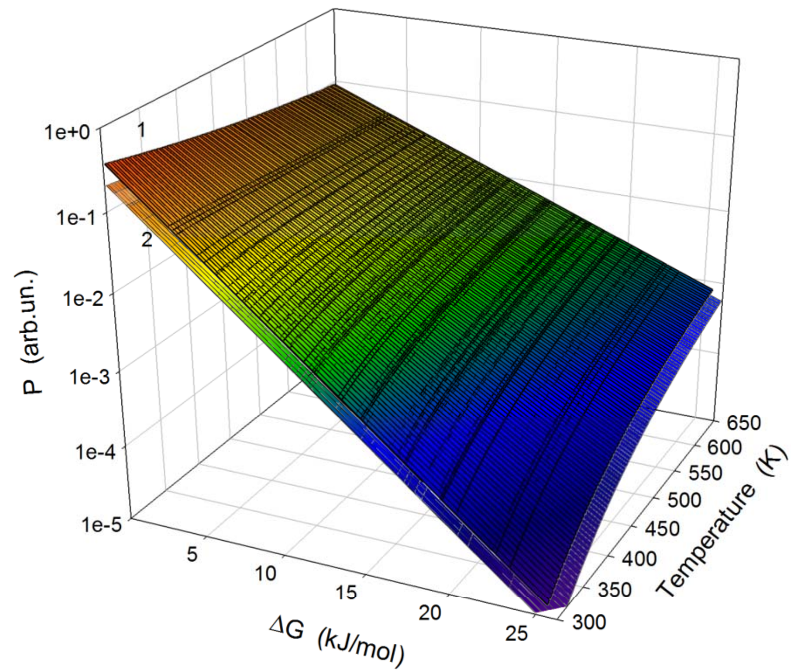
$$f(\Delta G) = (2\pi\sigma^2)^{-0.5}\sum_i \exp[-(\Delta G_i - \Delta G)^2 / 2\sigma^2]$$

at $\sigma = 0.5$ kJ/mol for 67 conformers with the cc-pVTZ basis set (lower curves) and 95 conformers with the cc-pVDZ basis set (upper curves); and (b) populations P of the conformers in the (1) gas and (2) liquid phases calculated for 67 conformers with cc-pVTZ.

