3.320: Lecture 14 (Mar 29 2005)

MOLECULAR DYNAMICS

> **You cannot step twice**
> **in the same river**
> ***Heraclitus*** (Diels 91)

ποταμῷ γὰϱ οὐκ ἔστιν ἐμϐῆναι δὶς τῷ
αὐτῷ καθ᾽ Ἡϱάκλειτον.

Newton’s coupled equations

$$m_i \frac{d^2 \vec{r}_i}{dt^2} = \vec{F}_i(\vec{r}_1, \cdots, \vec{r}_N)$$

$$\langle A \rangle = \frac{\int A \exp(-\beta E)\, d\vec{r} d\vec{p}}{\int \exp(-\beta E) d\vec{r} d\vec{p}} \Leftrightarrow \bar{A} = \frac{1}{T} \int_0^T A(t)\, dt$$

The Computational Experiment

- Initialize: select positions and velocities
- Integrate: compute all forces, and determine new positions
- Equilibrate: let the system reach equilibrium (i.e. lose memory of initial conditions)
- Average: accumulate quantities of interest

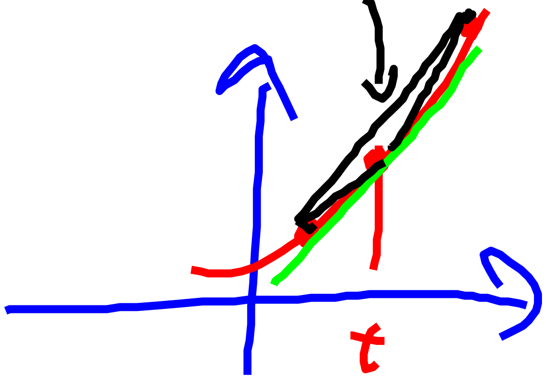
Initialization

- Second order differential equations: boundary conditions require initial positions and initial velocities
- Initial positions: reasonably compatible with the structure to be studied. Avoid overlap, short distances.
- Velocities: zero, or small. Then thermalize increasing the temperature

Integrate

- Use an integrator… (Verlet, leapfrog Verlet, velocity Verlet, Gear predictor-corrector)
- Robust, long-term conservation of the constant of motion, time-reversible, constant volume in phase space
- Choose thermodynamic ensemble (microcanonical NVE, or canonical NVT using a thermostat, isobaric-isothermic NPT with a barostat…)
- Stochastic (Langevin), constrained (velocity rescaling), extended system (Nose-Hoover)

Integrators



- (Simple) Verlet

$$\mathbf{r}(t+\Delta t) = \mathbf{r}(t) + \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2 + (1/6)\mathbf{b}(t)\Delta t^3 + O(\Delta t^4)$$

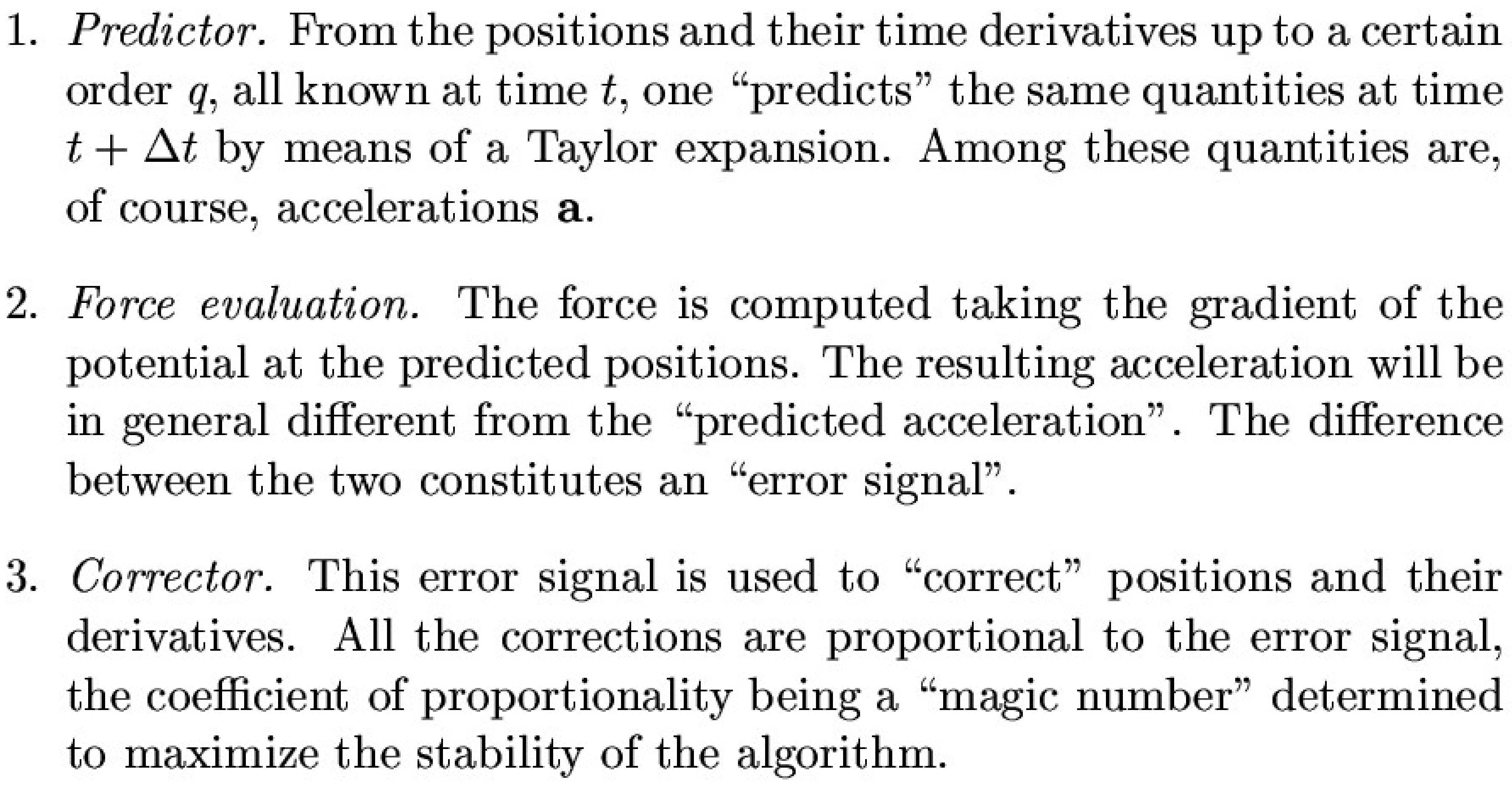
$$\mathbf{r}(t-\Delta t) = \mathbf{r}(t) - \mathbf{v}(t)\Delta t + (1/2)\mathbf{a}(t)\Delta t^2 - (1/6)\mathbf{b}(t)\Delta t^3 + O(\Delta t^4)$$

