Can a Computer Crystallize a Liquid? Molecular Simulation of a Continuous Trajectory from Liquid to Crystalline *n*-hexane

Angelo Gavezzotti

Supplementary Information

Details of Monte Carlo procedures

Virial pressure control

For isotropic box dimensions change in a rectangular box, a weak-coupling algorithm similar to those used in molecular dynamics simulations can also be used. The algorithm involves the equipartition kinetic energy, E_{kin}, the virial, W, calculated from derivatives of the potentials, and the current pressure, P, to estimate a variation factor μ for box periodicity such that $a' = \mu\, a$, $b' = \mu\, b$, $c' = \mu\, c$:

$$E_{\mathrm{kin}} = 1/2\, k_{\mathrm{B}}\, N_{\mathrm{dof}}\, T; \qquad P = 2/(3V)\,(E_{\mathrm{kin}} - W)$$
$$V^{\circ} = a\, b\, c; \quad V' = \mu^{3}\, \mathrm{V}^{\circ}; \qquad \mu = (1 + \mathrm{D}V/V^{\circ})^{1/3}$$

The number of degrees of freedom N_{dof} is determined in principle as the sum of rigid-body parameters of all molecules, plus internal degrees of freedom when present, *i.e.* $N_{\mathrm{dof}} = N(\mathrm{molecules})\,[6 + N(\mathrm{internal})] - 6 + 1$. The last two addends are the degrees of freedom of the whole box, and the box volume change d.o.f., respectively. The temperature is taken equal to the MC-Metropolis temperature parameter (see below), in absence of an actual estimate of the molecular velocities. Then if P° is the target pressure one gets:

$$\Delta P = P^{\circ} - P; \qquad \mu = [1 - (P^{\circ} - P)\beta]^{1/3}$$

where $\beta = (1/V^{\circ})\, \Delta V/\Delta P$ is the compressibility. As an order of magnitude, $\beta(\mathrm{water}) = 5 \cdot 10^{-10}\ \mathrm{m}^{2}\ \mathrm{N}^{-1}$, but this number is to be considered as an adjustable parameter in the range down to $3 \cdot 10^{-11}$.

The molecular virial is calculated as follows, if one recalls that in the atom-atom scheme interatomic forces project like the interatomic distance vectors and that derivatives *wrt* distances between molecular centers are equivalent to derivatives *wrt* interatomic distances. Let M and N be two different molecules with atom i on the former and atom j in the latter:

$$E(M,N) = \Sigma_{\mathrm{i,M;j,N}}\, E_{\mathrm{ij}}$$

$$F(M,N) = -\mathrm{d}E_{\mathrm{MN}}/\mathrm{d}R_{\mathrm{MN}} = -\Sigma\, \mathrm{d}E_{\mathrm{ij}}/\mathrm{d}R_{\mathrm{MN}} = -\Sigma\, \mathrm{d}E_{\mathrm{ij}}/\mathrm{d}R_{\mathrm{ij}} = \Sigma\, F_{\mathrm{ij}}$$

$$F_{\mathrm{ij}} = -\mathrm{dE}_{\mathrm{ij}}/\mathrm{R}_{\mathrm{ij}}$$

$$F_{\mathrm{x}} = |F|\, R_{\mathrm{x}}/R; \quad F_{\mathrm{x}}(M,N) = \Sigma\, F_{\mathrm{ij,x}}, \text{ etc. for } y, z$$

$$W(M,N) = -1/2\, \boldsymbol{F}(M,N) \bullet \boldsymbol{R}(M,N) = -1/2\, [F_{\mathrm{x}}(M,N)R_{\mathrm{x}} + F_{\mathrm{y}}(M,N)R_{\mathrm{y}} + F_{\mathrm{z}}(M,N)R_{\mathrm{z}}]$$

$$W_{\mathrm{TOT}} = \Sigma_{\mathrm{M,N}}\, W(M,N)$$

The current value of the virial is calculated to obtain in turn the current pressure, the correction factor μ, and the new box periodicities.

