Stationary properties of the entropy as a functional of the pair correlation and their application to DFT calculations of free energy[1] D.M. NICHOLSON, C.Y. GAO, Oak Ridge National Laboratory, D.J. KEFFER, University of Tennessee, Knoxville — We propose that within the class of pair potential Hamiltonians the excess entropy is a universal, temperature-independent functional of the density and pair correlation. This result extends Henderson's Theorem which states that the free energy is a temperature dependent functional of the density and pair correlation. The stationarity and convexity of the excess entropy functional are discussed and related to the Gibbs-Bogoliubov inequality and to the free energy. An approximate functional is given and compared to results from thermodynamic integration. We propose that a functional of this type, that is strictly applicable to pair potentials is also suitable for first principles calculation of free energies from Born-Oppenheimer molecular dynamics performed at a single temperature.

Donald Nicholson
Oak Ridge National Laboratory

Date submitted: 22 Dec 2009   Electronic form version 1.4