

# Theoretical prediction of the homogeneous ice nucleation rate: disentangling thermodynamics and kinetics

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## EXPLANATIONS ON HOW TO OBTAIN THE NUCLEATION FREE ENERGY

As discussed in Ref. [1], the zero excess for  $\Phi$  condition for the Gibbs dividing surface can be expressed in the following probabilistic form: if the reference system and the actual solid-liquid system both have  $n_s(\Phi)$  solid atoms and  $N - n_s(\Phi)$  liquid atoms, they should also both have the same distribution for  $\Phi$  [1], i.e.

$$\rho_{\text{sl}}(\Phi|n_s(\Phi), N - n_s(\Phi)) \equiv \rho_{\text{ref}}(\Phi|n_s(\Phi), N - n_s(\Phi)). \quad (1)$$

Eqn. (1) can then be used to link the free energy profile  $\tilde{G}(\Phi)$  and the free energy for a single solid cluster  $G(n_s(\Phi))$  relative to the bulk liquid:

$$e^{-\beta\tilde{G}(\Phi)} = \int_{n_{\text{cut}}}^{n^*} dn_s(\Phi) \rho_{\text{sl}}(\Phi|n_s(\Phi), N - n_s(\Phi)) N_s e^{-\beta G(n_s(\Phi))}, \quad (2)$$

This expression is valid for values of  $\Phi$  that satisfy  $\rho_{\text{sl}}(\Phi|n_s(\Phi), N - n_s(\Phi)) \approx 0$  for all  $n_s(\Phi) < n_{\text{cut}}$ . To avoid the numerical instabilities in the direct deconvolution process, Eqn. (2) can be solved numerically using a fixed-point iteration scheme [1]:

$$G(n_s(\Phi)) = \tilde{G}(\bar{\Phi}(n_s(\Phi))) + \frac{1}{\beta} \log N_s + \frac{1}{\beta} \log \int_{n_{\text{cut}}}^{n^*} dn \rho_{\text{sl}}(\bar{\Phi}(n_s(\Phi))|n, N - n) e^{-\beta[G(n) - G(n_s(\Phi))]}, \quad (3)$$

where  $\bar{\Phi}(n_s(\Phi)) = \int d\Phi \rho_{\text{sl}}(\Phi|n_s(\Phi), N - n_s(\Phi)) \Phi$ . Eqn. (3) can be solved iteratively by starting from the initial guess  $G_0(n_s) = \tilde{G}(\bar{\Phi}(n_s(\Phi)))$ , and by then plugging the old guess into the right-hand side so as to obtain a new estimate at each iteration.

As discussed in the main text, we computed the free energy profile  $\tilde{G}(\Phi)$  with respect to the extensive quantity  $\Phi$  of the system from umbrella simulations. We also computed the probability distributions  $\rho_{\text{sl}}(\Phi|n_s(\Phi), N - n_s(\Phi))$  from unbiased simulations of the bulk phases [1], and used the knowledge obtained from such simulations to convert  $\tilde{G}(\Phi)$  for the whole system into  $G(n_s(\Phi))$  using the iterative expression in Eqn. (3). We used  $n_{\text{cut}} = 50$ , and also assumed that the number of nucleation sites  $N_s$  was equal to the total number of atoms in the system  $N$ . We have also tried using  $n_{\text{cut}}$  equals 30, 100, 150, and 200, and confirmed that the free energy profile  $G(n_s(\Phi))$  obtained is not affected by the choice of  $n_{\text{cut}}$ .

## Notes on the sample PLUMED input file

Here we provide a sample input file for PLUMED. This input was used to run the umbrella simulations described in the main text.

