Breathing sphere polymer model

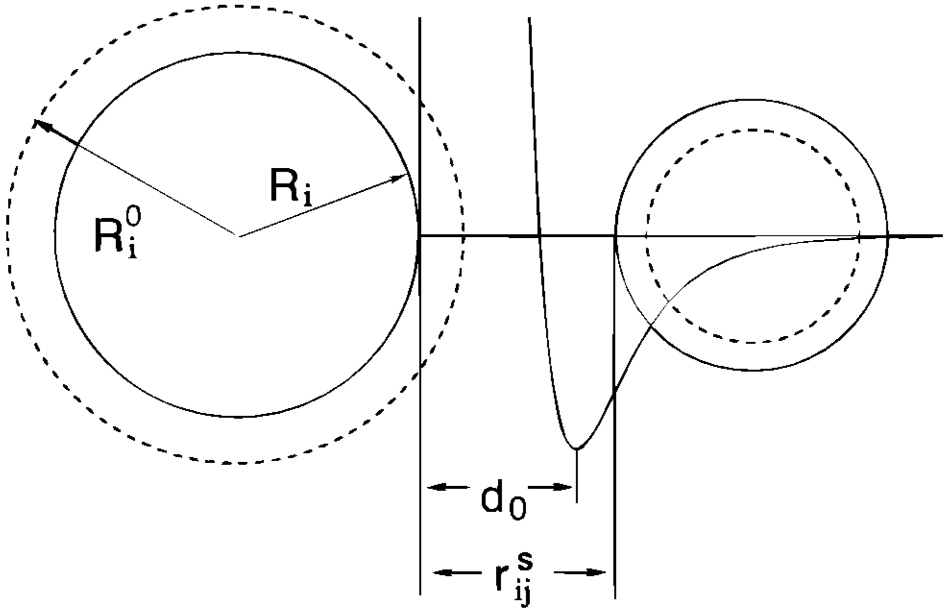
- So far on this course the basic object dealt with on this course has always been a single atom. But this does not necessarily need to be the case. In effects where some larger object is (at least usually) internally stable, it may be possible to treat this as a single object,

  In practice the range of problem where this approach works is likely to be limited. But in its range of applicability it can be very useful.

- As an example of such approaches we present here the “breathing sphere”-polymer model [L. Zhigilei, P. Kodali and B. Garrison, J. Phys. Chem. B **101** (1997) 2028; *ibid.,* **102** (1998) 2845]. In it one describes polymers with strong covalent internal bonds, and clearly weaker external interactions. Hence one can make the good assumption that the polymer does not break easily.

- In the model the polymers are described as spheres, but with a variable, time-dependent radius. Associated with a change of the radius is an energy, which is thought to be related to the vibrational modes of the molecule. In that way, part of the external interactions can be transferred to internal vibrational energy, and vice versa, which is known to correspond to the experimental situation.

- There are four size or distance quantities used to describe the spheres:



R_i^0 is the equilibrium size of the polymer 'particle', R_i its momentaneous size, d_0 the equilibrium distance between two spheres calculated from the external (!) radii , and r_{ij}^s the momentaneous distance measured from the external radii.

- The total Lagrangian in the model is

$$L = 1/2\sum_i m_i(\mathrm{d}r_i/\mathrm{d}t)^2 - \sum_{ij} U_r + 1/2\sum_i M_i(\mathrm{d}R_i/\mathrm{d}t)^2 - \sum_i U_R \quad (1)$$

where m_i is the normal mass of the particle, and M_i is an effective mass associated with its internal degree of freedom. Thus in the expression above the two first terms are the normal kinetic and potential energy, but the two latter one describe the internal energy.

- The interaction between spheres is described with the good old Morse potential:

$$U_r = \epsilon_n[\exp\{-2\alpha(r_{ij}^s - d_0)\} - 2\exp\{-\alpha(r_{ij}^s - d_0)\}] \quad (2)$$

where the variable, though, is the distance between the external radii r_{ij}^s .

