Coupling microscopic and mesoscopic scales to calculate thermodynamic properties of heterogeneous fluid systems including nanometric carbon clusters

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Molecular simulation of (parts of) a detonation wave

- Isentropic release of detonation products
- Reaction zone
- Neat explosive
- Shock front

**FOCUS**

Study of the detonation products mixture including a solid phase of carbon at chemical and thermodynamic equilibrium
The difficulty is to simulate simultaneously the chemical and phase equilibriums between the solid cluster and the fluid.

Here is how should be the « real » system
(No idea of how is the experimental system)
Previous Method:

• Chemical and thermodynamical equilibrium between two separated phases

Goal:

• Insert more physics in the carbon phase description

• Add a fluid/solid phase interaction: embed the carbon phase in the fluid (clusters <= 10^4 atoms)

What do we need?

• Study thermodynamic properties of carbon nanocluster (meso-particle), and build an adapted EOS for this carbon solid phase

• Define an interaction energy between the meso-particle and the fluid particles able to reproduce accurate microscopic simulation of the system

• Develop a method to simulate the chemical equilibrium between the meso-particle and the fluid phase
Investigation of thermodynamic properties of carbon nano-clusters

Molecular dynamic simulations using LCBOP II potential

Molecular dynamics simulations of nanocarbons at high pressure and temperature
G. Chevrot et al., Carbon 47, 3392-3402 (2009)
Approximate phase diagram for nanocarbons

ND = diamond core + fullerene-like surface:

\[
V_{ND} = N_C \times V_D + N_S \times V_S
\]

\[
E_{ND} = N_C \times E_D + N_S \times E_S
\]

\(N_C\) and \(N_S\): number of core and surface atoms

\(V_D\) and \(V_S\): diamond and surface atomic volumes

NO = concentric layers of fullerene:

\[
V_{NO} = \frac{4}{3} \pi \left( r_i + (n_c - 1)d + \frac{1}{2}d_i \right)^3
\]

\[
E_{NO} = \sum_{i=1}^{n_c} N_i E_{\text{ion}} \left( 1 - \frac{1}{R_i^2} \right)
\]

\(r_i\): inner shell radius
\(n_c\): number of shells
\(d_i\): interlayer distance
\(R_i\): radius of layer \(i\)
\(N_i\): number of atoms of layer \(i\)
\(E_{\text{ion}}\): extrapolated atomic energy for a layer of infinite radius

Equation of State for nano-clusters of carbon
Replace the all atoms cluster by a spherical meso-particle

N, V, E from the Equation of State
Need to define a potential interaction with the fluid particles

NPT simulations: Comparison to All Atoms simulations: Good accordance

Bourasseau et al., PCCP 13 (2011).
**Meso-particle reaction move**

The chemical reactivity between the meso-particle and the fluid is handled using a specific MC “reaction” move:

1- random choice of a chemical reaction involving the meso-particle
2- random extraction of reactant fluid molecules
3- random insertion of product fluid molecules
4- change the number of carbon atoms - modify E and V accordingly

\[
2 \text{ CO} \leftrightarrow \text{ CO}_2 + C_{\text{sol}}
\]

Same expression for acceptance probability:

\[
P_{\text{acc}} = \min \left[ 1, (P_0 \beta V)^{-1} \right] \exp \left\{ -\frac{\Delta f G_{\text{CO}_2}(T) - 2\Delta f G_{\text{CO}}(T) + \Delta f G_{C_{\text{solid}}}(T, P)}{RT} \right\} \frac{(N_{\text{CO}})(N_{\text{CO}} - 1)}{(N_{\text{CO}_2} + 1)} \exp(-\beta \Delta U)
\]

But \( \Delta U \) includes the interface energy.

Bourasseau et al., PCCP 13 (2011).
Comparison separated phases / meso-particle methods
What's wrong with the separated phases method used previously?

Main difference between the two methods:

In the “separated phases” method, fluid and solid phase volumes are infinite and not linked.

In the meso-particle method, volumes are linked because when the meso-particle grows, the fluid volume decreases.

This is as if in the second case, expansion of the solid phase is less efficient to fight the high pressure due to the fact that volume increase has to fight against fluid particles.

Modified expression for acceptance probability:

\[ P_{\text{acc}} = \min \left\{ \frac{1}{(P_0 \beta)^{-1} \left( V + V_{\text{solid}} \right)^{(N_{\text{fluid}})^{-1}}} \right\} \]

\[ \exp \left( -\frac{\Delta_f G^{\text{CO}_2}(T) - 2\Delta_f G^{\text{CO}}(T) + \Delta_f G_{\text{solid}}(T, P)}{RT} \right) \]

\[ \frac{(N_{\text{CO}})(N_{\text{CO}} - 1)}{(N_{\text{CO}_2} + 1)} \exp(-\beta \Delta U - \beta PV_{\text{solid}}) \]

Note the \(-\beta PV\) term.
Comparison separated phases (corrected) / meso-particle methods
Influence on a real case: Hugoniot curve of the detonation products of TATB

Bourasseau et al., JPC A (2011)
Conclusions:

- Heterogeneity of our systems can not be neglected
- There is a thermodynamic difference between the case where phases are separated and the case where the solid phase is inside the fluid phase. This difference has been underlined thanks to molecular simulations.
- It is possible to modify the constrains of the first case to get the same results as in the second one.

Perspectives:

- Apply those conclusions to thermochemical calculations
- MC and MD simulations of systems containing distributions of meso-particles: size distribution effects, diffusion/clustering kinetics, non-equilibrium processes (shock compression, release, …)