DENSITY FUNCTIONAL THEORY FOR STUDIES OF MULTIPLE STATES OF INHOMOGENEOUS FLUIDS AT SOLID SURFACES AND IN PORES.

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ABSTRACT

Two new versions of the density functional theory (DFT), which correspond to the canonical ensemble and the Gibbs ensemble respectively, are applied to study multiple equilibrium states and associated hysteresis on examples of capillary condensation of argon in nanopores of MCM-41 mesoporous molecular sieves and Kr adsorption on carbon. The canonical ensemble DFT (CEDFT) allows us to trace not only the stable and the metastable states along the hysteresis loop, but also the unstable states inside the hysteresis loop. The Gibbs ensemble DFT (GEDFT) allows us to determine precisely the points of equilibrium phase transitions in confined fluids.

INTRODUCTION

Multiple states of confined inhomogeneous fluids are well documented in surface science. They manifest themselves in step-wise phase transitions and hysteresis behavior, which are inherent to thin films between colloidal particles, soap films, wetting and adsorption films on solid surfaces, fluids in pores, etc. Some of the prominent examples are the capillary condensation phenomena in nanopores and the adsorption-desorption transitions in mono- and multilayers. Better understanding of the specifics of confined fluid transformations is needed in a variety of practical applications such as stability of colloids, fabrication of nanostructures, separations, lubrication, fluid flow and sorption in porous media.

The density functional theory (DFT) has been used by many authors for analyses of inhomogeneous fluids at solid surfaces and in pores (for a comprehensive review, see [1]). In particular in our earlier papers [2-5], we employed the non-local density approximation due to Tarazona [6] to model hysteresis phenomena such as capillary condensation/evaporation in MCM-41 mesoporous molecular sieves and phase transitions in adsorption multilayers on carbon.

Conventional versions of the DFT imply minimization of the grand thermodynamic potential with respect to the fluid density within fixed solid boundaries at the given temperature T and chemical potential μ. They correspond to the grand canonical (μ-V-T) ensemble and are below referred to as GCE DFT. In this paper, we apply two new versions of the DFT, which correspond to the canonical ensemble (CE DFT) and the Gibbs ensemble (GE DFT) respectively. We study capillary condensation of Ar in nanopores of MCM-41 mesoporous molecular sieves and Kr adsorption on carbon. The GCE DFT studies of these systems have been reported in the previous MRS meeting [5]. It was shown that GCE DFT qualitatively describes these phenomena and is in a satisfactory agreement with experimental adsorption/desorption.

CE DFT allowed us to trace not only the stable and the metastable states along the hysteresis loop, which can be done with GCE DFT, but also the unstable states inside the hysteresis loop. The obtained isotherms are alike the van-der-Waals S-shaped isotherms. Thermodynamic foundations for this type of isotherms have been discussed in the literature

earlier in mid-80s [7]. However, they were constructed for the first time only recently [8] by means of the canonical ensemble and the Gibbs ensemble MC simulations. The proposed DFT methods provide a better understanding of hysteresis phenomena in nanoconfinements. In systems with several consecutive phase transitions, the CE DFT isotherms exhibit multiple zigzags. The backward regions of the isotherms correspond to the unstable states inside the hysteresis loop(s). These unstable states cannot be realized in a physical or a numerical experiment unless density fluctuations, which drive the system to one of the metastable or stable states, are completely suppressed. In the developed DFT, the density fluctuations are suppressed by fixing the total amount of fluid molecules in the confinement.