Adding the two expressions gives

$$\mathbf{r}(t+\Delta t) = 2\mathbf{r}(t) - \mathbf{r}(t-\Delta t) + \mathbf{a}(t)\Delta t^2 + O(\Delta t^4)$$

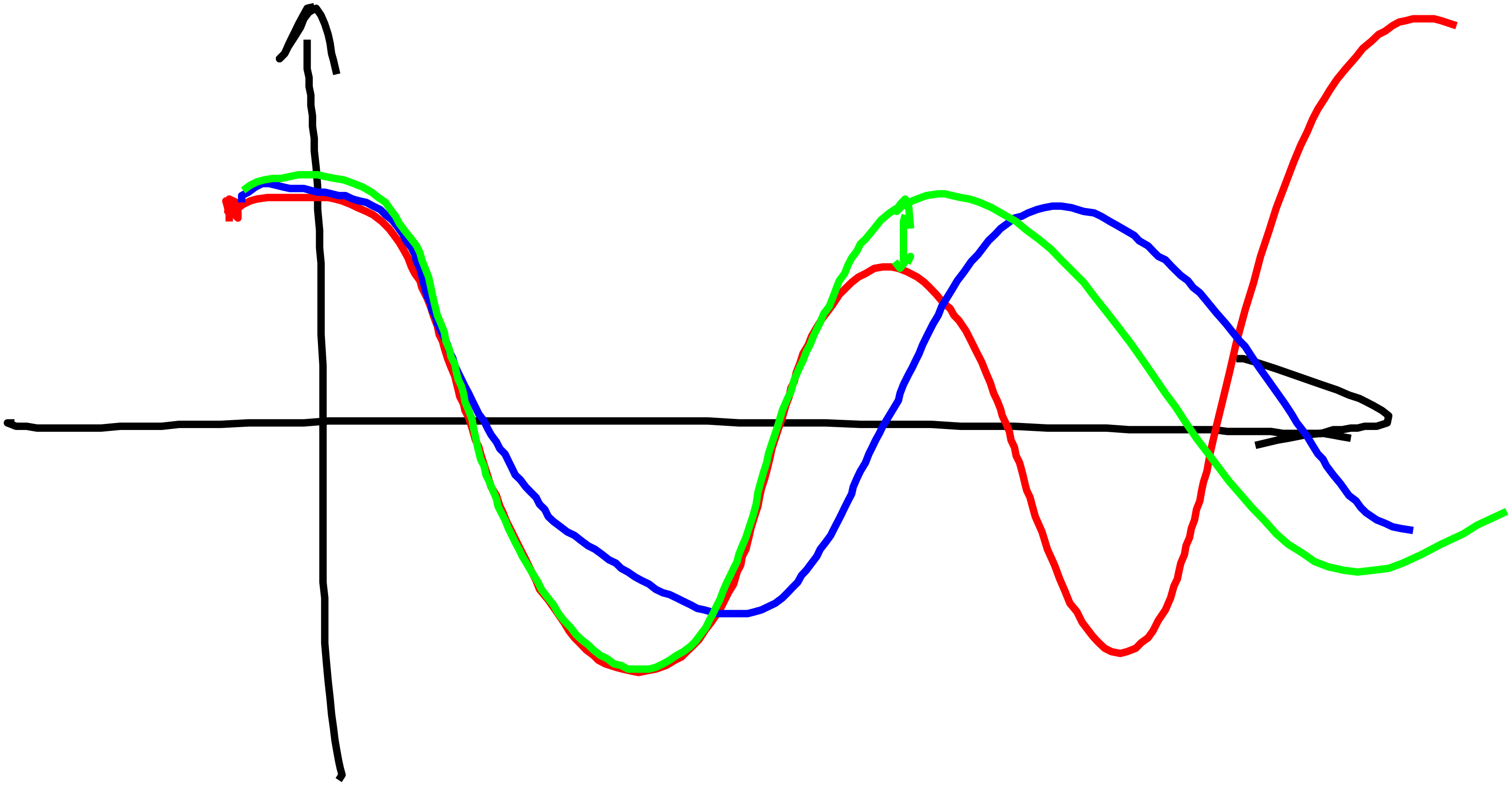
$$\mathbf{a}(t) = -(1/m)\nabla V(\mathbf{r}(t)) \qquad \mathbf{v}(t) = \frac{\mathbf{r}(t+\Delta t) - \mathbf{r}(t-\Delta t)}{2\Delta t}.$$

Gear Predictor-Corrector

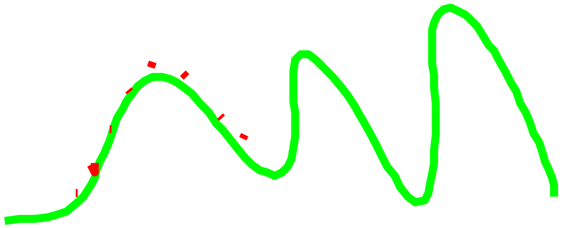


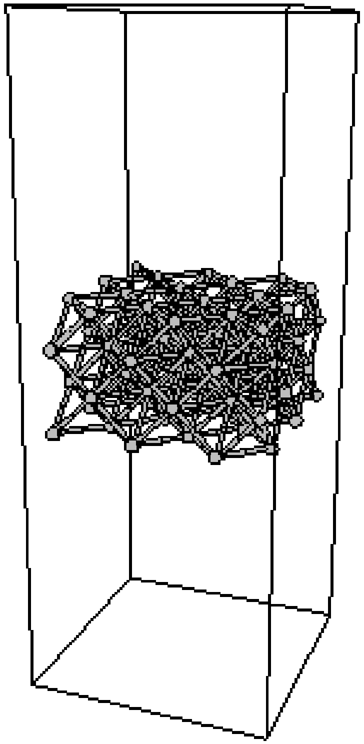
1. *Predictor.* From the positions and their time derivatives up to a certain order q, all known at time t, one "predicts" the same quantities at time $t + \Delta t$ by means of a Taylor expansion. Among these quantities are, of course, accelerations $\mathbf{a}$.
2. *Force evaluation.* The force is computed taking the gradient of the potential at the predicted positions. The resulting acceleration will be in general different from the "predicted acceleration". The difference between the two constitutes an "error signal".
3. *Corrector.* This error signal is used to "correct" positions and their derivatives. All the corrections are proportional to the error signal, the coefficient of proportionality being a "magic number" determined to maximize the stability of the algorithm.

