the physics of chemical bonding in crystals

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• why don't your fingers evaporate (at least, not very fast)?

• why can't you walk through a wall?

• Why, when you lift one end of a stick, does the other end come up too?
a molecule of aspirin hovering above a slab of aspirin crystal: do we understand what happens?
fcc argon

1,1-di-p-tolylethylene (a hydrocarbon)

(A.Gavezzotti et al., 1971)
glucose (a highly polar compound)


Cobalt octacarbonyl (organometallic)

Sumner et al., Acta Cryst. 1964, 17, 732
ionic crystals: fcc alkali halides

minerals: forsterite $\text{Mg}_2(\text{SiO}_4)$

Fujino et al., Acta Cryst. 1981, B37, 513
LSD in serotonin 5-HT2A receptor
models for the physical nature of the interaction

If all scientific knowledge were lost in a cataclysm, what single statement would preserve the most information for the next generation of creatures? Richard Feynman's answer: "All things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another"
the packing of organic molecules in crystals
the P2 space group:

...there are 'holes'.....
the P1- space group: that's better!

there is plenty of P1- organic crystal structures, and practically no P2 crystal structures
Experiment:
Condensed phases are, indeed, condensed but they do not collapse

*ergo:*
1) There are adhesion forces
2) There are repulsion forces

*Observed structures are equilibrium between attraction and repulsion forces*
Molecule-molecule interaction energies in the first coordination shell of organic crystals
Interaction energies in crystals of ionic compounds and zwitterions
Richard P. Feynman
"The force on any nucleus...in any system of nuclei and electrons is just the classical electrostatic attraction exerted on the nucleus in question by the other nuclei and by the electron charge distribution for all electrons"

"It now becomes quite clear why the strongest attractive forces arise when there is a concentration of charge between two nuclei... 
...van der Waals forces can also be interpreted as arising from charge distributions with higher concentration between the nuclei"
the Feynman picture: equilibrium of Coulombic forces

this is the fundamental chemical problem: where are the electrons? what do the nuclei do? bond-breaking and bond-making!
**Hellmann-Feynman theorem**

Can we just use Feynman's theorem to calculate molecular structures? We could, but that would be rather expensive because one needs a very high quality wavefunction.

We need a simpler model that can be applied to molecules of interest (drugs, non-linear optics materials, pigments, explosives), not to speak of big macromolecules.
Problems:
our wavefunctions and densities are not perfect for (at least) two reasons:
1) electron correlation is not well represented
2) we want to use the free molecule wavefunction to describe the molecule in the crystal

Thus, we miss:
1) terms deriving from coupling of electronic oscillations
2) terms deriving from the deformation of the density due to the crystal field
3) terms deriving from the lack of antisymmetrization when molecular wavefunctions overlap to some extent
Coulomb's formula:

$$U_{ab} = \left(\frac{1}{4\pi \varepsilon_0}\right) q_a q_b R_{ab}^{-1}$$

$q$ are charges
$R$ is distance between charges
if we knew the perfect wavefunction, that would be the end of the story
(note that, in 1939, Feynman could not imagine that one could calculate the electron distribution in molecules with relative ease)
Coulombic interaction
++, -- repulsive destabilizing
+- attractive stabilizing
strongly orientation-dependent
COULOMBIC ENERGY

In terms of central multipoles

The potential due to a charge distribution, at a distance $R$ from the center of charges, is expanded in a series of multipoles:

$$V(R) = A^0/R + (1/R^2)(A_x p_x + A_y p_y + A_z p_z)$$

$$+ (1/R^3)(A_{z2} d_{z2} + A_{xy} d_{xy} + A_{xz} d_{xz} + A_{yz} d_{yz} + A_{x2-y2} d_{x2-y2})$$

$$+ \text{higher terms over } 1/R^4, 1/R^5, ...$$

$A$ coefficients: radial dependence of the potential $p$ and $d$ functions are the spherical harmonics.

