



# The Physics of Soft and Biological Matter

## Crystal-liquid interfacial free energy via thermodynamic integration

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A novel thermodynamic integration (TI) scheme is presented to compute the crystal-liquid interfacial free energy ( $\gamma_{cl}$ ) from molecular simulations. A key problem in previous thermodynamic-integration based approaches was the irreversibility and hysteresis inherent in the scheme due to the movement of the crystal-liquid interface. Here, by a clever approach of using extremely short-ranged walls to confine the liquid and crystal phases, whose actual contribution to the total interfacial free energy is negligible ( $<0.4\%$ ), we have made this irreversibility redundant. Another feature of our scheme is the use of a frozen crystalline phase to act as a wall, instead of specially designed cleaving potentials (*J. Chem. Phys.*, 84, 5759 [1986]) or cleaving walls (*Phys. Rev. Lett.*, 85, 4751 [2000]). It is seen that this approach prevents the formation of metastable states during the transformation. Our technique is applied to compute ( $\gamma_{cl}$ ) of systems interacting via Lennard-Jones and repulsive inverse-power ( $\epsilon(\sigma/r)^{256}$ ) potentials. We obtain good agreement with previous works based on a cleaving-wall approach (*J. Phys. Chem. B*, 109, 17802, [2005]), non-equilibrium work methods (*J. Chem. Phys.*, 124, 034712 [2006]) and a metadynamics (*Phys. Rev. B*, 81, 125416, [2010]) simulation.