THERMODYNAMIC PROPERTIES OF A SHELL MOLECULE-GAS PARTICLES SYSTEM

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ABSTRACT. A Lennard-Jones potential is used to derive formulaefor the potential of interaction between shell macromolecules[1] and gas atoms. Calculations are carried as far as thespherical symmetry approximation. The potential of interaction determines the stability of a shell topological compound. When the distance R between a shell molecule and a gas atom is equal the radius l of the outer shell, the potential is the highest and determines a barrier, which must be lower than an energy of the trapped / by the shell molecule / atom to be released.

In the title system shell macromolecules[1] occur. For such molecules, formulae for the potential of interaction between them and gas atoms have been derived. In Fig. 1
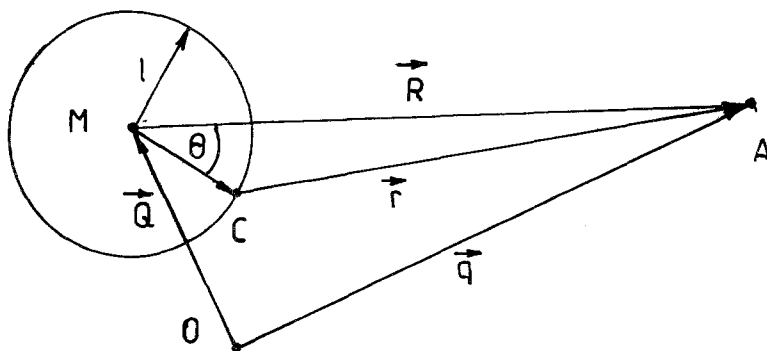

Figure 1. Schematic illustration of a shell molecule M interacting with a gas atom A. C - an atom of a shell; l - radius of the shell; O - the center of coordinate system; q,Q - positions of the atom and the molecule respectively; r - the distance between A and C; R - the distance between the centers of M and A.

a shell molecule M with the outer shell only and a gas
atom A interacting with it are schematically shown. For
simplicity we assume the shell molecule to be of a rigid
ball chemical structure and to be also a gas. We have two
simple relations

$$R = \vec{q} - \vec{Q} \qquad\qquad r^2 = R^2 + 1^2 - 2R1\cos\theta$$

A general potential of interaction between the shell mole-
cules and atoms can be written as

$$V = \sum_{i=1}^{n} \sum_{j=1}^{N} \Psi\left(q_i - Q_j\right)$$

where Ψ is a potential between an atom and a molecule.
This potential can be obtained in approximation if one
makes some simplifications. We can write an equation

$$\Psi\left(\vec{q},\vec{Q}\right) = \sum_{\text{over shells}} V_1\left(\vec{q},\vec{Q}\right) \qquad ,$$

The summation is performed over shells in a shell molecule.
V_1 is a potential of the interaction between a gas atom
and a shell of   radius 1.
We assume that the interaction is described by a Lennard -
Jones potential

$$u_{CA}\left(r\right) = \begin{cases} 4\varepsilon_{CA}\left[\left(\dfrac{\sigma_{CA}}{r}\right)^{12} - \left(\dfrac{\sigma_{CA}}{r}\right)^{6}\right] & r \leqslant r_o \\[4mm] 0 & r > r_o \end{cases} \qquad ,$$

where r_o is the cutoff distance, ε and σ are the Lennard -
Jones parameters. This is the site - site Lennard - Jones
potential, and u_{CA} denotes a potential between atoms A
and C (see Fig. 1). By "washing away" the potential u_{CA}
over a whole shell with a radius 1 we obtain the following
formula for the potential V_1

$$V_1\left(\vec{q},\vec{Q}\right) = V_1\left(|\vec{q} - \vec{Q}|\right) = V_1\left(R\right) = \int_S 4_g\varepsilon_{CA}\left[\left(\frac{\sigma_{CA}}{r}\right)^{12} - \right.$$
$$\left. - \left(\frac{\sigma_{CA}}{r}\right)^{6}\right]dS \qquad ,$$

where the integral is performed over a sphere of radius 1,
g is the average density of atoms on a shell instead of
a discrete number N of atoms on the shell

$$g = \frac{N}{4\pi 1^2} \quad .$$

If we introduce spherical coordinates we obtain

$$V_1\left(R\right) = 4\int_0^{2\pi} d\varphi \int_0^{\pi} 1^2 \sin\theta d\theta \frac{N\varepsilon_{CA}}{4\pi 1^2} \left(\frac{\sigma_{CA}}{r}\right)^{12} - \left(\frac{\sigma_{CA}}{r}\right)^6$$

$$= \int_0^{\pi} \sin\theta d\theta 2N\varepsilon_{CA}\left[\left(\frac{\sigma_{CA}^2}{R^2 + 1^2 - 2R1\cos\theta}\right)^6 - \right.$$

$$\left. - \left(\frac{\sigma_{CA}^2}{R^2 + 1^2 - 2R1\cos\theta}\right)^3\right] =$$

$$= 2N\varepsilon_{CA}\frac{\sigma_{CA}^2}{2R1}\left[\frac{1}{5}\left(\frac{\sigma_{CA}^2}{R^2 + 1^2 - 2R1\cos\theta}\right)^5 - \right.$$

$$\left. - \frac{1}{2}\left(\frac{\sigma_{CA}^2}{R^2 + 1^2 - 2R1\cos\theta}\right)^2\right]_{-1}^{+1} \quad .$$