Central multipoles may be appropriate for very small molecules, but not for large organic molecules.
the $n$-polar approximation means neglecting all multipoles or order $m>n$
for example, using a dipole means neglecting all multipoles $n>2$
this is appropriate when R is large compared with the dimension of the dipole (molecule)
this is never appropriate in liquids or in crystals
cholesterol
are these two nearby dipoles???
the concepts of central molecular dipoles and quadrupoles must be handled with great care
COULOMBIC ENERGIES
In terms of distributed multipoles
(A.J.Stone model)
Modelling the Coulombic energy

- In terms of **point-charge models**, the coulombic energy is

\[ E_{\text{coul}} = \frac{1}{4\pi\varepsilon_0} \sum \sum q_{i,A} q_{j,B} / R_{ij} \]

the q's are charged located at atomic nuclei; they come from:
1) Mulliken population analysis (variable with basis set)
2) ESP charges (more consistent)
3) ...............other recipes

- In terms of **central or distributed dipoles**, the coulombic energy is a sum of moment \( k \) to moment \( m \) terms, where each moment is a monopole, dipole, quadrupole moment.

(actual formulas are very complicated)
The best option: 
the charge density box 
- a molecular orbital calculation 
- computer programs available

\[ V(i), \rho(i); q(i) = V(i) \rho(i) \]
Coulombic potential energy: \textit{in terms of full density}

\[ E_{\text{coul}} = \iint \rho_A ((r_1)) \rho_B ((r_2)) / |r_1 - r_2| \, d^3r_1 \, d^3r_2 + \sum_k \int Z_k(A) \rho_B ((r_2)) / |r_k - r_2| \, d^3r_2 + \]
\[ + \sum_m \int Z_m(B) \rho_A ((r_1)) / |r_m - r_1| \, d^3r_1 + \sum_k \sum_m Z_k(A) Z_m(B) |r_m - r_k| \]

requires an analytical form for \( \rho \).

\[ E_{\text{coul}} = \sum_k \sum_m q_{k,A} ((r_1)) q_{m,B} ((r_2)) / |r_1 - r_2| + \]
\[ + \sum_k Z_k(A) \left[ \sum_m q_{m,B} ((r_m)) / |r_k - r_m| \right] + \]
\[ + \sum_k Z_k(B) \left[ \sum_m q_{m,A} ((r_m)) / |r_k - r_m| \right] + \sum_k \sum_m Z_k(A) Z_m(B) |r_m - r_k| \]

replaces the integrals with a summation, \( \rho \) by points
problems with the point charge models (and all localized-charge models):

"penetration" energies
Coulombic energy, kJ/mol

inter-ring distance, Å

point-charge

delocalized
POLARIZATION: deformation of the density on approaching another charge.

polar polarizer  neutral polarized
Polarization (electrostatic induction) energy

Polarizability is:
a measure of the propensity of a given electronic environment to yield under the action of an external electric field: displacement/restraint

the restraining force is coulombic attraction between the displaced charge and the nuclei polarizability is large when electrons are at a large distance from a weakly charged nucleus.
The energy involved in the polarization process is always stabilizing because the induced dipole always points in the stabilizing direction (compliance of the polarized medium to the polarizing field).

The energy required for 'turning on' a field $E$ onto a dipole $\mu = \alpha E$ is given by

$$E_{\text{pol}} = - \int_{0,\varepsilon} (\mu \, dE) = -\frac{1}{2} \alpha \, E^2$$

classical polarization: analogy with molecular orbitals mixing, including virtual orbitals sometimes called charge-transfer energy.
the electron game of chemistry

bond formation
spin pairing

close transfer
polarization

Pauli repulsion
avoidance of same spins
DISPERSION: fundamentally similar to polarization operates in any chemical system from NaCl to solid benzene the "glue of the world"!!!
Dispersion energy

fluctuating dipoles generate induced dipoles in a nearby electron distribution. The resulting effect can be described by a quantum mechanical coupling of oscillating dipoles.

(the resulting stabilization has to do with zero-point oscillator energies, and dispersion effects are a consequence of the uncertainty principle, like all zero-point energy effects are.)
The London Symphony orchestra:

"These very quickly varying dipoles...produce an electric field and act upon the polarisability of the other molecule and produce there induced dipoles...

we may imagine a molecule as represented by an orchestra of periodic dipoles ... These 'oscillator strengths' are the same quantities which appear in the 'dispersion formula'..."

Models for dispersion:

\[ \alpha \text{ molecular polarizability, } I \text{ ionization potential at a distance } R: \]

\[ E_{\text{disp}} \approx [ -I(\alpha)^2 ] (R)^{-6} \]

The dispersion energy is always stabilizing, like polarization energy is.