Population

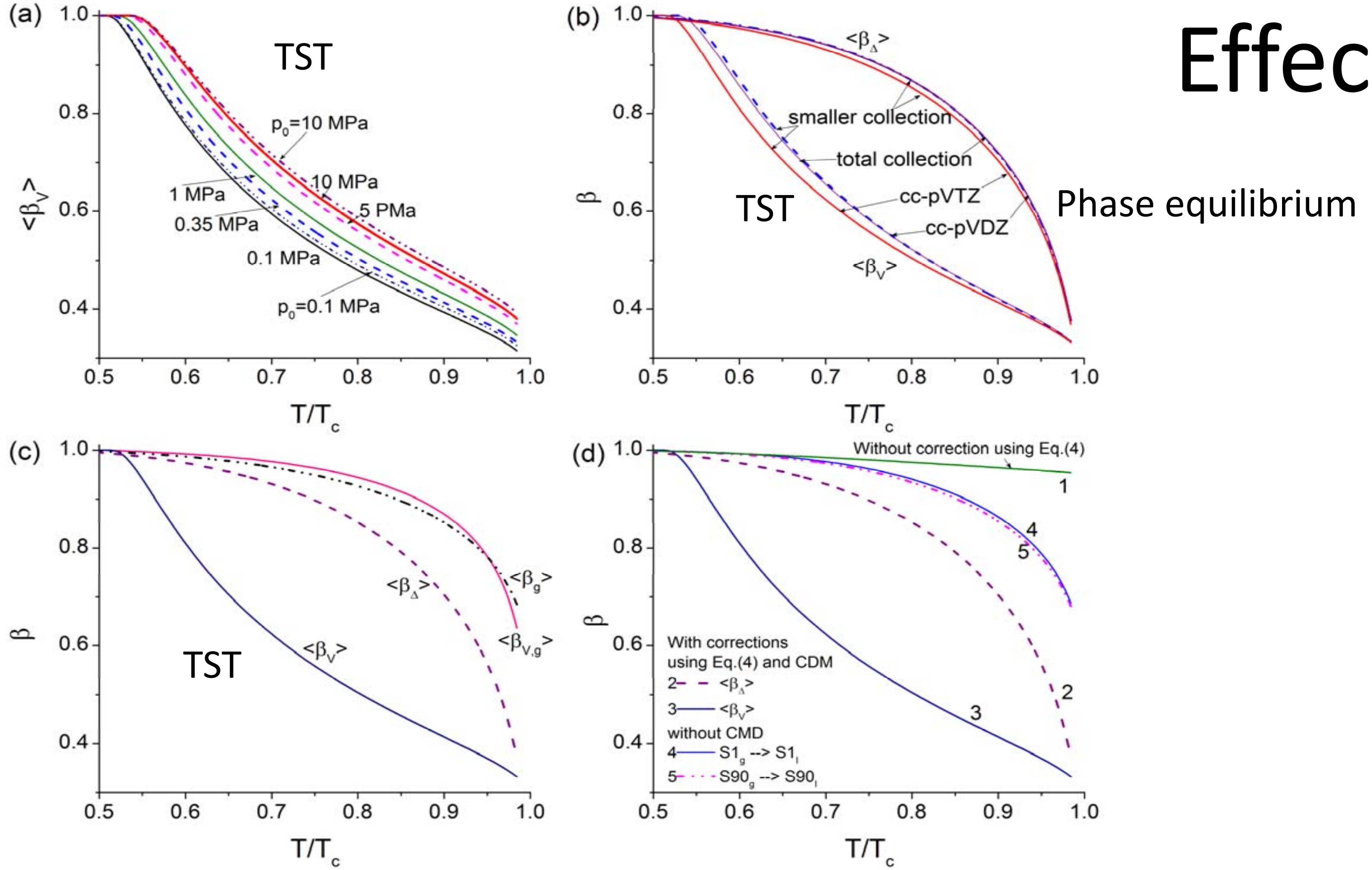


The populations (in linear scale) of the conformers in the (a) gas and (b) liquid phases calculated for 95 conformers with the cc-pVDZ basis set.