Radial density functions

Consider a pair of atomic species (atom-atom RDF), or pairs of molecular centers (center of mass RDF). N_i is the number of distances in a spherical distance bin of volume V_i, N is the total number of distance points and V is the total volume of the distance sphere. The radial density function *g(R)* is:

$$g(R_i) = (N_i/V_i) / (N/V)$$

N/V is the total number density of distances, corresponding to uniform and random distribution. g(R) is thus normalized and $g(R_i) > 1$ indicates a significantly high frequency of distances at R_i. RDF's are smoothed according to a numerical recipe.

Translational (diffusion) and rotational correlation

The diffusion coefficient *D* and rotational correlation function τ(rot) are estimated as follows. The standard time-dependent formulations are:

$$\tau (t) = [\Sigma_k \mathbf{u}_k(t)\cdot\mathbf{u}_k(0)] /N_{\mathrm{mol}}$$

$$D = (1/6) < |\mathbf{r}(t+\mathrm{D}t)-\mathbf{r}(t)|^2> / \Delta t$$

where **u**(t) is an orientation vector within the molecule, and **r**(t) is the position of a specified atom or of the center of coordinates at time *t*. The number of MC moves takes here the place of time, and an approximate scaling, with an estimate of the time equivalent of a MC move, results in 1Mmove approximately equal to 2 ps. The correlation functions are dimensionless numbers between 1 (complete correlation) and 0 (no correlation), and are averaged over all molecules in the box. They can be compared with experimentally determined correlation times, i.e. the time for the liquid to completely lose rotational memory. The *D* functions are averaged over the molecules within a radius of 25 Å from the overall center of the box.

Debye scattering profile

The scattering profile of a given simulation frame containing N_{mol} molecules can be calculated by the Debye equation

$$I(\theta) = N_{\mathrm{mol}} \Sigma f_k f_n (\sin kR_{kn})/(kR_{kn})$$

where *I* is the scattered intensity, θ is the scattering angle, and the summation runs on all pairs of atoms at distance R_{kn}. The *f*'s are the atomic scattering factors, and $k = 4\pi \sin\theta/\lambda$. For a crystalline system simulated in a computational box, the scattering profile should ideally be identical to the powder diffraction pattern, except that the limited size of the computational box introduces a large truncation error and a broadening of the peaks.

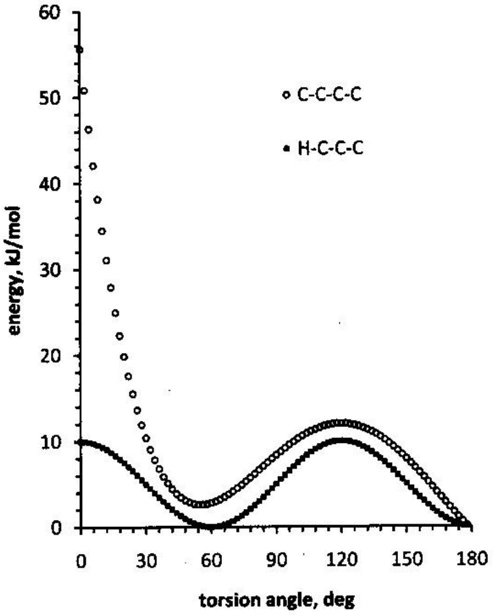

Figure S1. The torsional potentials: CCCC from a fitting of data from G.D.Smith and R.L.Jaffe, J.Phys.Chem. 1996, 100, 18718. HCCC is a cosine function.