CANONICAL ENSEMBLE DFT FOR INHOMOGENEOUS FLUIDS

Consider a closed system consisting of N molecules of fluid confined in a volume V surrounded by solid walls. The system is embedded in a bath of constant temperature T. The fluid is modeled as a hard sphere fluid with a given pairwise attractive potential, $\Phi_{ff}(\mathbf{r}_1, \mathbf{r}_2)$. The fluid-solid interactions are modeled by a given spatially varying external potential, $\Phi_{sf}(\mathbf{r})$. Equilibrium states of the closed system are defined by minimization of the Helmholtz free energy functional at constant $N, V,$ and T. The DFT implies that the intrinsic Helmholtz free energy, F_{int}, depends entirely upon given fluid-fluid interaction potential(s), $\Phi_{ff}(\mathbf{r}_1, \mathbf{r}_2)$, and is represented as a functional of the spatially varying fluid density $\rho(\mathbf{r})$. The external solid-fluid interaction potential, $\Phi_{sf}(\mathbf{r})$, does not affect the expression for intrinsic Helmholtz free energy functional, $F_{int}[\rho(\mathbf{r}), \Phi_{ff}]$, and makes an additive contribution, $F_{ext}[\rho(\mathbf{r}), \Phi_{sf}]$, into the total Helmholtz free energy, F:

$$F[\rho(\mathbf{r})] = F_{int}[\rho(\mathbf{r}), \Phi_{ff}] + F_{ext}[\rho(\mathbf{r}), \Phi_{sf}]$$ (1)

Equilibrium states in the canonical ensemble are obtained by minimization of the Helmholtz free energy functional (1) with respect to the fluid density $\rho(\mathbf{r})$, provided the total number of molecules is a given constant N:

$$\int_V \rho(\mathbf{r})d\mathbf{r} = N$$ (2)

This is a conditional extremum problem. To find a solution, one has to solve the Euler equation for the functional

$$\Omega[\rho(\mathbf{r})] = F[\rho(\mathbf{r})] - \mu \int_V \rho(\mathbf{r})d\mathbf{r}$$ (3)

Here, an additional unknown parameter, μ, is introduced. The Euler equation for the functional (3) reads

$$\mu = \frac{\delta F}{\delta \rho}$$ (4)

Here, $\frac{\delta}{\delta \rho}$ denotes the functional derivative. The right hand side of the Eq. (4) depends on an employed representation of the intrinsic Helmholtz free energy functional, $F_{int}[\rho(\mathbf{r})]$. Equations (4) and (2) represent a closed system for determination of two unknowns, a function $\rho(\mathbf{r})$ and a constant μ. This system implies a unique solution at given N. The solution gives the equilibrium

density profile $\rho(\mathbf{r}, N, V, T)$ and the value of $\mu(N,V,T)$, which turns out to be equal to the chemical potential of the corresponding N,V,T state. Therewith, the functional $\Omega[\rho(\mathbf{r}, N, V, T),$ $\mu(N,V,T)]$ is equal to the grand potential. While the obtained chemical potential, μ, is a single-valued function of N, there is no one-to-one correspondence. On the contrary, the function $N(\mu)$ can be non-monotone and exhibit S-shaped swings in the regions of phase transitions.

The points of equilibrium transitions, μ_e, can be defined from the Maxwell's rule of equal areas by integrating along the S-shaped isotherm between the coexisting states (1) and (2):

$$\int_{N_1(\mu_e)}^{N_2(\mu_e)} \mu dN = \mu_e (N_2 - N_1) \tag{5}$$

GIBBS ENSEMBLE DFT FOR EQUILIBRIUM TRANSITIONS

The Gibbs ensemble [9], is the canonical (N-V-T) ensemble for a two-phase system. Unrestricted exchange of volume and mass between the phases provides mechanical and chemical equilibrium. Consider N_Σ molecules of a fluid, which may be distributed between similar pores. Suppose the pores may be in two different states, which are characterized by distinct fluid density profiles, $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$. Let V_1 and V_2, and N_1 and N_2 be the volumes of pores in the states 1 and 2 and the numbers of molecules in these pores respectively. The total volume of pores, $V_\Sigma = V_1 + V_2$, and the total number of molecules, $N_\Sigma = N_1 + N_2$, are fixed. The phase volumes and the numbers of molecules in phases are variable. The problem is to find an equilibrium phase distribution at given V_Σ and N_Σ, and also the equilibrium conditions in terms of chemical potential μ.