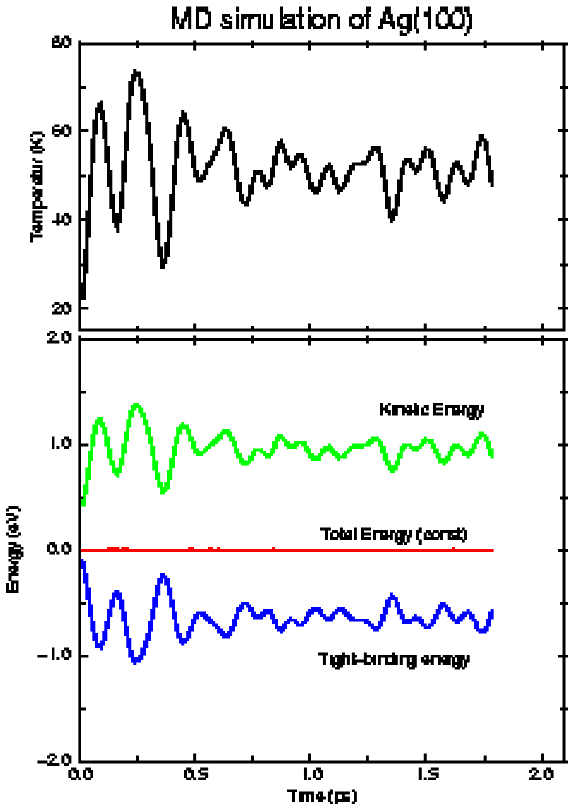
Lyapunov Instabilities



Time Step

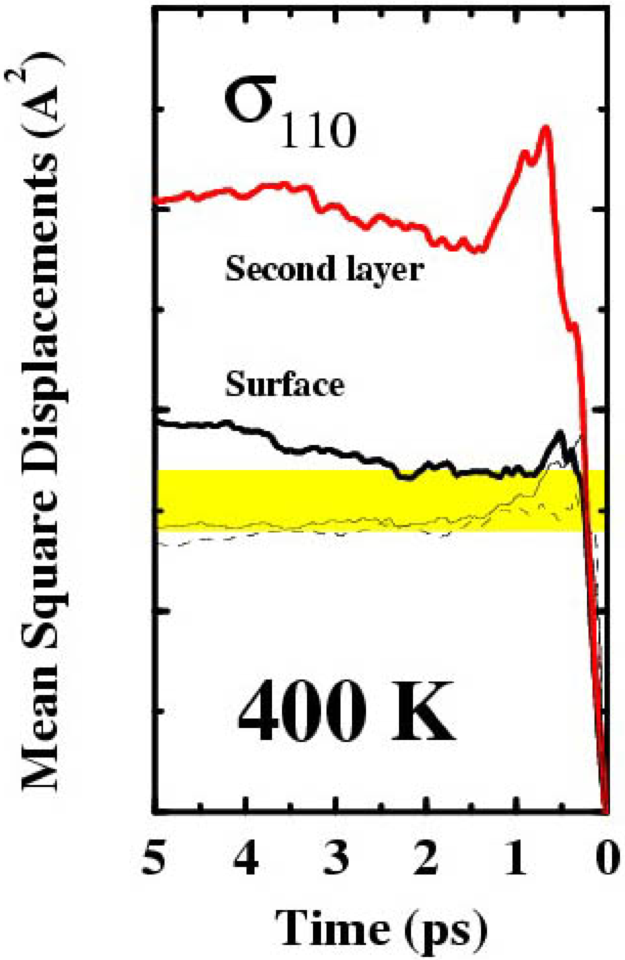





MD simulation of Ag(100)
Temperature (K)
80
60
40
20
Energy (eV)
2.0
1.0
0.0
−1.0
−2.0
Kinetic Energy
Total Energy (const)
Tight-binding energy
0.0
0.5
1.0
1.5
2.0
Time (ps)

Thermodynamic equilibrium ?

- Drop longer and longer initial segments of your dynamical trajectory, when accumulating averages



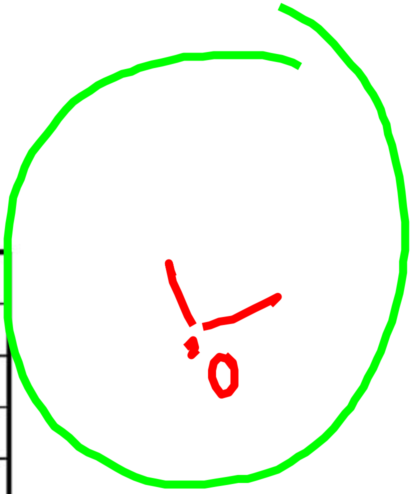
Accumulate averages

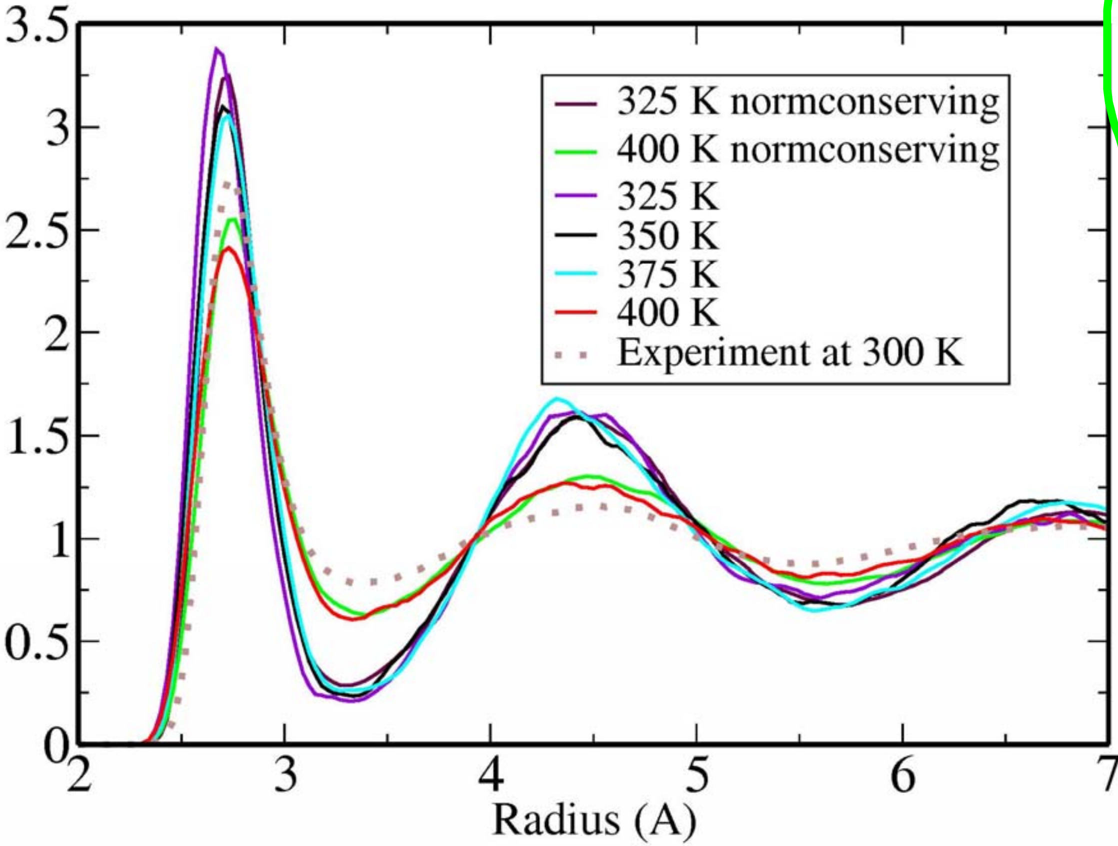
- Potential, kinetic, total energy (conserved)
- Temperature ($K=3/2\ N\ k_B T$)
- Pressure
- Caloric curve E(T): latent heat of fusion
- Mean square displacements (diffusion)
- Radial (pair) distribution function