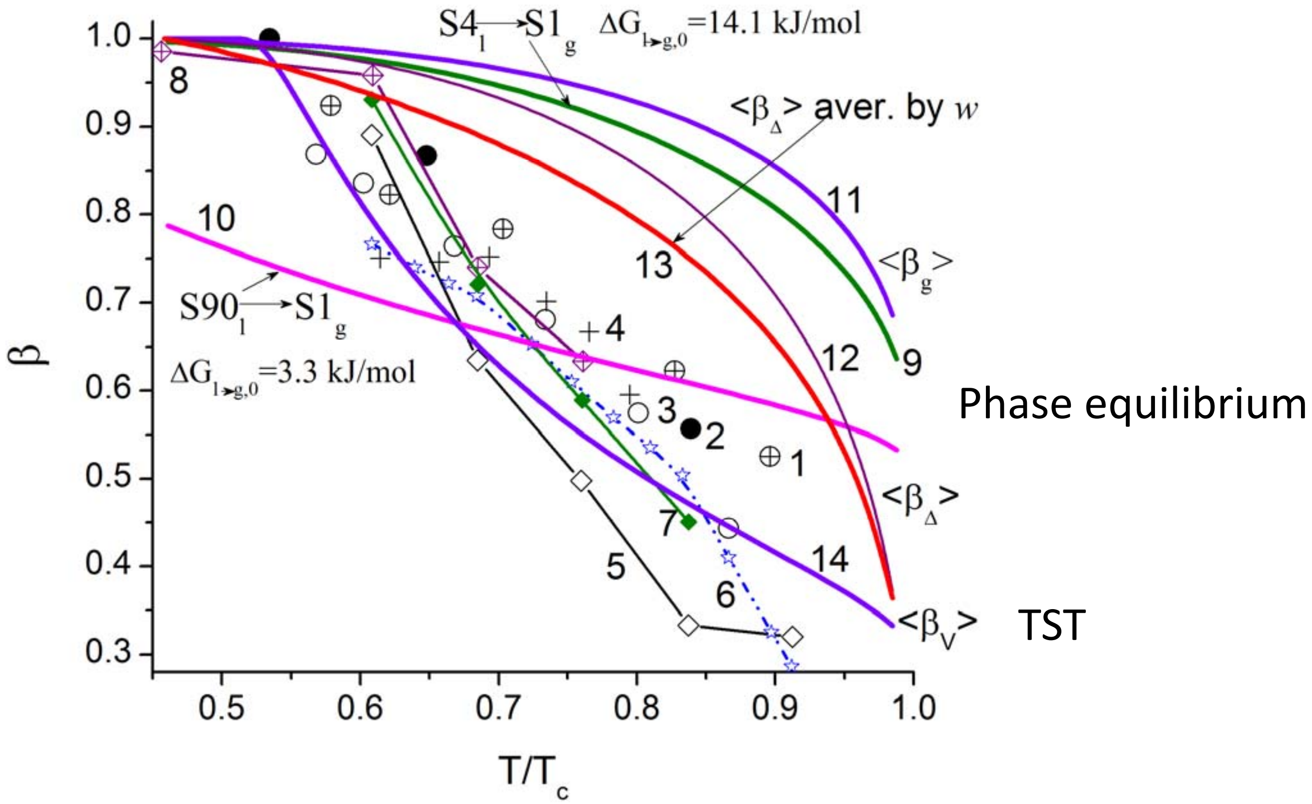
The populations (in log-scale) of the conformers in the (1) gas and (2) liquid phases calculated for 95 conformers with the cc-pVDZ basis set.