The equilibrium states in the GE are found by minimization of the total Helmholtz free energy of the two-phase system,

$$F_\Sigma(\langle\rho\rangle) = \alpha F[\rho_1(\mathbf{r})] + (1-\alpha)F[\rho_2(\mathbf{r})] \Rightarrow \min, \tag{6}$$

at the condition

$$\alpha \int_V \rho_1(\mathbf{r})d\mathbf{r} + (1-\alpha)\int_V \rho_2(\mathbf{r})d\mathbf{r} = \langle\rho\rangle V . \tag{7}$$

Here, we introduced the unknown portion of pores in the state 1, $\alpha = V_1/V_\Sigma$, and the fixed average density $\langle\rho\rangle = N_\Sigma/V_\Sigma$.

The solution of this problem gives the density profiles $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ in the equilibrium states and the chemical potential μ of equilibrium transition. Therewith, $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ fulfill the equation (6), and μ is determined form the condition of equality of the grand potentials in the equilibrium states,

$$G(\rho_1(\mathbf{r})) = F[\rho_1(\mathbf{r})] - \mu\int_V \rho_1(\mathbf{r})d\mathbf{r} = G(\rho_2(\mathbf{r})) = F[\rho_2(\mathbf{r})] - \mu\int_V \rho_2(\mathbf{r})d\mathbf{r} . \tag{8}$$

In order to demonstrate capabilities of the proposed CE DFT and GE DFT methods, we present below several prominent examples. Detail description of the techniques will be given elsewhere.

EXAMPLES.

In Figs. 1-4, we present two prominent examples of multilayer adsorption and capillary condensation hysteresis: 1) Ar adsorption on MCM-41 mesoporous molecular sieve; calculations were performed at Ar boiling temperature 87 K (T^*=0.739) in a cylindrical pore of 14.2 σ_{ff} (internal diameter 4.4 nm), and 2) Kr adsorption on carbon; calculations were performed at O_2 boiling temperature 90 K (T^*=0.547) in a slit-shaped pore of 14 σ_{ff} (internal diameter 4.7 nm). We used the Tarasona's representation of the Helmholtz free energy [6] with the parameters for fluid-fluid and solid-fluid interaction potentials, which were employed in our previous paper [5]. We employed the Broyden's method for solution of nonlinear set of equations [10]. On these examples, we observe formation of consecutive adsorption layers prior to spontaneous (spinodal) capillary condensation. Equilibrium capillary condensation transition links a liquid-like state on the desorption branch with a two-layer adsorption film on the adsorption branch. Multilayer adsorption is also associated with spinodal transitions (most prominent for Kr adsorption) and equilibrium coexistence of distinct states. We observed up to five states at the same chemical potential.

CONCLUSIONS

We studied multiple equilibrium states of inhomogeneous confined fluids and associated hysteresis phenomena by means of new versions of the density functional theory, which correspond to the canonical ensemble and the Gibbs ensemble respectively. On the examples of capillary condensation of Ar in nanopores of MCM-41 mesoporous molecular sieves and Kr adsorption on carbon, it was shown that the proposed CE DFT and GE DFT methods provide a better understanding of hysteresis phenomena in nanoconfinements. They allow us to generate continuous adsorption isotherms, including unstable states inside the hysteresis loop, and to determine precisely the points of equilibrium and spinodal phase transitions in confined fluids.