Three Main Goals

- Ensemble averages (thermodynamics)
- Real-time evolution (chemistry)
- Ground-state of complex structures (optimization)
    - Structure of low-symmetry systems: liquids, amorphous solids, defects, surfaces
    - Ab-initio: bond-breaking and charge transfer; structure of complex, non trivial systems (e.g. biomolecules)

Correlation Functions





$$g(r) = \rho^{-2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r}_i)\,\delta(\mathbf{r}_j - \mathbf{r}) \right\rangle = \frac{V}{N^2} \left\langle \sum_i \sum_{j \neq i} \delta(\mathbf{r} - \mathbf{r}_{ij}) \right\rangle$$

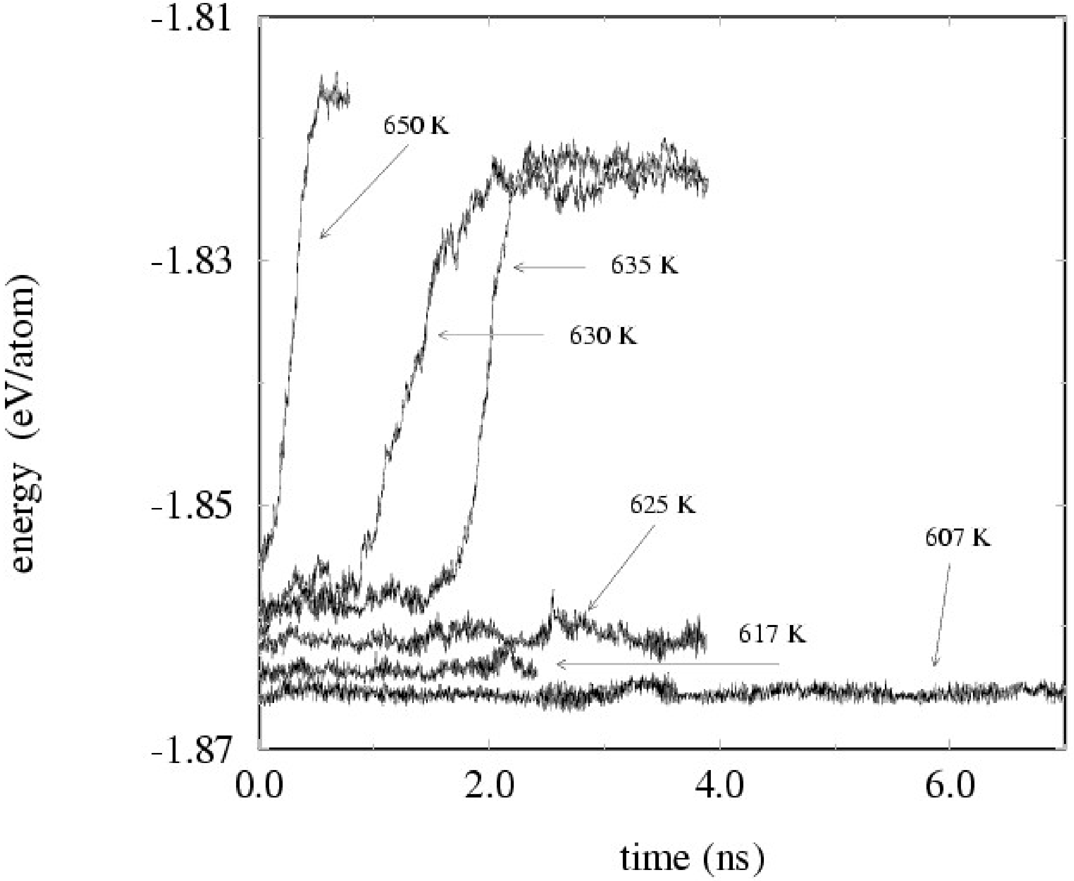
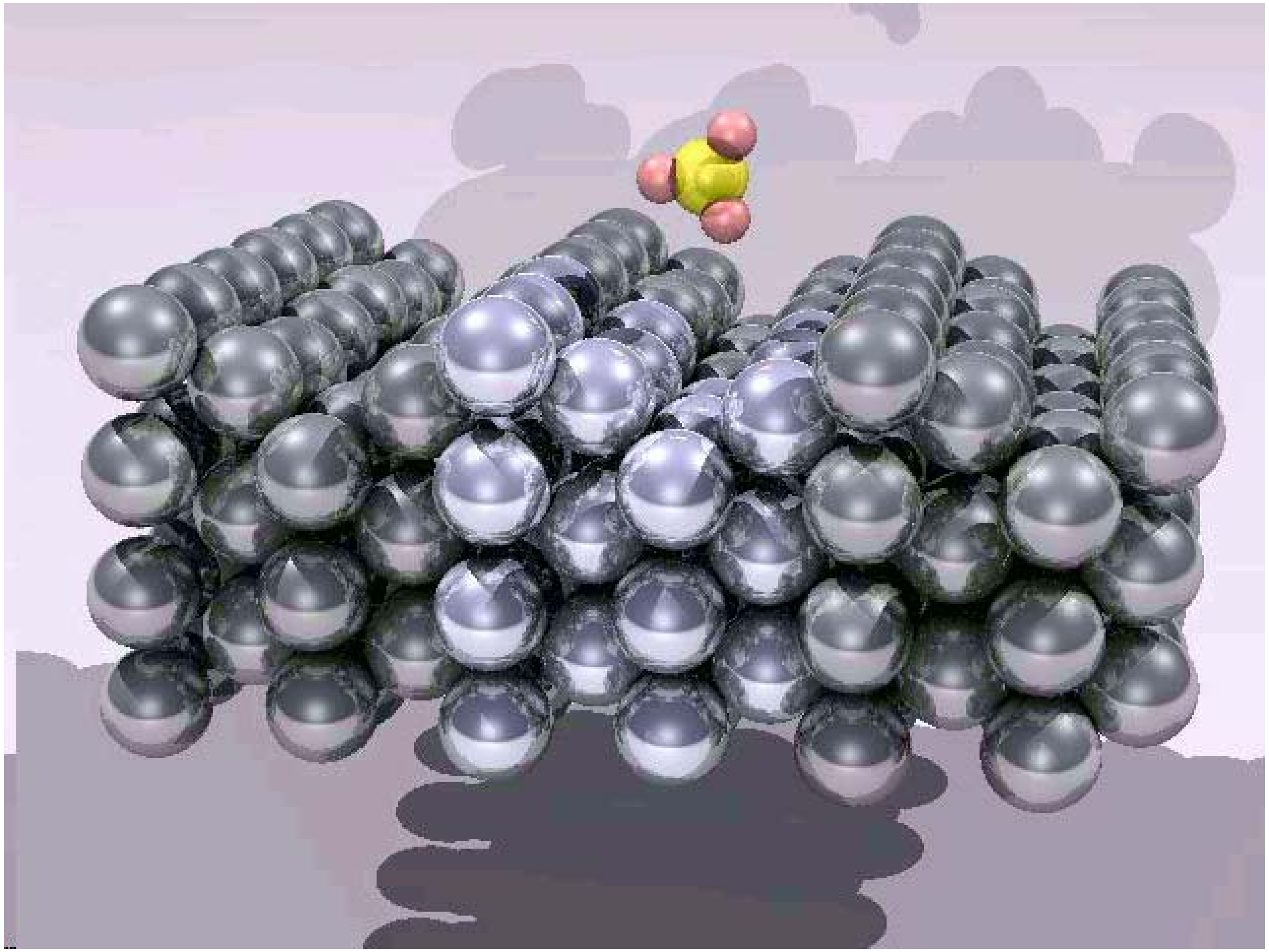
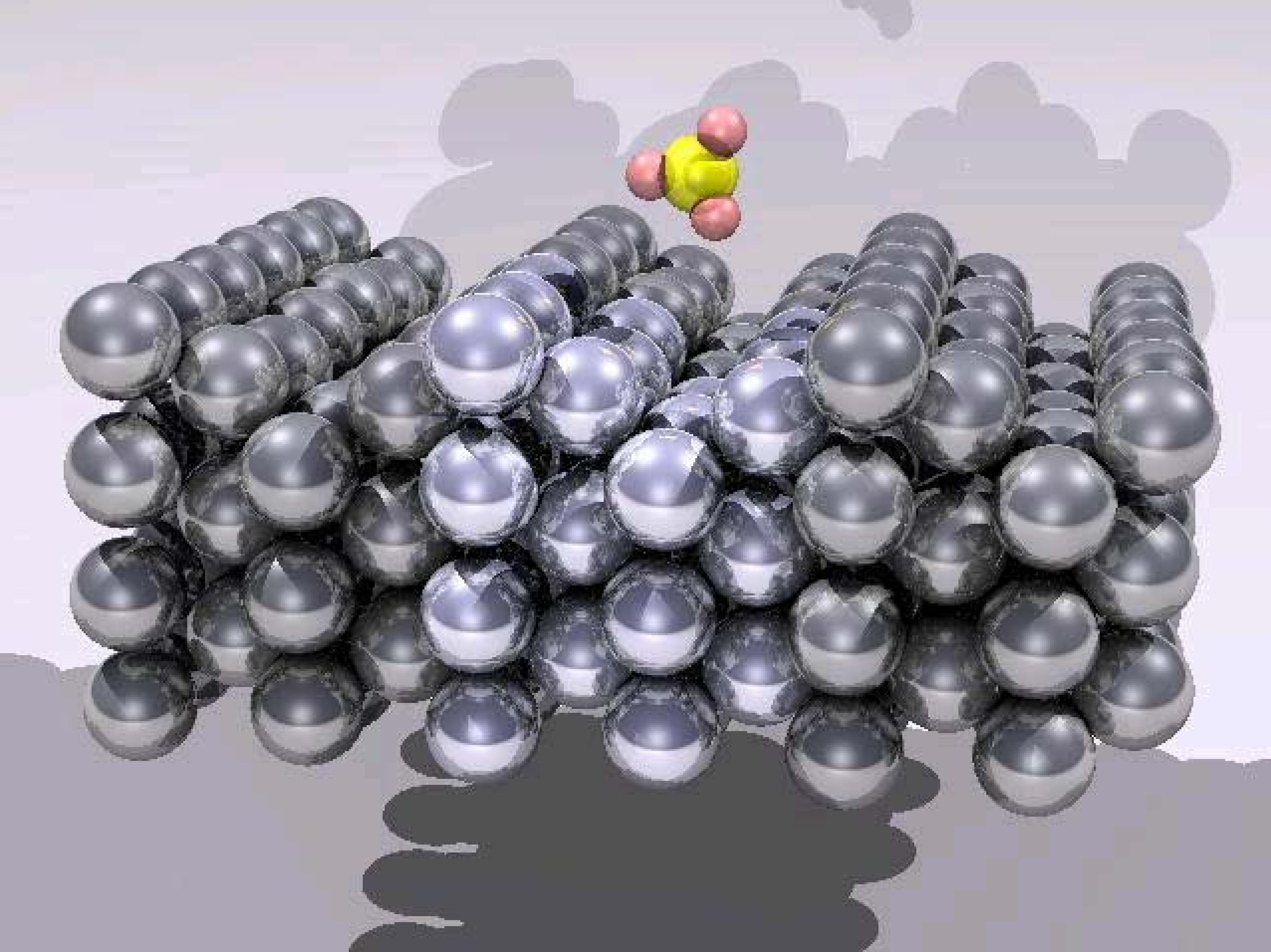