Fritz London

(...although Einstein had already proposed polarizability as a source of cohesion: *Annalen der Physik*, 1901, 309, 513)
REPULSION!
Exchange-overlap-Pauli repulsion

Short-range repulsion has no classical analogy. Consider two 1s atomic orbitals, $a$ and $b$, with electrons 1 and 2 (unpaired spins); S is the overlap integral:

$$
\Phi^o = a(1)b(2) \quad \text{large distance, no antisymmetrization}
$$

$$
\Phi_{as} = (1-S^2)^{-1} \left( 1/2 \right)^{1/2} \left[ a(1)b(2) - a(2)b(1) \right] \quad \text{antisymmetrized}
$$

The difference between the expectation energies calculated with each of the two wavefunctions is

$$
E_{as} = (1-S^2)^{-1} (\Delta E' - K_{ab})
$$

$\Delta E'$ includes a number of corrections to the total electronic energy, while $K_{ab}$ is the $ab|ba$ exchange integral.
• antisymmetrization is the mathematical equivalent of the exclusion principle (no two electrons with same quantum numbers in the same region of space)

• $E_{as}$, the energy arising from antisymmetrization, is called the exchange-repulsion energy because it is overall destabilizing; it is zero when $S=\text{overlap}=0$.

• **Confusion:** exchange integrals give a stabilizing contribution to the energy, so that one has exchange stabilization in many-electron systems

• but the exchange integral also gives the largest contribution to $E_{as}$ for repulsion
A model for the repulsion energy:

\[ S_{AB} = \text{electron density overlap} \]

\[ E_{rep} = A S_{AB}^\gamma \]

reasonable: energy proportional to overlap, with \( A \) and \( \gamma \) parameters
the total intermolecular energy is the sum of these separate terms:

\[ E_{\text{tot}} = E_{\text{coul}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{rep}} \]

One often speaks of "van der Waals" energies more appropriately one should speak of Coulomb-London-Pauli energies
$P = \frac{RT}{(V_m - b)} - \frac{a}{V_m^2}$

Johannes Diderik van der Waals (1837-1923)

"I don't know anything about dispersion and this guy London!"
emphasize again: this is a MODEL for the analysis and interpretation of intermolecular forces, in terms of chemically significant molecular properties (there are other methods)

chemical interpretations; for example, coulombic end polarization energies are large in molecules with a permanent polarization (easily recognizable in their formula).
Energies are in kJ/mol.
energies are in kJ/mol
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naphthalene crystal

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naphtoquinone crystal

\begin{align*}
\text{E}_{\text{coul+pol}} & : -4.9 \quad -3.2 \quad -18.1 \quad -16.8 \\
\text{E}_{\text{disp}} & : -45.7 \quad -37.1 \quad -8.6 \quad -10.2 \\
\text{E}_{\text{tot}} & : -36.7 \quad -30.3 \quad -15.0 \quad -12.0
\end{align*}
Methods in Molecular Dynamics and Monte Carlo simulation

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a pre-crystallization system

solvent

solute

impurity

?
solvent
solute
impurity

phase separation
formation of micelles (nuclei, particles)
two key points in solution chemistry and crystallization:
- can I "see" the micelles/nuclei?
- are there differences between solute molecules in a homogeneous solution and in the micelle?

a simple calculation:
take a molecule, volume of say 300 Å³
space occupation factor is about 0.6
assume a spherical particle with N molecules
surface layer: 1.2 times the molecular diameter
particle diameter, micron

text: number of molecules

graph: red dot line
The graph shows the percentage of surface molecules (blue line) and bulk molecules (red line) as a function of the number of molecules. The x-axis represents the number of molecules, ranging from 0 to 1000. The y-axis represents the percentage, ranging from 0 to 100%.

- The percentage of surface molecules decreases as the number of molecules increases, approaching but not reaching zero at the highest number of molecules.
- The percentage of bulk molecules increases as the number of molecules increases, approaching 100% at a lower number of molecules compared to the surface molecules.