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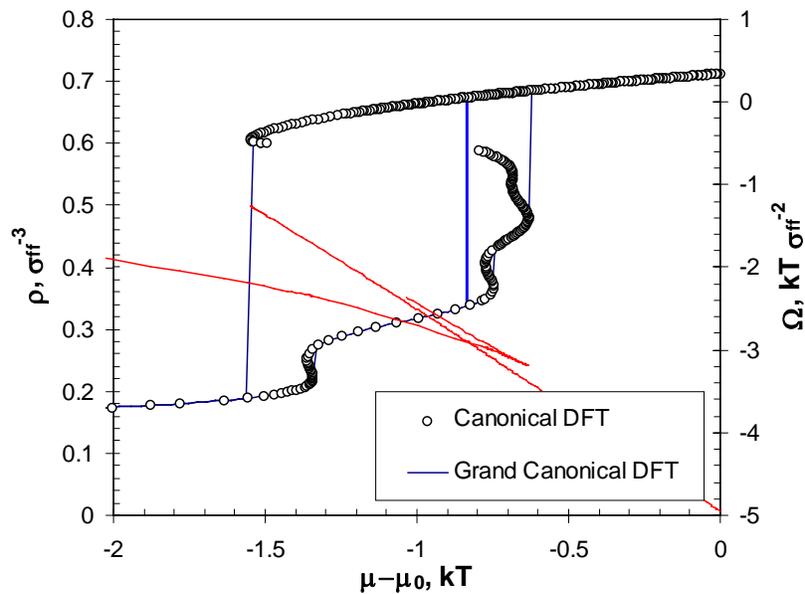
Fig. 1. Ar in 14.2 σ_{ff} (4.4 nm) cylindrical pore at 87.3 K (T^*=0.739). In the stable and metastable states, the GCE DFT isotherm (line) coincides with the CE DFT isotherm (points). The GE DFT gives the vertical line of equilibrium capillary condensation transition. The point of equilibrium transition, $\Delta\mu$=-0.835 kT, corresponds to the intersection point of the Grand Potential (zigzag thin line). The leftmost and rightmost vertical lines, which bound the hysteresis loop, correspond to the spinodal transitions in the GCE DFT.
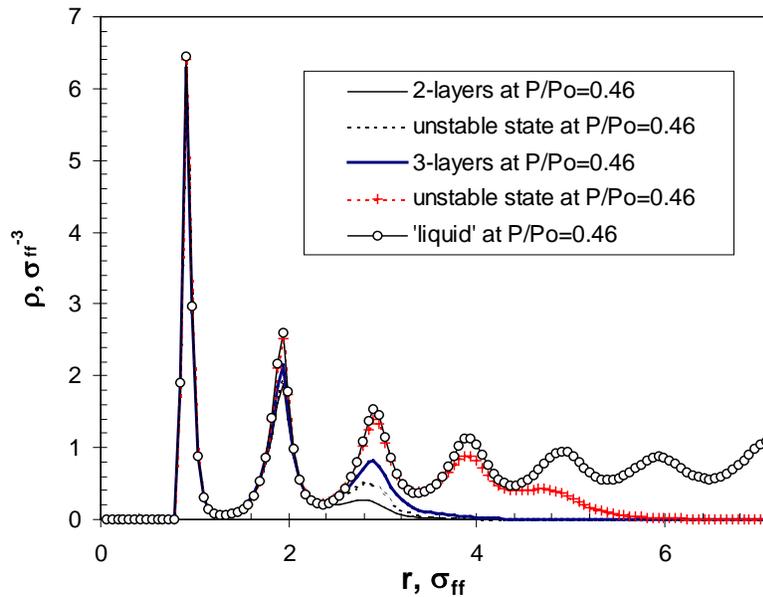

