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Derivation of all thermo-poro-mechanical moduli from atomistic fluctuations

L. Brochard[a*]

[a] Laboratoire Navier, Ecole des Ponts/Univ. Gustave EIffel/CNRS, Champs-sur-Marne, France
[*] corresponding author: laurent.brochard@enpc.fr

Abstract:

Fluctuations of thermodynamic quantities are ubitquitous in molecular simulations at the atomistic scale but their magnitudes relative to the statistical averages vanish in the limit of large macroscopic systems (thermodynamic limit). From a practical point of view, these fluctuations are detrimental to the accuracy of statistical averages estimated from molecular simulations. But, these fluctuations can also be used to estimate additional thermodyanmic properties. Indeed, it is well known that the fluctuations of a state parameter are related to the second order derivatives of the thermodynamic potential minimum at equilibrium (e.g., compressibility, thermal expansion and heat capacity for a fluid). Otherwise, said one can fully derive the constitutive behavior of a system by estimating the magnitudes of the fluctuations. While fluctuation formulas are well established for basic systems (e.g., a pure fluid), for porous media, only the heat of adsorption is commonly estimated from fluctuations, and the formula used assumes that the solid is rigid. In this work, we revisit the Biot-Coussy theory of thermo-poro-elasticity in a framework suitable to derive fluctuation formulas. All the thermo-poro-elastic moduli are related to fluctuations that are straightforward to compute by molecular simulation, i.e., there is no need to define any porosity, or specific surface, which would be ambiguous at the molecular scale. The moduli estimated are tangent moduli, i.e., correspond to a non linear formulation of the constitutive equations. Interestingly, the fluctuation formulas are perfectly general, and apply even if the fluid is adsorbed. As a consequence, the derived moduli can characterize unusual thermo-poro-mechanical couplings due to adsorption (e.g., fluid pressure dependent Biot coefficient or bulk modulus). This framework is also used to revisit the concept of heat of adsorption and to derive a new fluctuation formula that extends the usual one to deformable porous media.