The graph illustrates the distribution of molecules between the surface and the bulk as the number of molecules increases.
human hair: 100 micron
microscope resolution: 0.2-0.5 micron
...the particles are small!!

experimental techniques:
- IR, NMR
- microcalorimetry
- turbidimetry
- synchrotron light scattering/diffraction...

they all provide partial information
Molecular Dynamics or Monte Carlo: evolutionary simulation

simulation in which the system changes its structure and energy vs. static simulation: energy of one configuration
Molecular dynamics (MD): part 1

for each atom (atomic nucleus):
- three positional coordinates, \( \mathbf{x} \)
- three components of momentum, \( \mathbf{p} = m \mathbf{v} \)

for \( N \) molecules each with \( M \) atoms:
6 x \( N \) x \( M \) coordinates defining **phase space**

**orders of magnitude:**
50000 molecules with 20 atoms
total energy of the system:

$$E(\text{tot}) = E(\text{potential}) + E(\text{kinetic})$$

$$E(\text{potential}) = \sum \text{(atoms)} \ (U(R))$$

stretch, bend, torsion, intermolecular

$$E(\text{kinetic}) = \sum \text{atoms} \ (1/2 \ mv^2) = \frac{3}{2}RT$$
an intermolecular force:
two Lennard-Jones particles at a distance $R$:

potential: $U = A \ R^{-12} - B \ R^{-6}$
with $A$, $B$ empirical parameters

force: $F = -\frac{dU}{dR} = 12 \ A \ R^{-13} - 6 \ B \ R^{-7}$

an intramolecular force:

potential $U = \frac{1}{2} k(R-R^\circ)^2$

force $F = -\frac{dU}{dR}$ (can you work it out?)
MD Part 2: the NPT ensemble

$N$ particles move in a “computational box” at constant pressure $P$ and temperature $T$ under the action of the forces generated by their own potentials (Coulomb, polarization, dispersion, repulsion, stretching, bending, torsion...).
computational box: acetonitrile

liquid

partly ordered
Pressure = \frac{2}{3V} [E(\text{kinetic}) - \text{virial}]

\text{virial} = -\frac{1}{2} \sum_k \sum_j R(k,j) F(k,j)

sum of distances between atoms \times forces

\text{pressure and volume control:}
if pressure is too high, decrease all distances
(reduce volume of computational box)

E(\text{kinetic}) = \sum \text{atoms} \left( \frac{1}{2} m v^2 \right) = \frac{3}{2}RT

\text{temperature control:}
if T is too high, decrease all velocities

\text{exercise: check that for an ideal gas, } PV = RT
MD part 3: dynamic equations

\[ F = ma = \frac{d^2R}{dt^2} \]

Newton's equation of motion

its solution gives the position and velocity of each atom as a function of time (trajectory)
position of all atoms, energies; T, P, V; as a function of time in any process

BUT:

- the timescale problem  
  (nanoseconds versus seconds/hours)
- the size problem  
  \(10^5\) molecules against \(10^{23}\)
- the potential energy problem  
  energies and forces are parametric formulas
Monte Carlo

even simpler:
1) prepare a starting configuration (computational box)
2) compute starting energy $E^\circ$
3) move one particle at random or change volume, and compute $E'$
4) accept move if $E' < E^\circ$ or if $\exp(-\Delta E/kT) >$ a random number between 0 and 1
   (“Metropolis” criterion)

Result:
for a large number of moves, a Boltzmann ensemble

there is no time in MC but e.g. rotation of a molecule by $2^\circ$, or
one MC move, takes $\approx 10^{-15}$ s or $10^{-6}$ picoseconds
a few examples of evolutionary simulation in crystallization processes
a look at solution: why does this molecule pick up acetone solvent at crystallization?

hydrogen-bond distance between diol and acetone in solution, from MD simulation

(A.G. Chem Eur J 2000, 6, 2288; crystal structures by Nassimbeni et al., 1992)
what do molecules do when they aggregate into a crystal from the melt?

MD is deterministic (Newton’s equations)

MC is limited only by the fantasy of the operator (and/or adherence to statistical mechanics)

an example: non-equilibrium MC simulation of disentaglement of long-chain molecules ($n$-hexane): the Metropolis criterion is enforced only after increase of an order parameter within the computational box
MC view of liquid \(n\)-hexane: fully isotropic, gauche population
MC view of “symmetrized” phase: anisotropic, all \textit{trans}
suggestion from the MC simulation:* 
as the dissimmetry parameter decreases the box expands 
to make room for molecules as they straighten up, so the density has a temporary decrease

*A.Gavezzotti (2009), rejected by three major Journals)
what is surface tension?

