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

Supplementary material - Sensitivity of solid phase stability to the interparticle potential range : studies of a new Lennard-Jones like model

Computational details of the calculations reported in the main article are provided here, for both the LSMC and thermodynamic integration simulations. In particular, all parameter values are made explicit by providing our simulation input files (see folder `Simulations` of this supplementary material). Moreover, raw simulation results of the Lattice-Switch Monte-Carlo (LSMC) simulations are provided in the file `Simulations/LSMC/data.txt` and those of the thermodynamic integration calculations can be found below in Table S1.

1 Lattice-Switch Monte-Carlo calculations

The Lattice-Switch Monte-Carlo simulations were performed with the program DL_MONTE version 2.07 [1]. In these simulations, we have used $\epsilon = 1\ k_B$K and $\sigma = 1$ Å. With this choice of ϵ, the physical temperature T and the reduced temperature $T^* = k_BT/\epsilon$ are identical

1.1 DL_MONTE input files

For performing LSMC simulations in DL_MONTE, the following files must be provided : CONTROL, FIELD, CONFIG.1, CONFIG.2, and CONFIG. Note that DL_MONTE operates with physical units rather than the reduced units quoted in the main paper. Our input files for a simulation at $T = 0.1$ and $p = 1.7$ katm (state point near the first hcp-fcc transition) are provided in folder `Simulation/LSMC`. Information on the parameters used for other transition lines, temperatures and system sizes are given in the file `README_LSMC.txt` inside the `LSMC` folder.

The FIELD file

The FIELD file contains options for energy units as well as the potential used during the simulation. Since we use the directive '`UNITS K`', the energies in the output files are in k_BT units, i.e. in reduced units since $\epsilon = 1k_BT$.
We have modified DL_MONTE's source code to operate with the Lennard-Jones like (**ljl**) potential. The use of this potential is specified by the following line :

```
LJ core  LJ core  ljl 1.0 1.0 2.0
```

where the three numbers correspond to ϵ, σ and r_c respectively. For more information regarding available options, the reader is referred to the DL_MONTE manual [2].

The CONTROL file

The CONTROL file contains the simulation main directives. The DL_MONTE tutorial[3] is a good resource to understand the LSMC directives in DL_MONTE.

A LSMC simulation starts with the computation of the bias function. The tutorial explains how to determine the range of order parameter over which the bias function should be determined. Here, we only give parameters values relevant to our calculations for the case of the first transition line at $T = 0$ and $p = 1.7$ katm. Results and other parameters are listed in the "README_LSMC.txt". The `switchfreq` is the frequency at each the simulation attempts a lattice-switch move. Here, its the number of atoms of the simulation cells $N = 216$. The number of steps is fixed to 200000 sweeps. The following lines are LSMC directives :

```
fed method TM tri 4320000 4320   # Nout Nupdate
fed order param ps 200 -15 15 1  # Nbins xmin xmax npow
```

Configuration files

CONFIG.1 and CONFIG.2 files contain the two candidates configurations at $T = 0$ between which the system will switch. The CONFIG file contains the concatenation of CONFIG.1 and CONFIG.2 in order (not necessarily at $T = 0$). For the simulation with $N = 216$, these CONFIG files are provided in the tutorial page. Configuration files for hcp and fcc for other system sizes and densities can be generated by using a script provided with the program *MonteSwitch*[4] (see files `lattice_in_hcp_fcc.f95` and `kinds_mod.f95`).

1.2 Calculations of the uncertainties

Uncertainties on the coexistence pressure are calculated from the uncertainty in the difference of the volumes of the coexisting phases, $\sigma_{\Delta V} = \sigma_{V_{hcp}} + \sigma_{V_{fcc}}$ and from ΔG, the latter being determined via a block analysis. Then

$$\sigma_p = \left|\frac{\sigma_{\Delta G}}{\Delta V}\right| + \left|\frac{\Delta G\,\sigma_{\Delta V}}{(\Delta V)^2}\right|. \tag{1}$$

The uncertainty on the coexistence density is deduced from the uncertainty on the coexistence pressure by using the equation of state $p = f(\rho)$:

$$dp = \frac{df(\rho)}{d\rho} d\rho \quad \Rightarrow \quad \sigma_\rho = \sigma_p / f'(\rho). \tag{2}$$