The above formulae can be written only in the case, when

$$r^2 \leqslant r_0^2 \Leftrightarrow \frac{R^2 + 1^2 - r_0^2}{2R1} \leqslant \cos\theta$$

and this equality should hold for all $\cos\theta$ so we get

$$\frac{R^2 + 1^2 - r_0^2}{2R1} \leqslant -1 \quad .$$

$$\text{If} \quad -1 \leqslant \frac{R^2 + 1^2 - r_0^2}{2R1} \leqslant 1$$

the integral can not be performed over the whole sphere, but over a part of it only. Then we get

$$
V_1\left(R\right) = 2N\varepsilon_{CA}\ \frac{\sigma_{CA}^2}{2R1}\left[\frac{1}{5}\left(\frac{\sigma_{CA}^2}{R^2 + 1^2 - 2R1\cos\theta}\right)^5 - \right.
$$

$$
\left. - \frac{1}{2}\left(\frac{\sigma_{CA}^2}{R^2 + 1^2 - 2R1\cos\theta}\right)^2\right]\frac{1}{\dfrac{R^2 + 1^2 - r_o}{2R1}} \quad .
$$

If $\dfrac{R^2 + 1^2 - r_o^2}{2R1} \gg 1$ we get $V_1\left(R\right) = 0$.

So we get the following final result

$$
V_1\left(R\right) = N\varepsilon_{CA}\ \frac{\sigma_{CA}^2}{R1}\left[\frac{1}{5}\ \sigma_{CA}^{10}\left(\frac{1}{\left(R - 1\right)^{10}} - \frac{1}{\left(R + 1\right)^{10}}\right) - \right.
$$

$$
\left. - \frac{1}{2}\ \sigma_{CA}^4\left(\frac{1}{\left(R - 1\right)^4} - \frac{1}{\left(R + 1\right)^4}\right)\right] \quad r_o \geqslant R + 1
$$

$$
V_1\left(R\right) = 0 \qquad\qquad\qquad\qquad\qquad\qquad r_o \leqslant |R - 1|
$$

$$
V_1\left(R\right) = N\varepsilon_{CA}\ \frac{\sigma_{CA}^2}{R1}\left[\frac{1}{5}\ \sigma_{CA}^{10}\left(\frac{1}{\left(R - 1\right)^{10}} - \frac{1}{r_o^{10}}\right) - \right.
$$

$$
\left. - \frac{1}{2}\ \sigma_{CA}^4\left(\frac{1}{\left(R - 1\right)^4} - \frac{1}{r_o^4}\right)\right] \quad \begin{array}{l}|R - 1| \leqslant r_o \\ \qquad \leqslant R + 1\end{array}
$$

The potential V_1 can be used in the calculation of the partition function and then in the determination of the free energy of the system. However, the potential V_1 itself, especially that of the outer shell of a shell molecule, is important and determines the stability of a shell topological compound which is a topological isomer of two
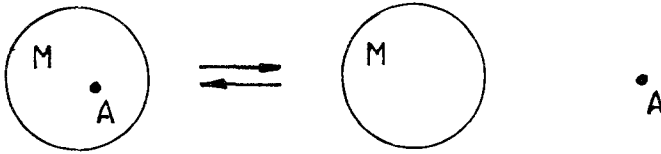
systems (Fig. 2).

Figure 2. Topological isomers: an atom A trapped inside a shell molecule M (left), and the atom located outside the molecule (right).

The left isomer illustrates just the topological compound, i.e. an atom A is located inside a shell molecule M. It means R is less or equal 1. When R equals 1 the potential V_1 is the highest and determines the barrier, which must be lower than the energy of the trapped atom to be released. In general, the potential V_1 is connected with the energy barrier, which determines the permeability of the outer shell of a shell molecule for small particles. This is important if we predict (and we really do) the shell molecule to play a role, in the future, as a cavity forming component in a synthetic enzyme system. We suppose this problem should also be important in the revers osmosis system using microporous membranes[2].

References

1. M. Maciejewski, J.Macromol.Sci.-Chem., 17, 689 (1982).
2, T. Matsuura, Y. Taketani, and S. Sourirajan, in Synthetic Membranes, vol. 2, A.F. Turbak, Ed.; American Chemical Society, Washington D.C. 1981, paper 19.