**Exploring Polymorphism: the Case of Benzene**

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Crystal structure prediction is one of the most challenging problems in theoretical chemistry. The standard approaches focus on the minimization at T=0 of lattice energies. Here instead we concentrate on the finite temperature, finite pressure Gibbs free energy, thus fully accounting for entropic effects. This is achieved by combining the Parrinello-Rahman variable cell approach with metadynamics[1], a novel powerful sampling method. We apply this scheme to an old and difficult problem, the prediction of benzene polymorphs[2]. Only the knowledge of the molecular structure and a reasonable intermolecular potential are necessary. We find seven stable crystalline structures of benzene. Comparison with the experimental data shows an unambiguous correspondence between our structures and those revealed by Raman spectroscopy and X-ray diffraction, so that for the first time the benzene phase diagram appears to be completely accessible. These results demonstrate that metadynamics is a powerful tool that shows definite promise for solving the problems of crystal structure prediction or search for polymorphs and suggest that the smoothness of the free energy surface, as compared to the enthalpy surface, may facilitate the task even when using extremely accurate force fields.

[1] Laio A., Parrinello M., *PNAS,* 2002, **99**, 12562-12566. [2] Raiteri P., Martoňák R., Parrinello M., *Angew. Chem. Int.Ed., in press.*

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