We derive now Eq. (1), which is an upper bound on the error. To obtain this upper bound, we use the following two standard rules: (1) add absolute errors when performing an addition or subtraction and (2) add the relative deviations when computing a product or ratio, e.g. $|\mathrm{dZ/Z}| = |\mathrm{dX/X}| + |\mathrm{dY/Y}|$) if $Z = X/Y$. According to the first rule, the upper bound for the uncertainty of a quantity $X - Y$ is

$$\sigma_{X-Y} = \sigma_X + \sigma_Y. \tag{3}$$

The second rule is a consequence of the first rule and of the logarithmic derivative

$$d\ln(x) = dx/x. \tag{4}$$

From Eq. (3) we get

$$dP_{i+1} = dP_i + d\left(\frac{\Delta G_i}{\Delta V_i}\right). \tag{5}$$

From Eq. (4) we get

$$d\left(\frac{\Delta G_i}{\Delta V_i}\right) = \frac{\Delta G_i}{\Delta V_i} d\ln\left(\frac{\Delta G_i}{\Delta V_i}\right).$$

From the properties of the logarithm, we have

$$d\ln\left(\frac{\Delta G_i}{\Delta V_i}\right) = \frac{d\Delta G_i}{\Delta G_i} - \frac{d\Delta V_i}{\Delta V_i}.$$

Inserting this expression in Eq. (5), we find

$$dP_{i+1} = dP_i + \frac{d\Delta G_i}{\Delta V_i} - \frac{\Delta G_i d\Delta V_i}{(\Delta V_i)^2} \tag{6}$$

By taking absolute values, we get :

$$\sigma_{P_{i+1}} = \sigma_{P_i} + \left|\frac{\sigma_{\Delta G_i}}{\Delta V_i}\right| + \left|\frac{\Delta G_i \sigma_{\Delta V_i}}{(\Delta V_i)^2}\right| \tag{7}$$

The phase diagram was computed with LSMC simulation at constant pressure, so $\sigma_{P_i} = 0$. We thus find the upper bound given by Eq. (1). The uncertainties on ΔV were computed with pymbar ([5],[6]).

2 Thermodynamic integration calculations

The TI calculations were performed using GROMACS version 2018, compiled in double precision. In these simulations, we have used the Lennard-Jones parameters $\epsilon = 0.99768$ kJ.mol^{-1} and $\sigma = 0.34050$ nm (values for argon). The factor ϵ/k_B that intervenes when computing a reduced temperature is thus equal to $\epsilon/k_\mathrm{B} = 119.9933$ K.

We implemented the Wang et al.[7] potential as a tabulated potential. The corresponding file (`table.xvg`) is provided with the other simulation input files (see section 2.1).

The TI calculations were performed by using the same methodology as in Ref. [8]. The supplementary material of Ref [8] provides *bash* scripts to compute the different contributions A_0, ΔA_1 and ΔA_2. We adapted these scripts to the more recent version 2018 of gromacs. We improved also the script that computes ΔA_1 by using the `-rerun` option of gromacs's program `mdrun`. This improves vastly the performance of the calculation of ΔA_1. The script that computes ΔA_2 with a 15 point Gauss-Legendre quadrature needs an input file (`landas.dat`) which lists the 15 "intermediate" spring constants and the associated weights for the numerical integration (including a factor arising from the change of variable). We provide a Python script, `calc_GaussLegendre_xi_wi.py`, that computes these "intermediate" spring constants and weights.

2.1 Simulation input files

The folder `Simulations/TI` contains the simulation input files, as well as analysis scripts that we used to compute the free energy of the hcp and fcc phases for the state point $T = 0.1$ and $\rho = 1.20$. These files are stored in 4 subfolders :

- `1-EinsteinCrystal` : simulation of an Einstein crystal with one fixed atom and $(N-1)$ independent harmonic oscillators.
- `2-U_LJ` : 0-step "simulation" to calculate $E_\mathrm{pair}^{(T=0)}$, which is the sum of the pair interactions in the perfect crystal at $T = 0$.
- `3-DeltaA1` : calculation of ΔA_1 using Bennet's formula. It uses the results from the two previous simulations.
- `4-DeltaA2` : calculation of ΔA_2. This involves 15 simulations with various spring constants.