- U_R is used to describe the internal modes of freedom, which is associated with a change of radius (“breathing”). The form is fairly simple,

$$U_R = k_1 \Delta R_i^2 + k_2 \Delta R_i^3 + k_3 \Delta R_i^4 \qquad (3)$$

  where $\Delta R_i = R_i - R_i^0$ i.e. the difference between the equilibrium and momentaneous radius. The constants k can be used to finetune how efficiently the internal vibrational energy is transferred to external kinetic energy.

- Zhigilei, Garrison & co have used this model to simulate laser ablation of organic compounds. In this process a laser is used to irradiate some material, in which case the light energy is first transferred to internal vibrational energy and then to external kinetic energy, which will essentially make a surface layer of the material to blow up.

  The technique is used e.g. in surgery to remove thin layers of human tissue in a controlled manner, and in mass spectrometry to obtain large, free organic molecules. In the so called MALDI technique (Matrix Assisted Laser Desorption Ionization) the desired molecules are set into a matrix of smaller molecules, which are chosen so that they efficiently absorb laser light. The developers of this technique got the Nobel prize in chemistry in 2002.

- Zhigilei simulates this process by selecting the model parameters so that they can describe both large and small molecules, using values which correspond to typical experimental situations.

  The matrix molecules were described with the parameters $d_0 = 3$ Å, $\varepsilon_n = 0.1$ eV, $\alpha = 1$ Å^{-1} , $R_i^0 = 1.4$ Å and $m = 100$ Daltons (1 Dalton = 1 u). These correspond to e.g. nicotine or mustard acid. The large molecules, on the other hand, had $R_i^0 = 10$ Å and $m = 2000$ Daltons.

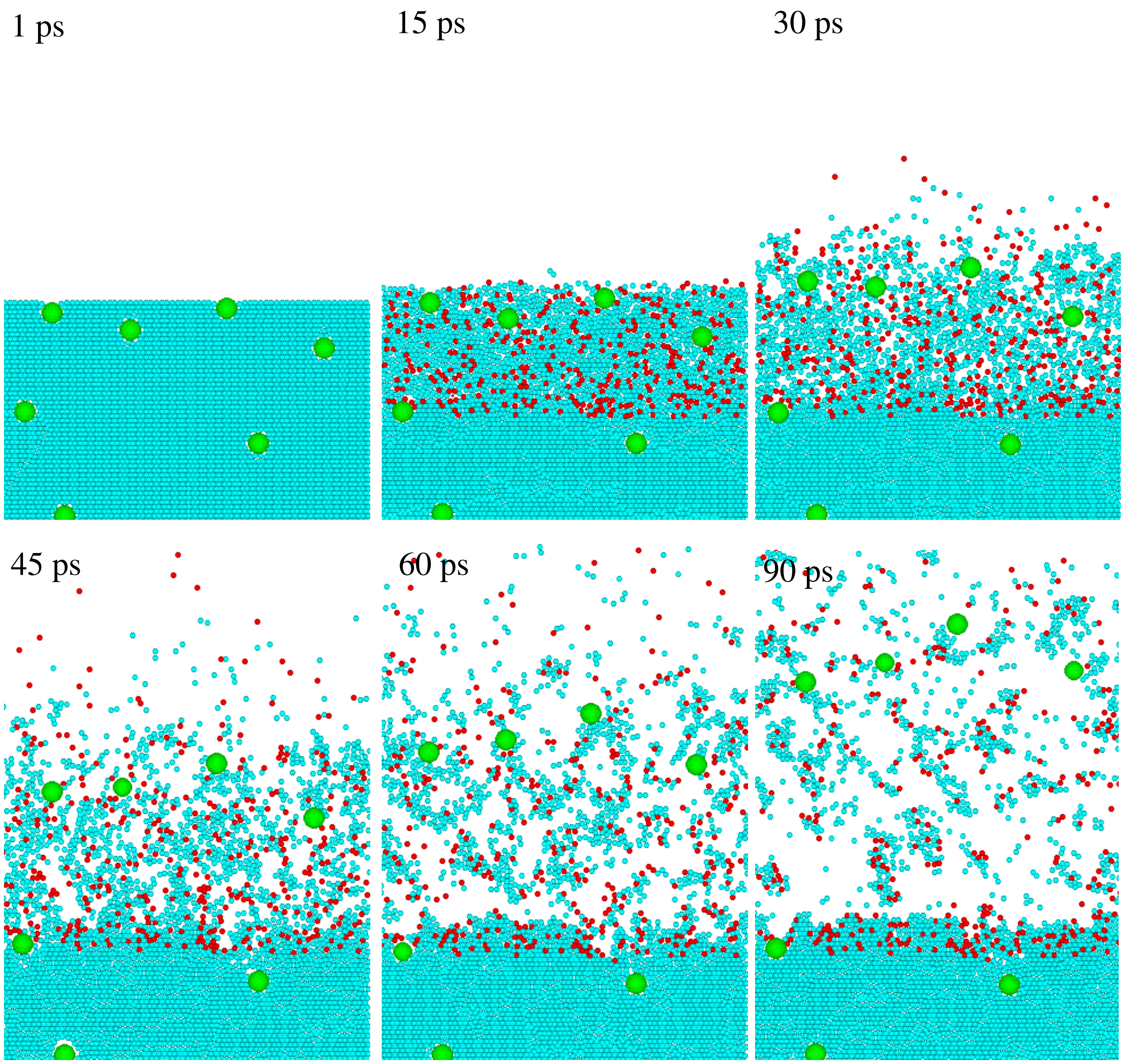
  The parameters of the internal potential were $k_1 = 30$ eV/Å^2 , $k_2 = -60$ eV/Å^2 , $k_3 = 60$ eV/Å^2 and the inertia parameter M_i was either 5000 or 3200 Daltons depending on whether the simulation was in 2 or 3 dimensions. With these parameters the cooling time of excited molecules was obtained to be of the order of 10 ps.