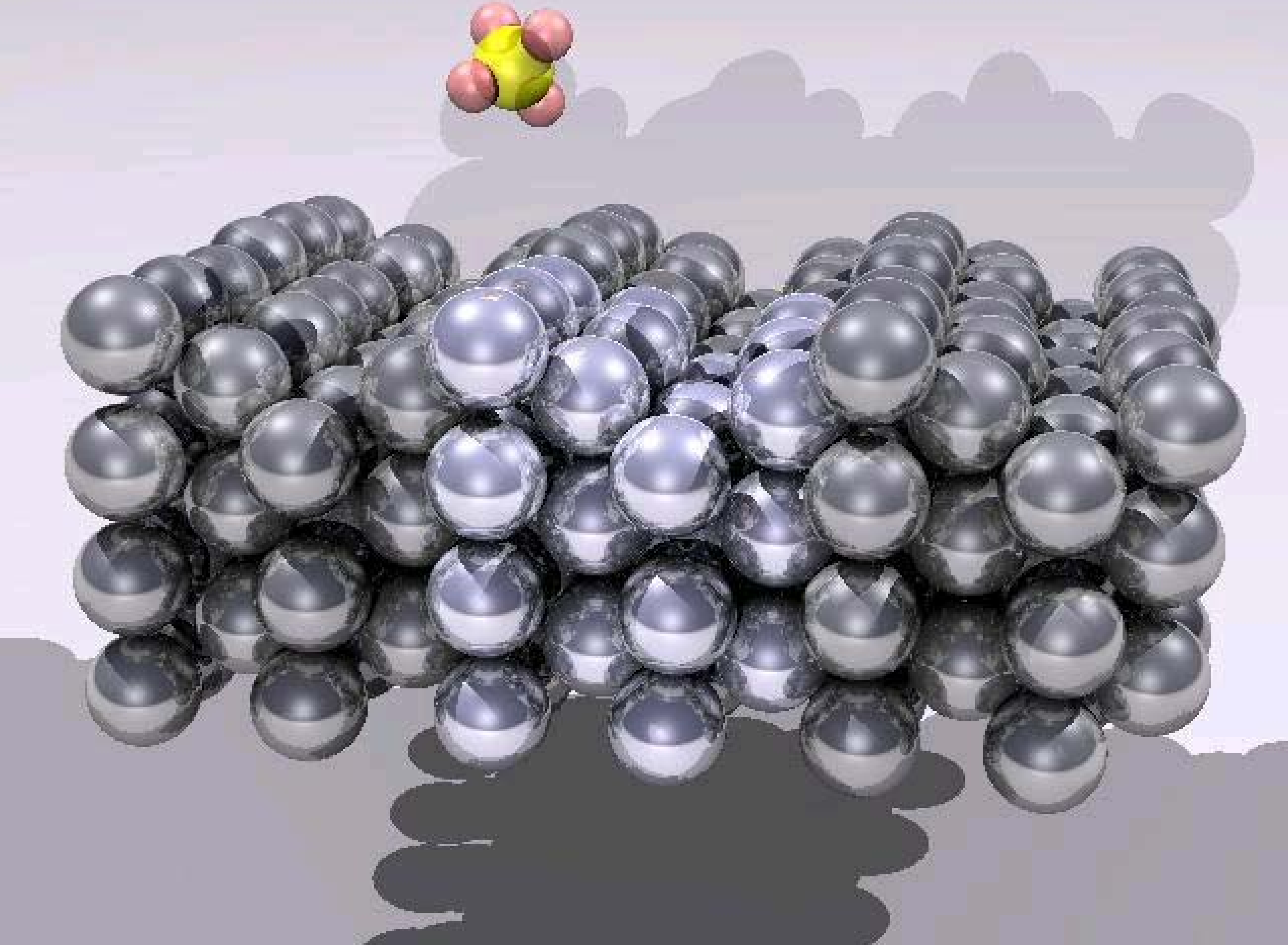
Figure 5.13: Time evolution of the total energy of Pb(100) (sample of 32 layers, 200 particles per layer). At 607 K ($\sim T_m$ in this simulation) the surface is incompletely melted, and survives in this metastable state until $T \leq 625\,\mathrm{K}$. The energy increase between 607 K and 625 K mostly reflects the increase of the quasi-liquid layer thickness, from ~ 1.3 to ~ 3 ML. For $T \geq 630\,\mathrm{K}$ the slab melts and irreversibly releases the latent heat corresponding to ~ 26 layers.

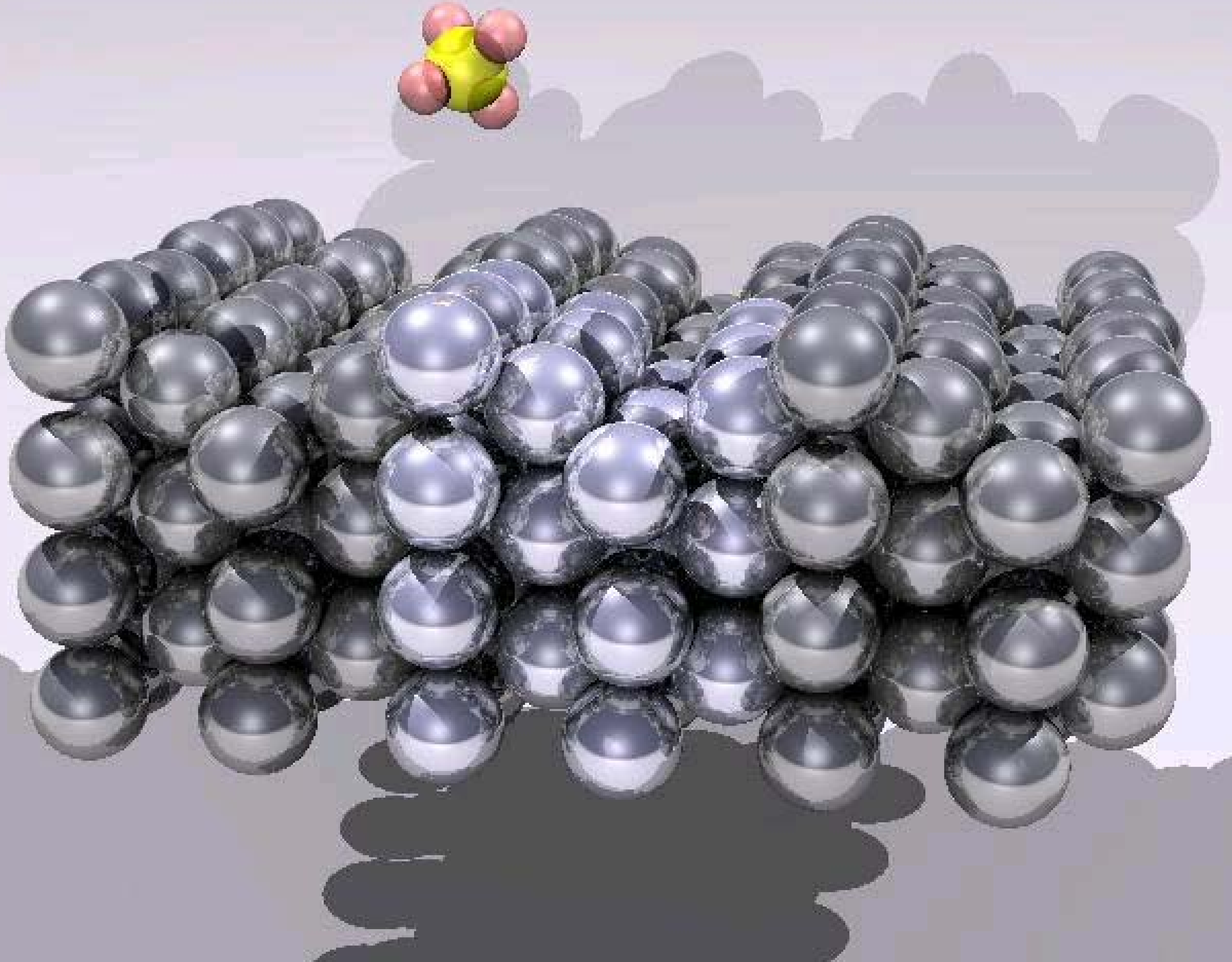
Source: Di Tolla, Francesco. "Interplay of Melting, Wetting, Overheating, Faceting, on Metal Surfaces: Theory and Simulation." Ph.D. Thesis, International School For Advanced Studies (SISSA), Trieste Italy, 1995. Courtesy of SISSA. Used with permission.