Effects I



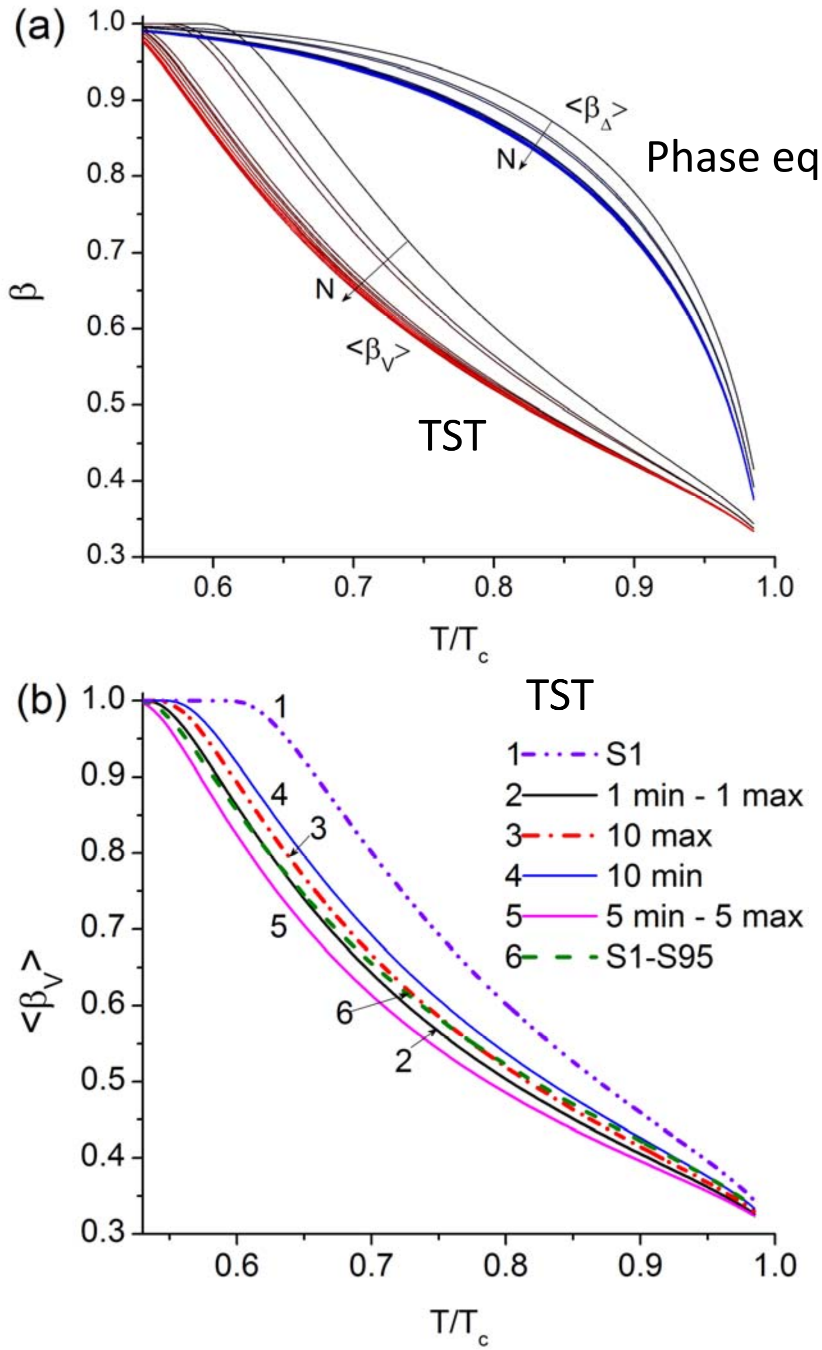
Comparison of (a) effects of pressure (shown in Figure) in the gas phase on at a constant pressure or at p ~ T (p_0 is shown, dot-dot-dashed lines); (b) $<\beta_V>$ & $<\beta_\Delta>$ for smaller (67 conformers) and total (95 conformers) collections with cc-pVTZ and cc-pVDZ; (c) $<\beta_V>$ & $<\beta_{V,g}>$ with $<\beta_V>$ & $<\beta_g>$; and (d) & without (curve 1) or with corrections (curve 2) based on the dependence of vaporisation enthalpy of *n*-dodecane on temperature and considering orientation of a molecule at a surface of liquid dodecane parallel to a surface ($\Delta G_{g\rightarrow l}$ = 5/8 ΔG_s), (curve 3), and curves 4 and 5 correspond to corrected ECC but without CDM for transfer of S1 and S90, respectively. Conformers: (a-d) 67 calculated with cc-pVTZ by ωB97X-D and SMD/ωB97X-D and (b) 95 calculated with the cc-pVDZ basis set at (a) different pressures or (b-d) constant pressure of 0.35 MPa.