First compute the Q6 bond order parameter for each water molecule.

```
Q6 ...
LABEL=q6
SPECIES=1-8192 SWITCH={CUBIC D_0=0.33 D_MAX=0.37}
LOWMEM
... Q6
```

The following comment computes locally averaged Q6 for all the particles that are within a cutoff radius. The value for m6.morethan-1 is used as the global order parameter  $\Phi$  described in the paper.

```
LOCAL_AVERAGE ...
LABEL=m6
SPECIES=q6
SWITCH={CUBIC D_0=0.33 D_MAX=0.37}
MEAN
MORE_THAN1={SMAP R_0=0.2 D_0=0.18 A=8 B=8}
LOWMEM
... LOCAL_AVERAGE
```

```
DUMPMULTICOLVAR STRIDE=1000 DATA=m6 FILE=m6.xyz
```

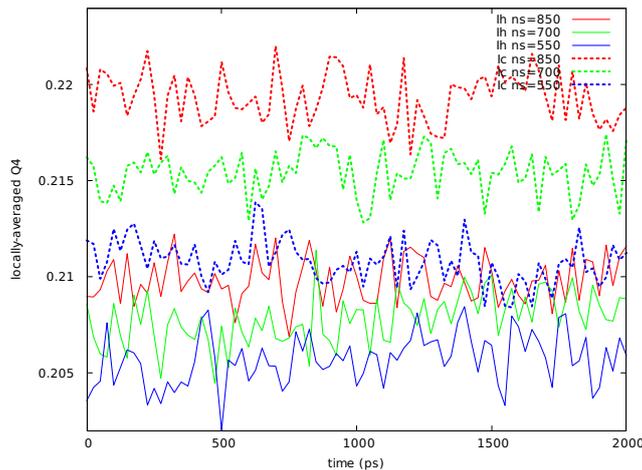


FIG. 1: The time evolution of  $\overline{Q_4}$  during the umbrella sampling simulations with  $\kappa = 0.005$ .

The following comment adds a harmonic restraint on the collective variable in the form

$$V_{\text{bias}}(\Phi) = \frac{\kappa}{2} (\Phi - \bar{\Phi})^2, \quad (4)$$

where  $\kappa$  denotes the spring constant, and  $\bar{\Phi}$  is the center of the umbrella potential. In order to sample all relevant values of  $\Phi$  in a quasi-uniform manner, we used about 50 windows with different values of  $\bar{\Phi}$ , while adjusting the spring constant  $\kappa \in (0.005, 0.1)$  according to the gradient  $d\tilde{G}(\Phi)/d\Phi|_{\Phi=\bar{\Phi}}$ .

```
RESTRAINT ARG=m6.morethan-1 AT=NUMBER KAPPA=0.01 LABEL=res
```

```
PRINT STRIDE=10 ARG=m6.*,res.bias FILE=COLVAR
FLUSH STRIDE=10
```

```
ENDPLUMED
```

The following comments compute locally averaged bond order Q4. This order parameter differentiates ice Ic and Ih structures.

```
Q4 ...
LABEL=q4
SPECIES=1-8192 SWITCH={CUBIC D_0=0.33 D_MAX=0.37}
LOWMEM
... Q4
```

```
LOCAL_AVERAGE ...
LABEL=m4
SPECIES=q4
SWITCH={CUBIC D_0=0.33 D_MAX=0.37}
MEAN
LOWMEM
... LOCAL_AVERAGE
```

### Monitoring the cubicity of the ice nucleus

In order to obtain the nucleation free energy profile for pure Ih or Ic ice nuclei, we rely on the fact that the formation of stacking disorders during the umbrella sampling simulations has a time scale that is longer than the local equilibration time. To confirm this, we plotted the time evolution of the locally-average bond order parameter  $\overline{Q_4}$  that is able to differentiate the two ice phases, as well as visually inspected the snapshots collected during the simulations. From Fig. 1, it can be seen that there is no drift of the mean values of  $\overline{Q_4}$  during 2 nanosecond runs of the umbrella sampling simulations, indicating that the cubicity of the ice nuclei remain stable.

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[1] B. Cheng and M. Ceriotti, The Journal of Chemical Physics **146**, 034106 (2017).