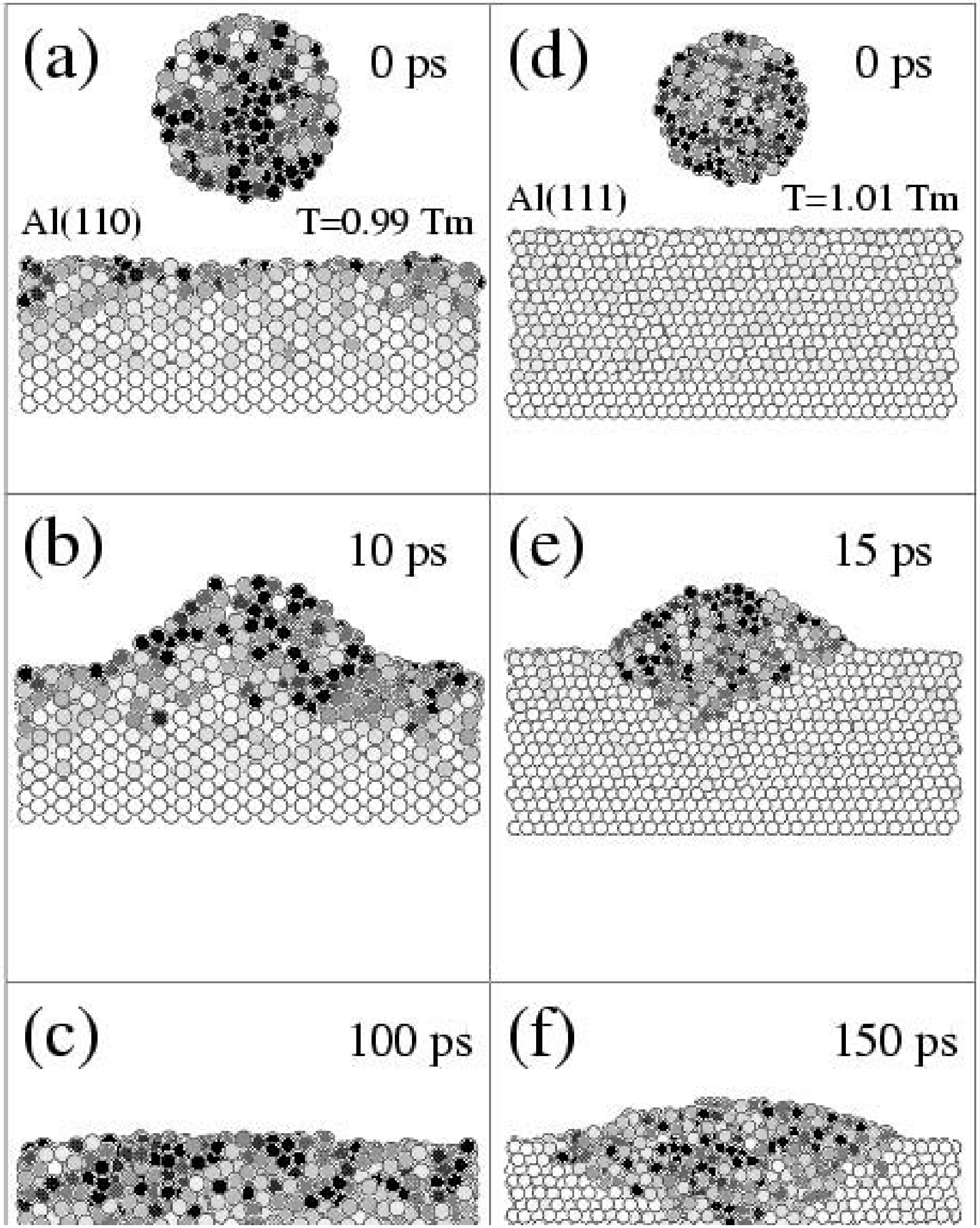
Cold catalysis of methane ?