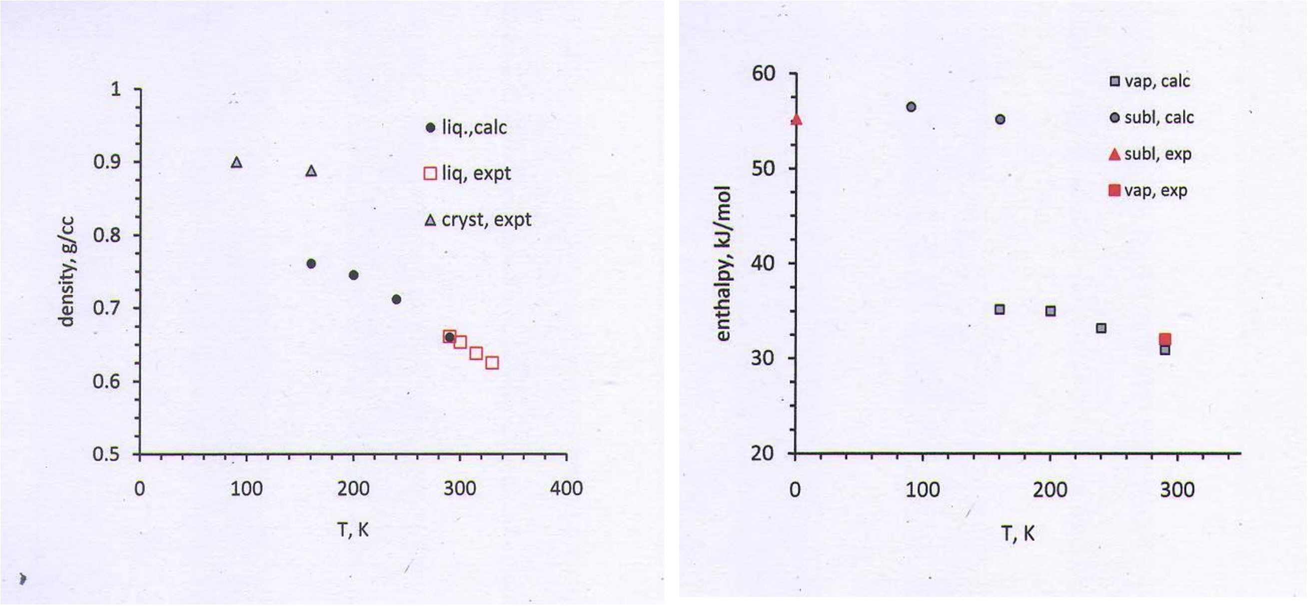

Figure S2. Left: calculated and experimental density of n-hexane. Right: calculated and experimental phase change enthalpies.

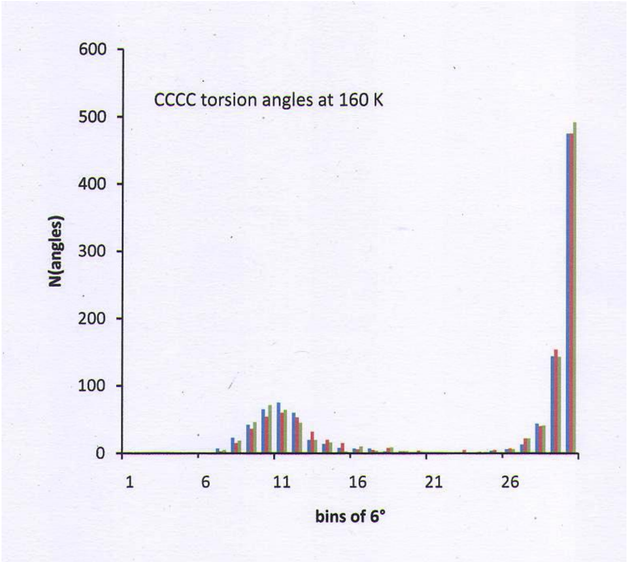

Figure S3. Distribution of the four torsion angles (one color bar for each) in liquid n-hexane at 160 K. The abscissa is the torsion angle from 0 to 180° in bins of 6°.