- The ablation process itself is described by letting some randomly chosen matrix molecules have internal energy which corresponds to the energy the laser gives to the molecules. The laser wavelength used was 337 nm (photon energy 3.68 eV, i.e. just in the UV-region) and the duration of the pulse 15 ps.

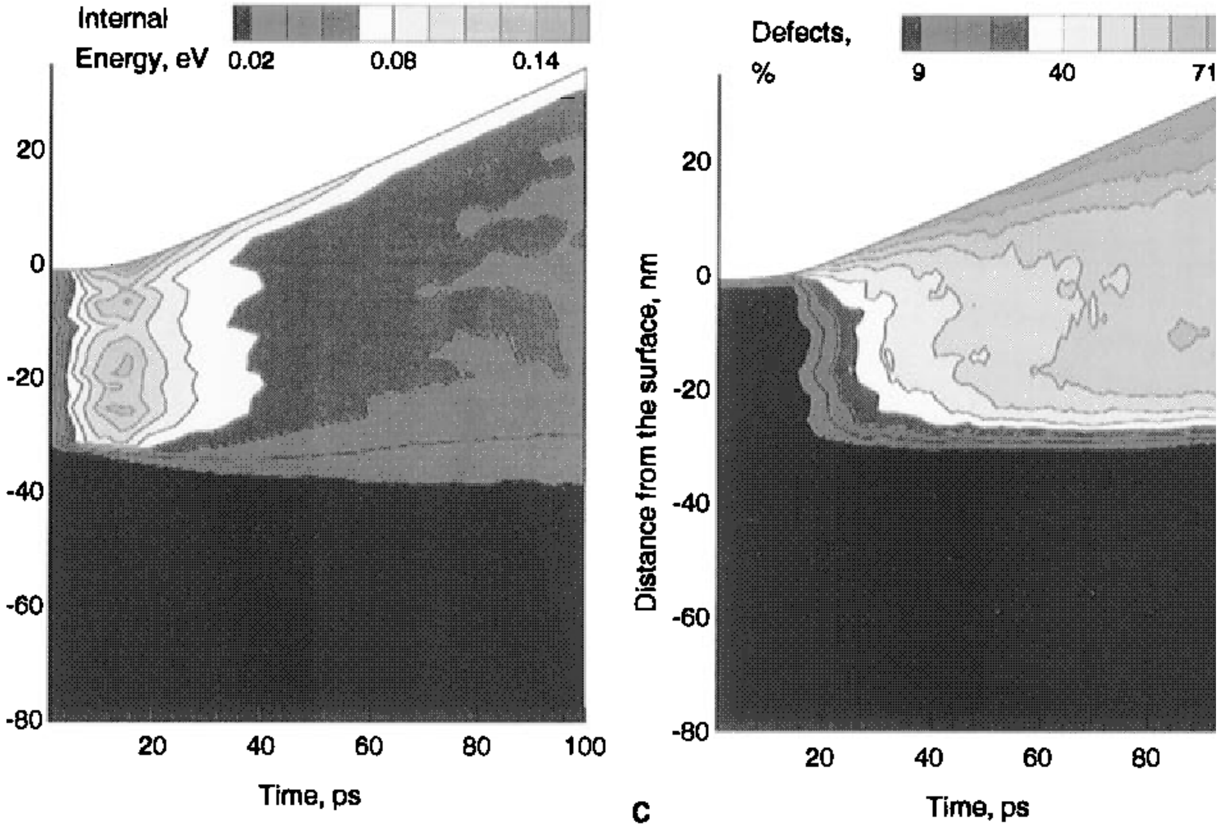
- Using these relatively simple simulations Zhigilei and Garrison have been able to clearly increase the understanding of the ablation processes, which was previously described primarily with analytical models involving lots of questionable approximations and assumptions.

- A few example results:

  The process itself (red atoms are the exited matrix molecules):



- In addition to pretty pictures, the simulations also gave useful information on the explosion process and the nature of the material sputtered out:



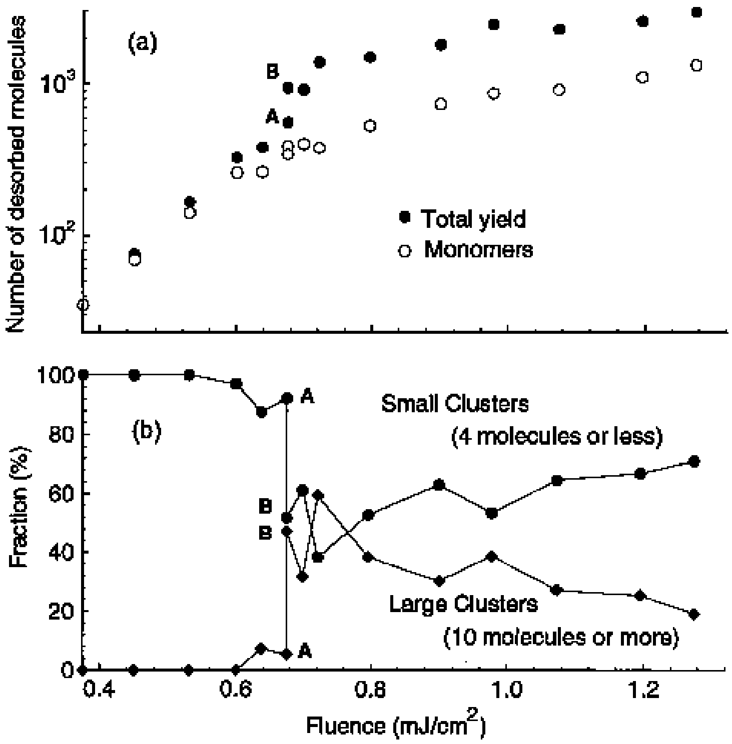


Figure 2. Desorption yield (a) and plume composition (b) vs fluence for the 3D simulation. Figure adapted from ref 28.