the result of anisotropic intermolecular interaction on the surface molecules of an aggregate
**start:** a slab of crystalline succinic anhydride

after 10 picoseconds MD at 100 K

after 280 picoseconds MD at 250 K
periodic boundary conditions:
replicas of the system prevent part of the anisotropy
why does a crystal melt?

higher T and anisotropic libration produce a decrease in density molecules are more and more free to librate until a catastrophic “collective libration” destroys the crystal
melting: if $T$ is sufficiently high, practically any trajectory through phase space will lead to the liquid crystallization: only very few well specified paths will lead back to the crystal. No crystallization has ever been observed in MD - time problem!!!

question/exercise:

can you explain why is it that anisotropic libration produces a decrease in density, while harmonic libration does not?*

*Note: the answer “ah, but that’s obvious!” is not acceptable)
what happens when a solute crystallizes out of a solution?

ask MD, but remember the time and size problems and the potential energy problem
first example
succinic anhydride
in a nonpolar solvent (yellow dot)

the starting box
for a MD simulation
of a homogeneous solution (periodic boundary)
the box after some nanoseconds of MD simulation
solute starts its aggregation into micelles
a close-up of the micelles (solvent removed)
a 10-500 molecule entity cannot have a crystalline form because of surface/interface tension. No solvent can stabilize a crystalline form.
the first step in crystal nucleation must be phase separation into small droplets

(an emulsion, if you wish)
second example
acetic acid in a nonpolar solvent
the starting box

after 0.2 nanoseconds:
delete boundary conditions
after about 2 nanoseconds...

note:
no coalescence is observed without solvent (it is not a matter of long-range interactions between solutes... but of constrained diffusion)
coalescence of organic compounds from solution: cluster size: N = 2 to 100
oligomers in solution
N = 100 to 10,000 phase separation nanoparticles with distinction between possibly crystalline core and surface

▪ solvent interfacial tension may still influence the core structure
▪ kinetic competition for size and structure
N = $10^4$ to $10^7$

**mesoparticles**

- solvent influence presumably over
- almost visible

- crystalline core develops: crystal seed

- crystalline core does not develop: oil or wax

- crystal growth proper, **macroparticles**
  powder or single crystal
case studies in crystal formation (organic crystals)

what molecular simulation has to say
experiment:
a true crystal
periodic symmetric
powder diffraction: diffracted intensity

angle $\theta$
semi-ordered phase

disordered, semi-crystalline

liquid

intensity, arbitrary units

angolo $\theta$
some definitions

are definitions useful/necessary?
‘flower a shoot of the sporophyte of a higher plant that is modified for reproduction and consists of a shortened axis bearing modified leaves
solid
a body that does not flow and has an elastic response to strain, preserves its outer shape for a time longer than a human lifetime.

crystal proper
• a solid in which the molecule is repeated over domains (10000-100000 times the size of a single molecule) by 3D translationally periodic symmetry operations.
• X-rays: single-crystal yields more than $5N$ sharp independent Bragg spots for an $N$-parameter molecule
• structure solution and refinement proceed smoothly: no large thermal parameters, no superposition of partial atom occupancies, the final $R$-factor must not exceed 0.07-0.10
• powder: has sharp separate peaks
defective crystal

- shows less than $5N$ Bragg spots, or a powder pattern with broad peaks, or a diffractogram with fuzzy features
- Refinement of the X-ray crystal structure: R-factor that may not decrease below 0.07 without a repeated intervention by an experienced crystallographer
- arise from: high thermal motion, rotational or translational diffusion, or structural disorder, poor crystallization, domain structure, dislocations, etc., twinning.

Presumably, defective crystals are often present together with proper ones in crystallization batches
amorphous material
- a solid without translationally periodic symmetry operations of any dimensionality
- shall not give well resolved Bragg peaks.

glass
an amorphous material that exhibits some characteristic singularities in thermodynamic functions and orientational correlation properties ("glass transitions")

solvate
a solid whose constituent chemical species is \( A^X B^Y \) where
- \( A \) is a higher molecular weight component (the host),
- \( B \) is a lower molecular weight component (the guest);
- \( X \) is a small integer, and \( Y \) is any number \( >0 \).
**nucleation:**
formation of the first molecular aggregates