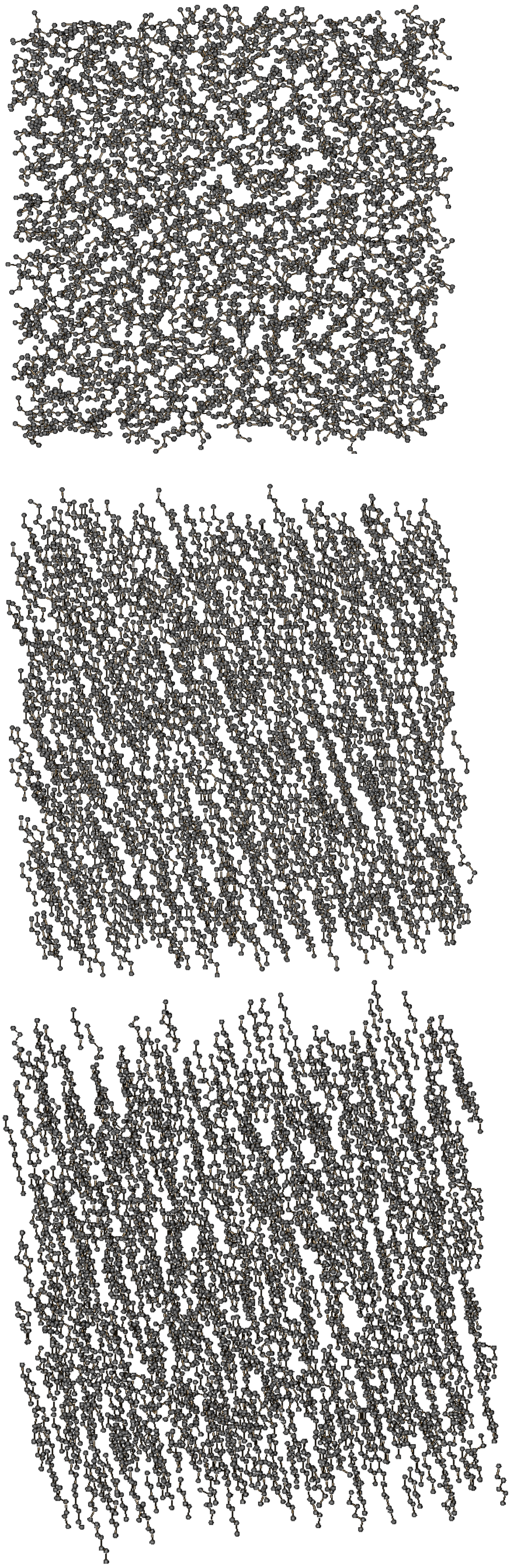

Figure S4. Top to bottom: final frames for liquid, symmetrization with tolerance 10^{-6}, and symmetrization with tolerance 10^{-5}. Hydrogen atoms omitted