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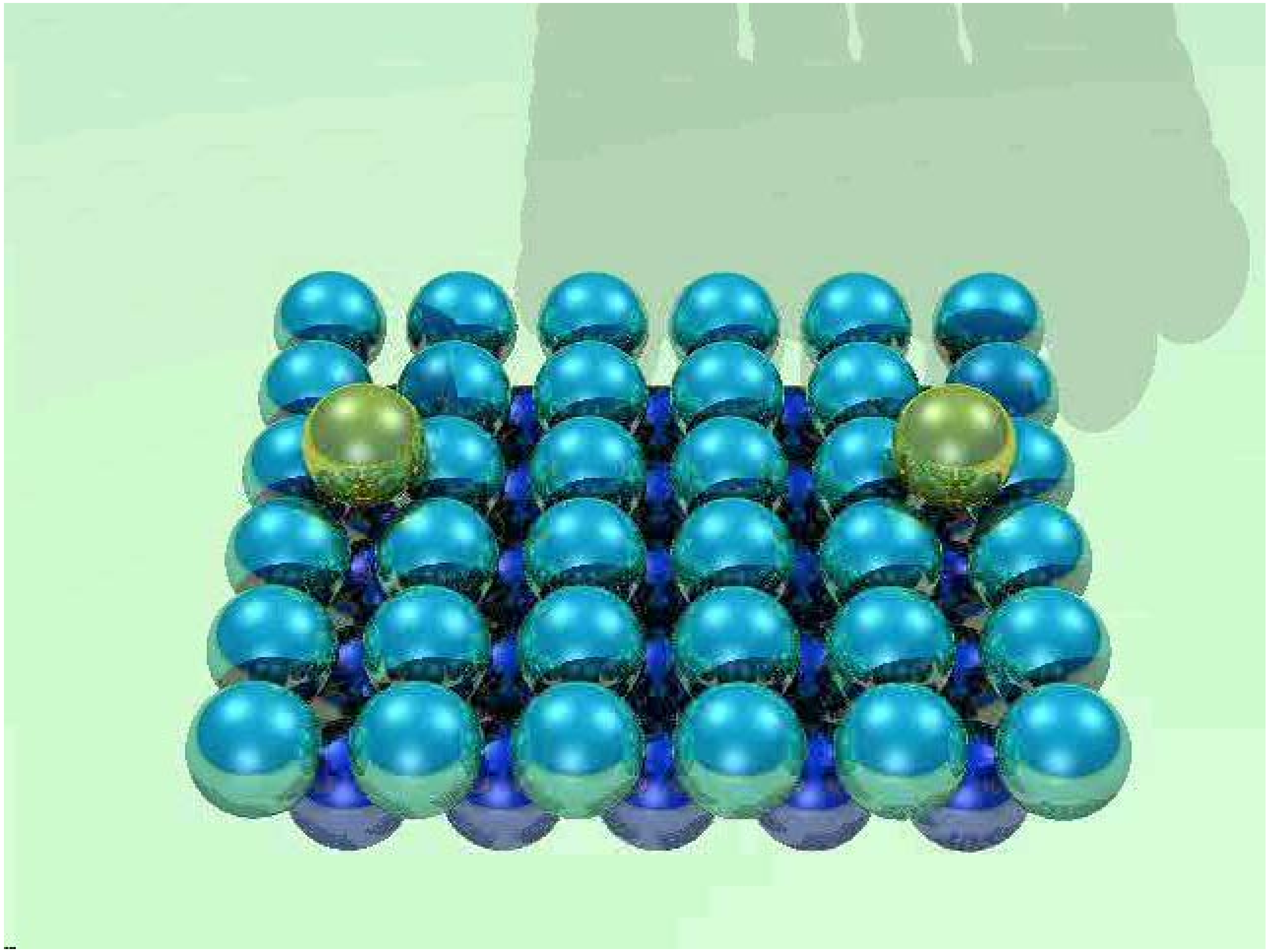
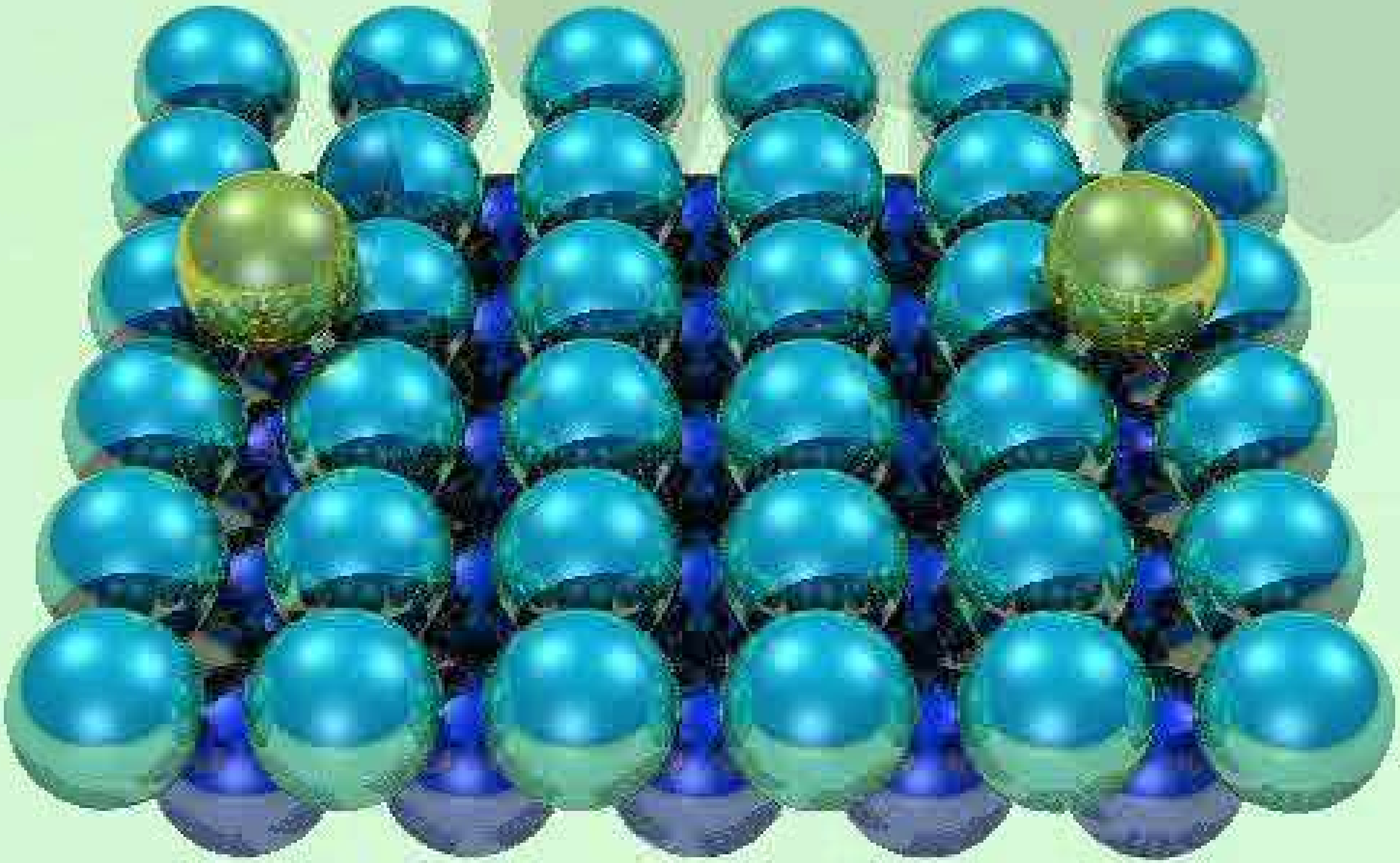
Diffusion of Adatoms





Bibliography

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