Fig. 2. Density profiles of Ar in 14.2 σ_{ff} (4.4 nm) cylindrical pore at 87.3 K (T^*=0.739). The five profiles correspond to multiple states at P/Po=0.46 ($\Delta\mu$=-0.76 kT). Three equilibrium states: the absolutely stable liquid-like state after the capillary condensation (circles); the metastable coexisting two-layer adsorption film and the three-layer adsorption film (lines). Two unstable states: the two-and-a-half-layer (dashed line) and the four-and-a half-layer (crosses).
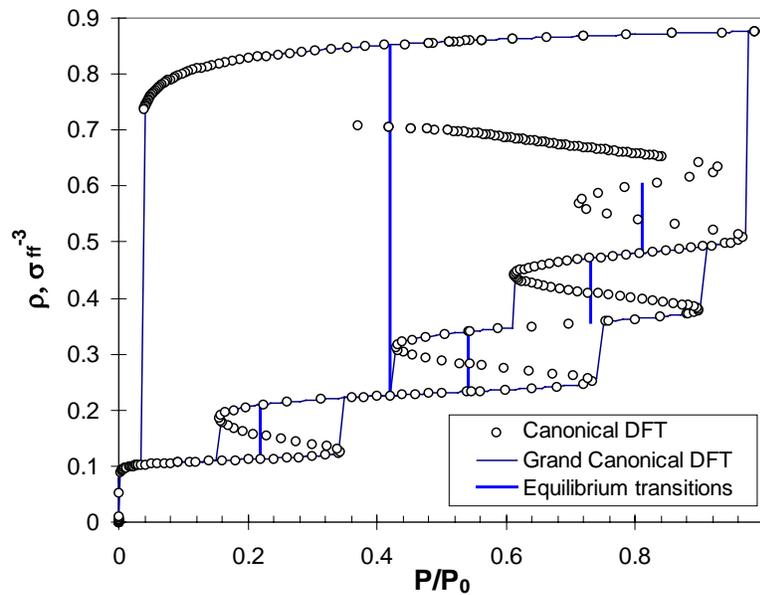
Fig. 3. Isotherm of Kr in a 14 σ_{ff} (4.7 nm) slit-shaped pore of carbon at 90 K (T^*=0.547). In stable and metastable states the GCE DFT isotherm (line) coincides with the CE DFT isotherm (points). The GE DFT gives the vertical lines of equilibrium transitions between the coexisting phases. We observe four consecutive layering transitions and the capillary condensation transition.
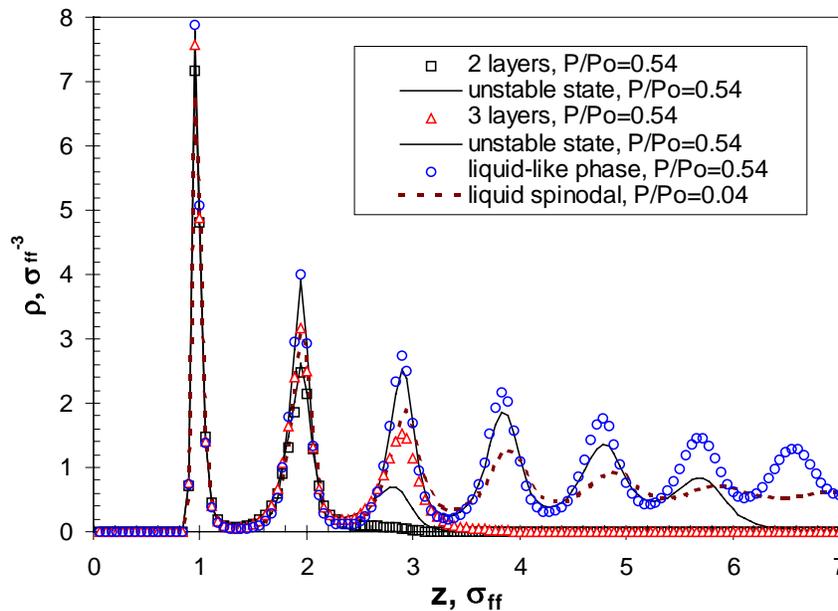

Fig. 4 Density profiles of krypton in 14 σ_{ff} (4.7 nm) slit-shaped pore at 90 K (T^*=0.547). Five states correspond to the relative pressure of P/Po=0.54. Three equilibrium states: the absolutely stable liquid-like state after the capillary condensation (circles); the metastable coexisting two-layer adsorption film (squares) and the three-layer adsorption film (triangles). Two intermediate unstable states (lines): the two-and-a-half-layer state and the six-layer state. A density profile near the liquid spinodal point, P/Po=0.04, (dotted line) is presented for comparison.