Corresponding states theory for property prediction at the nanoscale

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The Principle of Corresponding States was first proposed by van der Waals in 1881, based on his equation of state. The Principle made it possible to predict the vapor pressure curve, including the critical and normal boiling points, of liquids for which no measurements exist, based on experimental data for other liquids. It quickly found use in this way for predicting liquid properties for hydrogen and helium, neither of which had been liquefied at the time. When these light gases were later liquefied the predictions were found to be accurate. A more powerful derivation of the Principle is based on statistical thermodynamics, which makes clear the assumptions involved and provides a path to improve the theory so that it is more generally applicable. Subsequent generalizations of the theory of corresponding states, in particular that due to Pitzer, provide the basis for the prediction of many physical properties of homogeneous gases and liquids, and are widely used in process simulation. However, these correlations are not applicable to highly inhomogeneous or nanoscale systems, such as small drops, nanoparticles, adsorbed thin films on solid substrates, polymer brushes, etc.

A statistical mechanical analysis of the properties of a highly inhomogeneous nanoscale system shows that the equilibrium properties (adsorption isotherms, isosteric heats, phase change conditions, etc.) are determined by a small number of dimensionless parameters, including the dimensionless width, H, of the nanophase and a *microscopic wetting parameter*, α_w, that is defined in terms of intermolecular forces and solid structure; α_w is a measure of wetting that applies at all scales and for any kind of adsorbed film (gas, liquid or solid) [1,2].

We illustrate the usefulness of this approach using examples drawn from both experimental and molecular simulation studies of gas-liquid and liquid-solid phase separations [3,4], and pressure enhancement in nanopores [5-7], with emphasis on simple pore geometries. These examples illustrate the central role played by wetting, and also the breakdown of some concepts and macroscopic laws, such as the equations of Kelvin, Laplace and Gibbs-Thomson, for nano-phases confined within small pores. They also suggest consistency tests for experimental data that should be applied in the event of capillary condensation or other phase changes in mesoporous materials.

The approach can be extended to account for geometric or energetic wall roughness [8], and to adsorbate molecules that interact with site-site potentials having both Lennard-Jones and point charge sites.

MELTING POINT SHIFT IN PORES
EFFECT OF PORE WIDTH AND WETTING PARAMETER

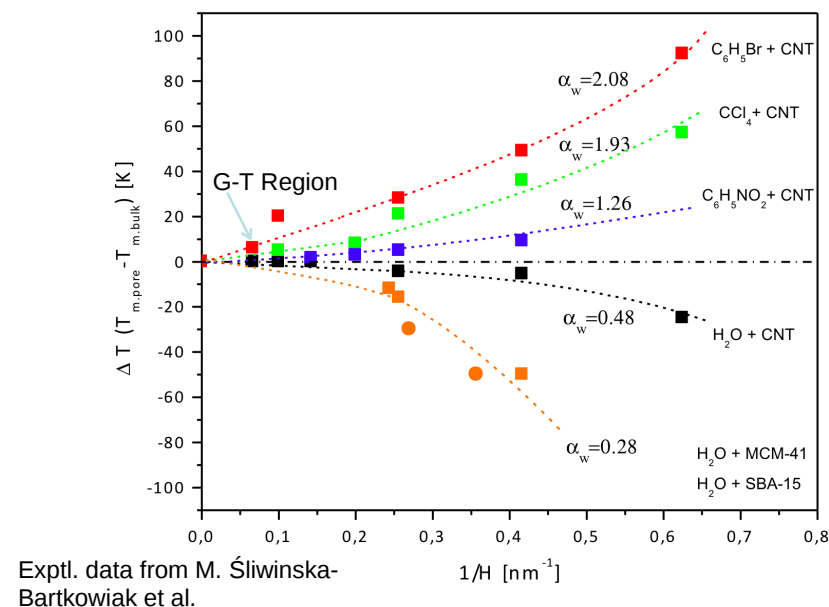Exptl. data from M. Śliwinska-Bartkowiak et al.

Figure 1. Experimental results for the effect of confinement in cylindrical pores on the melting point of various adsorbates. Here CNT = carbon nanotube and α_w is the microscopic wetting parameter; high values of α_w indicate strong wetting. For large pore widths the temperature shift is approximately linear, as required by the Gibbs-Thomson equation.

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