Effects II



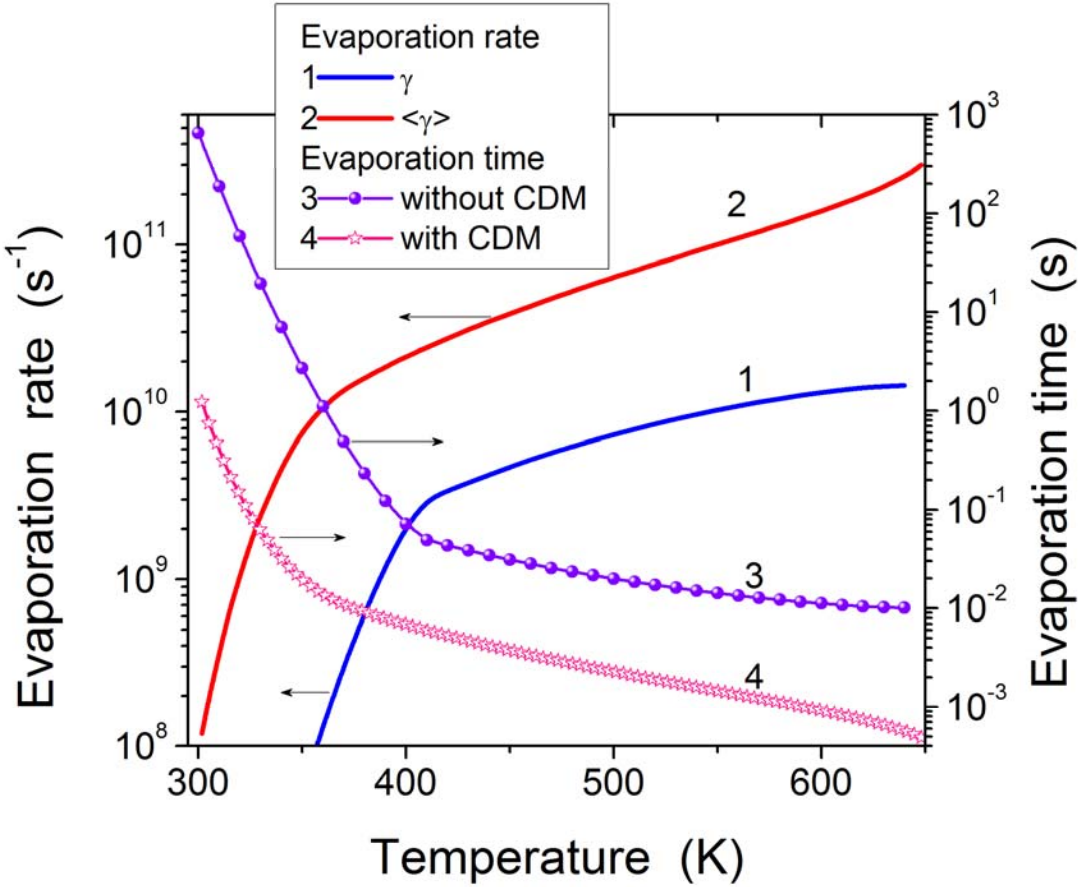
Comparison of the values of the evaporation coefficient, predicted by MD FF (symbols (1-4) refer to the models for structureless LJ fluids with various input parameters, curves with symbols (5-8) refer to the results obtained based on the simplified model of *n*-dodecane molecule (including united atom model)[6] curves 5 and 6 (TST), curves 7 and 8) and QC (9-14 curves) for processes $S4_l \rightarrow S1_g$ (9) and $S90_l \rightarrow S1_g$ (10) with $\Delta G_{l\rightarrow g}$ = 14.1 and 3.3 kJ/mol at T_0 = 298.15 K, respectively, and curves calculated based on the averaging of the contributions of 67 conformers for (11), at w = 5/8 (12) and the results of arithmetical averaging of the values of the coefficients referring to various w (w = 1/4, 1/3, 1/2, 5/8, 3/4, and 1) (13), and at 0.35 MPa (14). QC calculations were performed using ωB97X-D/cc-pVTZ and SMD/ωB97X-D/cc-pVTZ.

Effects III



(a) The values of and various numbers of conformers: N = 1, 5, 10, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, and 95 (arrows indicate the directions of increasing N; calculations were performed using ωB97X-D/cc-pVDZ). (b) The values of for N = 1 (S1; curve 1), N = 2 (curve 2 referring to the case when the summations are performed over the conformers with minimal G for S12 and maximal G for S94), N=10 (curve 3 referring to the case when the summations are performed over 10 conformers with maximal G (S94, S84, S90, S83, S86, S76, S32, S80, S87, and S64), N=10 (curve 4 referring to the case when the summations are performed over 10 conformers with minimal G (S36, S8, S67, S21, S23, S1, S3, S5, S2, and S12), N=10 (curve 5 referring to the case when the summations are performed over 5 conformers with maximal G (S94, S84, S90, S83, and S86), and over 5 conformers with minimal G (S1, S3, S5, S2, and S12), N=95 (curve 6). QC calculations were performed using ωB97X-D/cc-pVDZ and SMD/ωB97X-D/cc-pVDZ.

Evaporation rate *vs*. CDM



Comparison of the evaporation rate γ (curves 1 and 2) and evaporation time (curves 3 and 4 without condensation) of *n*-dodecane nanodroplet (droplet radius 2.65 μm and number of molecules 1.46×10^8, pressure 3.5 MPa) without (curves 1 and 3) and with (curves 2 and 4) taking into account CDM for 67 conformers calculated using ωB97X-D/cc-pVTZ and SMD/ωB97X-D/cc-pVTZ.

Conclusion

Changes in the interaction of a dodecane molecule with the surroundings in the surface layer of a droplet affect ECC more strongly than the conformerisation and cross-conformerisation of the molecules in gas and liquid phases or pressure in the gas phase.
Thus, temperature and the surroundings effects at a surface of droplets are the predominant factors affecting the ECC values for *n*-dodecane molecules.