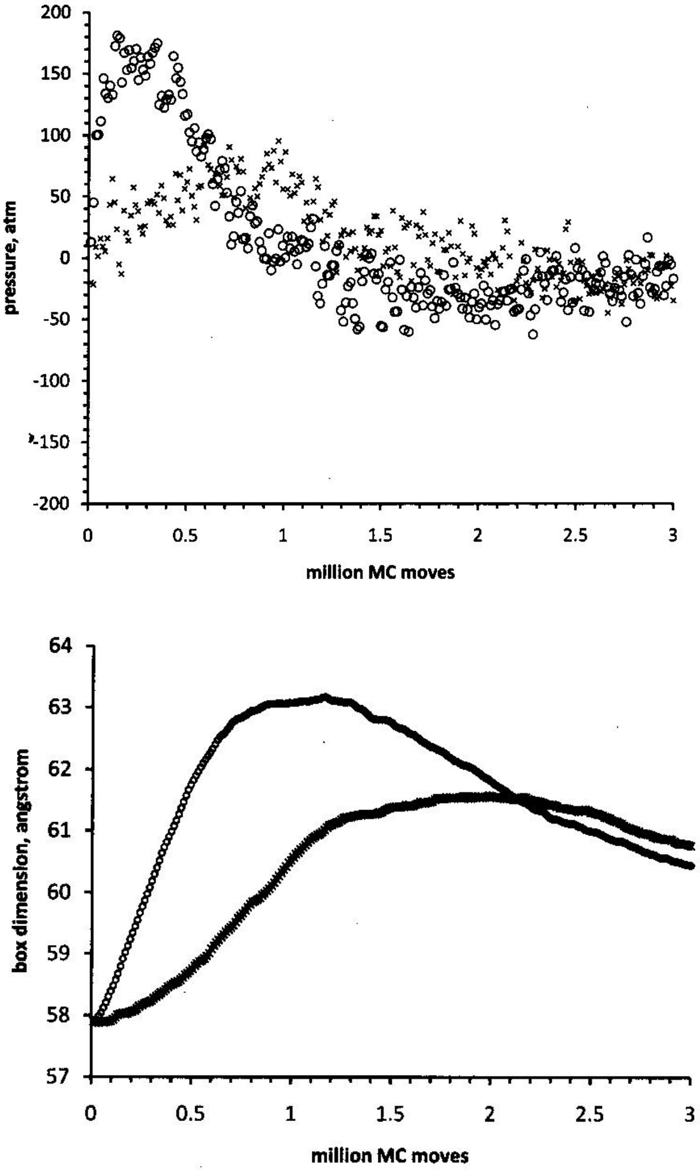

Figure S5. Top: pressure evolution during the symmetrizations at tolerance 10^{-6} (higher) and 10^{-5} (lower curve). Bottom: Same, trajectory of the box dimension (Å).

