The internal-energy functional for classical liquids

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An overview of two different variational formulations of classical statistical mechanics is given. In standard classical density functional theory for inhomogeneous liquids the Helmholtz excess (over ideal gas) free-energy functional plays the central role, and examples of recent approximate functionals for non-additive hard sphere mixtures are described briefly [1,2]. In an extended framework, besides the one-body density the local entropy distribution constitutes a trial field. Using Levys constrained search method, it is shown that the grand potential is a functional of both distributions, that it is minimal in equilibrium, and that the minimizing fields are those at equilibrium. The functional splits into a sum of entropic, external energetic, and internal energetic contributions. Several common approximate Helmholtz free-energy density functionals, such as the Rosenfeld fundamental measure theory for hard sphere mixtures, are transformed to internal-energy functionals. The variational derivatives of the internal-energy functional are used to generalize dynamical density-functional theory to include the dynamics of the microscopic entropy distribution, as is relevant for studying heat transport and thermal diffusion.

[1] *Rosenfeld functional for non-additive hard spheres*
    M. Schmidt, J. Phys.: Condens. Matt. **16**, L351 (2004).
[2] *Density functional for ternary non-additive hard sphere mixtures*
    M. Schmidt, J. Phys.: Condens. Matt. **23**, 415101 (2011).
[3] *Statics and dynamics of inhomogeneous liquids via the internal-energy functional* M. Schmidt, Phys. Rev. E **84**, 051203 (2011).