In each folder, there is a script with a name with form `calc_*.sh`, namely `calc_traj.sh`, `calc_U_LJ.sh`, `calc_deltaA1.sh` and `calc_deltaA2.sh` respectively. By executing these scripts one after another, one obtains the values of ΔA_1 and ΔA_2 at $T = 0.1$ and $\rho = 1.20$. The file `README_TI.txt` explains how to adapt the simulation input files and the scripts to compute the free energy at another temperature or density.

2.2 Numerical results

Table S1 complements Table 1 of our article by providing some supplementary information: the maximal spring constants used and the contributions $A_0 + k_BT\ln(N\Lambda_T^3/V)$, ΔA_1 and ΔA_2 to the free energy (see eq. (4) of the paper). Notice that the free energies A_hcp and A_fcc in Table S1 are in reduced units and per particle, while the free energy differences are expressed in units of Nk_BT in Table 1 of our article.

Table S1: Maximal spring constant k_E (in kJ.mol^{-1}.nm^{-2}) and contributions A_0, ΔA_1 and ΔA_2 (in units of Nk_BT) to the free energy A (in reduced units per particle) for the HCP and FCC phases of the LJL solid. The free energies from Ref. [7] are in reduced units per particle.

T	ρ	k_E	A_0	HCP				FCC			
				ΔA_1	ΔA_2	A_{hcp}	Ref.[7]	ΔA_1	ΔA_2	A_{fcc}	Ref.[7]
0.1	1.16	448956	16.9685	−58.5914	−7.6207	−4.9244	−4.9469	−58.5298	−7.6608	−4.9222	−4.9241
0.1	1.20	448956	16.9686	−55.1582	−7.4295	−4.5619	−4.5848	−55.1715	−7.4706	−4.5674	−4.5691
0.1	1.24	448956	16.9686	−50.9641	−7.2604	−4.1256	−4.1487	−51.0673	−7.2883	−4.1387	−4.1404
0.1	1.28	448956	16.9687	−46.0015	−7.0965	−3.6130	−3.6363	−46.1907	−7.1128	−3.6335	−3.6350
0.1	1.32	448956	16.9687	−40.2637	−6.9318	−3.0227	−3.0455	−40.5135	−6.9455	−3.0491	−3.0505
0.204	1.20	300000	15.2966	−27.0255	−6.8378	−3.7877	−3.8324	−27.0318	−6.8673	−3.7950	−3.7981
0.308	1.20	300000	14.6795	−17.8933	−6.8486	−3.0993	−3.1615	−17.8980	−6.8760	−3.1092	−3.1084
0.4	1.20	300000	14.2879	−13.7737	−6.8442	−2.5321	−2.6178	−13.7771	−6.8707	−2.5441	−2.5479
0.503	1.20	300000	13.9447	−10.9492	−6.8442	−1.9360	−2.0334	−10.9523	−6.8670	−1.9490	−1.9437
0.607	1.00	130000	12.4102	−10.7382	−6.6478	−3.0203	−3.1014	−10.7019	−6.6787	−3.0170	−2.9764
0.607	1.10	200000	13.0556	−10.2554	−6.7341	−2.3879	−2.4896	−10.2328	−6.7591	−2.3893	−2.3660
0.607	1.20	300000	13.6631	−9.0699	−6.8439	−1.3663	−1.4806	−9.0724	−6.8699	−1.3836	−1.3706
0.802	1.0	140000	12.1039	−8.1180	−6.7466	−2.2141	−2.3336	−8.0958	−6.7628	−2.2093	−2.1676
0.802	1.1	200000	12.6383	−7.7568	−6.7286	−1.4815	−1.6116	−7.7395	−6.7536	−1.4876	−1.4465
0.802	1.20	300000	13.2458	−6.8598	−6.8449	−0.3683	−0.5123	−6.8624	−6.8646	−0.3861	−0.3619

References

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[2] A. V. Brukhno and J. Grant and T. L. Underwood. *DL_ Monte Manual.* Version 2.07. 2023. URL: `https://dl_monte.gitlab.io/dl_monte_manual`.

[3] *DL_ MONTE tutorial.* `https://dl_monte.gitlab.io/dl_monte-tutorials-pages/tutorial7.html`. [Online; accessed 5-Nov-2023].

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