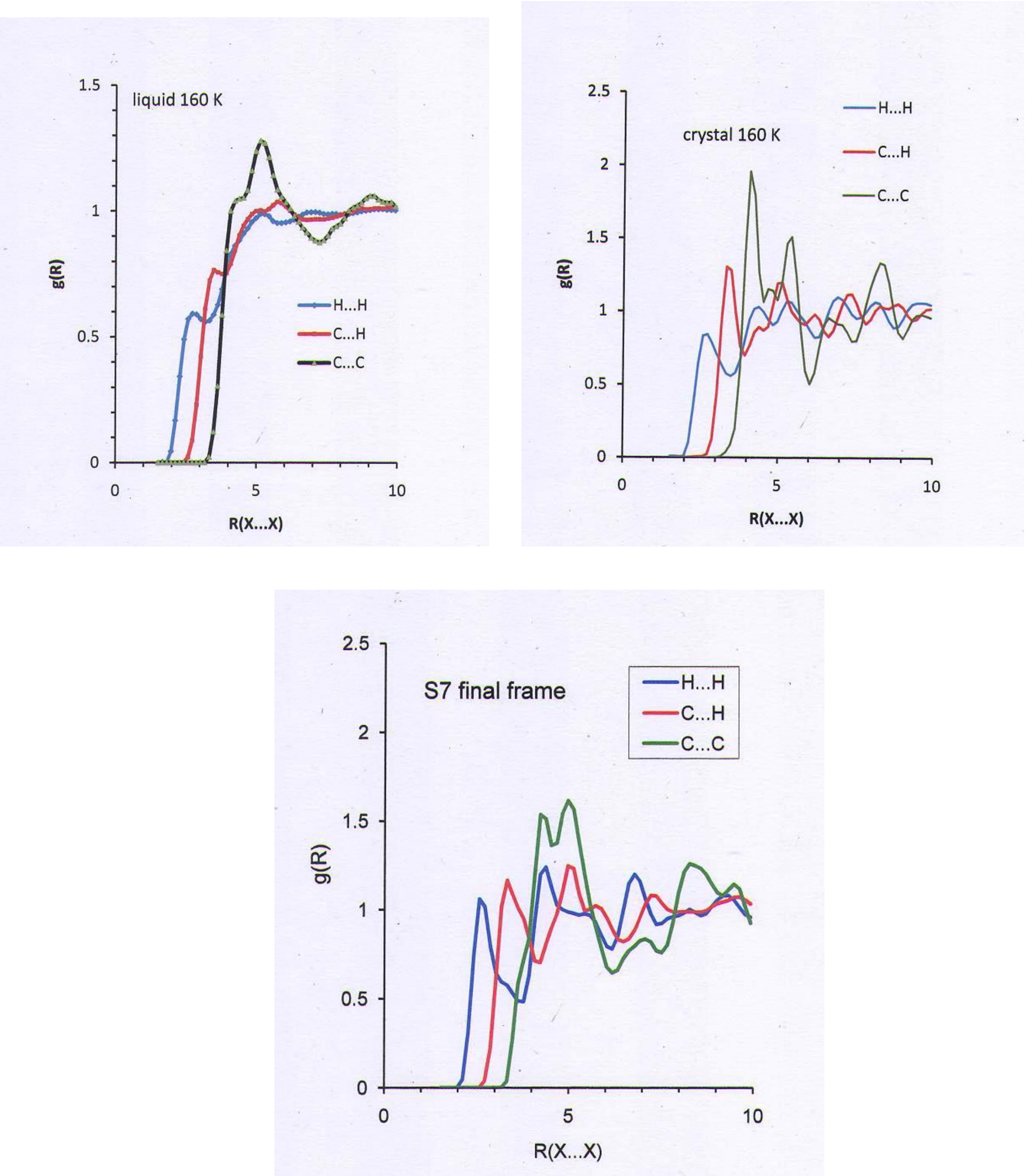

Figure S6. Atom-atom radial distribution curves for liquid, crystalline and after-symmetrization n-hexane.

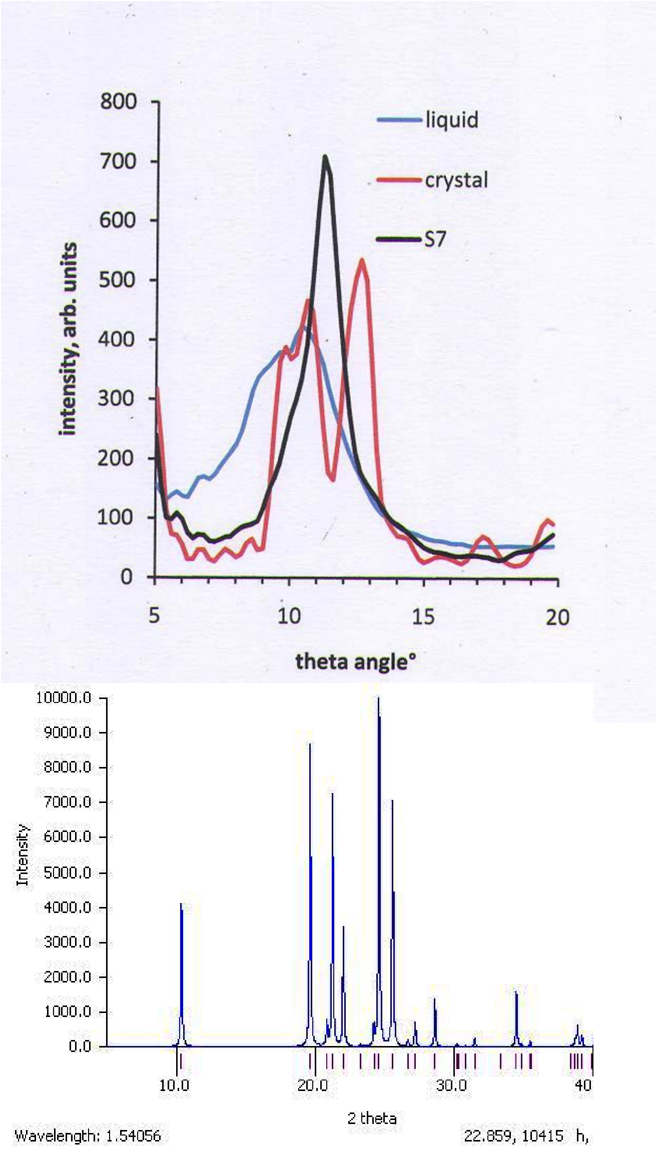

Figure S7. Top: Debye scattering profiles for liquid, crystalline and after-symmetrization n-hexane. The very low resolution of all curves in comparison with the calculated spectrum for the real crystal (bottom) is due to truncation effects over the small size of the computational boxes.