**growth:**
epitaxy over an already formed crystalline entity

**mesoscopic (macroscopic) theories:**
invoke nucleation free energy, roughening transitions, etc.

**atomic level theories:**
attempt at a view of the behaviour of all particles involved in the process
impurity → solvent → bulk crystal → surface → solute
the timescale problem...

crystal formation
solution diffusion, encounter: ns
nucleation: ???
growth: from seconds
up to months

protein folding
loop closing: 10 ns
α-helix: 200 ns
β-hairpin, folding: 10 μs
first step: condensation into a liquid-like micelle ("phase" (?) separation)

solute:
fast rotation on the diffusive timescale (nanoseconds)
The molecule has 'attachment points', A, B, C, D.

A 'likes' B,
C 'likes' D

but links are flexible; translational pre-organization followed by symmetry to close small voids (or solvent pickup).

Second step: organization within the micelle.
**Polymorphs**

a set of crystals with identical chemical composition made of molecules with the same molecular connectivity, (possibly with different conformations) with distinctly different three-dimensional translationally periodic symmetry operations.

If so, there can be real polymorphism only if both forms are proper crystals of the same chemical species. Modulations and transitions from proper to defective crystal, with molecular arrangements remaining largely unchanged, are not polymorphic transitions*

*Lawyers of Pharma Companies do not like this
the crystallization problem
for organic materials:
crystal forces are weak, often scarcely directional
many choices are possible
the transition from non-symmetric to symmetry-organized phases
is often uncertain or equivocal
molecular simulation?
static simulation: generate crystal structures, calculate lattice energies

Each point in this graph is a possible crystal structure.
glycine polymorphs: DFT calculations
many structures have the same lattice energy

Parsons et al., Cryst. Growth Des. 2005, 5, 1437
evolutionary simulation
molecular dynamics or Monte Carlo

a typical run: 10,000 atoms
for each step compute \((10^4)^2 = 10^8\) distances
for 100,000,000 steps,
0^{16} times Pythagora’s theorem...
Model systems: the LennardJonesium
an ensemble of spherical particles interacting with
a soft isotropic radial potential

Anwar et al., Mode of action and design rules for additives
that modulate crystal nucleation, Angew.Chem.Int.Ed 2009,48,1596
real life: ritonavir
a famous case of catastrophic polymorphism in the pharmaceutical industry

ritonavir, form 1, said to be metastable

form 2, said to be stable
a gallery of situations in crystal growth based on Monte Carlo simulation of a test compound growth from the gas phase, no solvent

not a spherical particle, but not ritonavir either....
the [001] direction with an artificial splitting between two layers
an idealized slab of the crystal structure.....

...and a snapshot of what would happen in reality to such a small fragment! remember thermal motion!.. (from MC simulation)
a molecule hovering above an idealized crystal slab
Monte Carlo simulation under parametric intermolecular potentials (dispersion/Coulombic)
rigid molecules, surface constrained to stand still
a sample output from a MC simulation:

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</tr>
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</table>
molecule landed on the surface
(an instantaneous snapshot)

adsorption/absorption?

what pulls the molecule down?
what keeps it down?
attachment speed:
\[ d = 10 \, \text{Å} = 10^{-9} \, \text{m} \]
\[ t = 10^4 \, \text{move} \cdot 2 \cdot 10^{-6} \, \text{ps/move} = 2 \cdot 10^{-14} \, \text{s} \]
\[ v = \frac{d}{t} = 50 \, \text{km/s} \]
free gas-phase molecule: 1 km/s at 300 K
particle is accelerated under the attractive potential

bulk cohesion energy: \(-21865/392 = -56 \, \text{kJ/mol}\)
attachment energy: \(-21865+21805 = -60 \, \text{kJ/mol}\)

(est’d heat of sublimation 75 kJ/mol; potential energy for removing one molecule from bulk crystal 150 kJ/mol)
energy oscillations:
surface diffusion
arrows: attempted desorption
100,000 moves 400,000 moves 800,000 moves

surface reconstruction
solvent
solute
“wet” surface
MUCH more difficult

the molecule is still swimming freely aloft after some million MC steps

long before the solute-solute potential comes into play the molecule has to fight against solute-solvent steric barriers (diffusion barrier)
Computer software: free download for academic institutions
http://users.unimi.it/gavezzot

Graphics: E.Keller, SCHAKAL