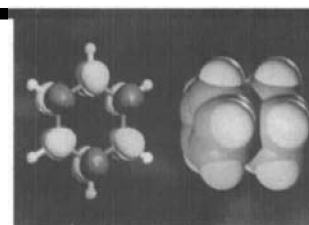


COMPUTATIONAL CHEMISTRY COLUMN

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Bulk Properties of Liquids and Molecular Properties in Liquids from a Combination of Quantum Chemical Calculations and Classical Simulations

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The next three columns are devoted to a common theme, namely bulk properties of liquids and molecular properties in liquids obtained from a combination of quantum chemical calculations and classical simulations. In the following we hope to show, how different fields of computational chemistry, which were completely separated three decades ago, have begun to overlap. Furthermore, before another three decades elapse, it is likely that they will merge to such an extent, that calculations of the condensed phase will be performed as routinely as single-molecule calculations today. This is another example which justifies the evolution of the new term 'Computational Chemistry'.

In this first column, we shall explore the historical background leading to this overlap, how we should promote its development in chemical education, and why we predict such a rapid evolution.

In the second column we will discuss the calculation of bulk properties of the fluid phase; what tools do we use, what further research is necessary to make these instruments of practical use.

Finally, in the third column, we will treat the calculation of molecular or nuclear properties in the fluid phase, i.e., solvent effects on a single molecule's properties.

Part I. Historical and Educational Aspects

Historical Background

Three quarters of a century ago, physical chemistry consisted of thermodynamics, kinetics, and electrochemistry. In addition, the foundation of statistical thermodynamics were laid, but only limited possibilities existed to connect microscopic with macroscopic properties, simply, because microscopic properties of molecules were not understood. Similarly, the

microscopic interaction between molecules was only accessible to empirical approaches as theoretical concepts were completely missing. Therefore, the theory of liquids was limited to special idealized cases.

Chemical reactions take place mostly in the liquid phase. If we deal with weak intermolecular interactions, the nuclear movements are mainly classical, but for

stronger interactions a proper description requires quantum mechanics. It is clear, that we cannot expect to describe reactions where bonds are broken and formed, by a purely classical theory. So one had to wait for quantum mechanics in the middle of the twenties to get a step further in the description of chemical reactivity.

Naively, one could have expected that with the arrival of quantum mechanics physical chemists would soon solve the important problems of nuclei moving on potential surfaces, *i.e.* for chemical reactions in both the gas and liquid phase. How wrong! Looking back one notices two important fields evolving and dominating physical chemistry for several decades: spectroscopy on the experimental side and quantum chemistry describing the electronic structure (at fixed nuclear positions!) on the theoretical side. Instead of investigating the movements of nuclei, chemists started to study the movements of electrons! How did they miss their real goal so badly?

Intramolecular as well as intermolecular interactions are evidently due to coulombic interactions of nuclei and electrons. Therefore, one has no chance to understand chemistry before one understands the electronic structure. Although, it is possible to separate the nuclear from the electronic motion in most cases (*Born-Oppenheimer* approximation), in order to obtain the potential surface for the nuclear problem, one has first to solve the electronic problem. Quantum chemistry leads immediately to complicated equations, which could not be solved exactly for real chemical problems. Therefore, it was very important to have experimental spectroscopic data available, to test approximations and fit empirical parameters in the quantum chemical methods. These methods in turn helped to interpret and under-

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stand the spectra more deeply. To be sure, there were very useful spinoffs in terms of analytical methods in the experimental field or accurate methods for calculating properties of single molecules, but we should not be deceived that this is not the real goal of chemistry.

About one quarter of a century ago, quantum chemistry was enriched by methods to efficiently search for minima and saddle points on potential surfaces necessary to study reactions at least in the gas phase. Roughly at the same time, techniques for simulations of thermodynamic ensembles within the framework of classical mechanics emerged and were applied, mainly with empirical intermolecular potentials, to study liquids. Although, the full quantum chemical treatment of liquids and, hence, the correct treatment of reactions in liquids is still not feasible, these two developments brought a wealth of new possibilities within reach. Much work has to be done to exhaust these areas and to further improve the techniques now available. In this and the two following columns we deal with the second of these new fields: the study of liquids by a combination of quantum chemical calculations and classical simulations.

Promotion in Chemical Education

The ability to compute properties of the condensed phase quantitatively also has important impacts on chemical education, because it fills a gap between microscopic and macroscopic world. Many students who decide to study chemistry probably do so in the hope of understanding macroscopic properties of matter. In their studies they are soon confronted with the microscopic behavior of matter and with professors, telling them, that only *via* the microscopic they will understand macroscopic problems. They learn about spectroscopies which provide information on the structure of molecules, the strength of bonds, and the electric currents in rings. After a few years they will forget to ask questions about macroscopic properties, believing that they are part of the microscopic world, breaking bonds with their hands, and their heads buzzing from watching electrons flying about. The professors are happy, because in most cases they are unable to make any connection with the macroscopic world. Perhaps an exaggeration, but is it really far from the truth? It is up to the reader to count the examples where she learnt to connect microcosms with macrocosms quantitatively. I am convinced, that there are not many.

As it becomes feasible to calculate bulk properties of liquids and properties of

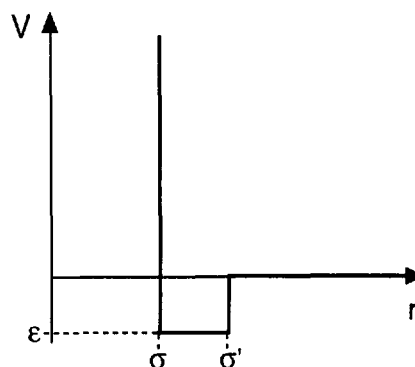
BOX 1

A Potential Obtained from Quantum Chemical Calculations Approximated by a Crude Model

In the boxes we give examples of macroscopic properties, accessible to measurements, obtained from microscopic properties. All examples are based on a potential for argon recently published by *D.E. Woon* (*Chem. Phys. Lett.* **1993**, *204*, 29). Molecular dynamics simulations based on this potential yield quite accurate results for many bulk properties as will be shown in the next column. Here we will use the potential to construct a crude model, which will allow several predictions with simple calculations without using a computer. These examples are better suited to show chemists, who are not specialized in this field, the connections between the microscopic world of quantum chemistry and the macroscopic world they met in the laboratory.

From *Woon's* potential we use the depth $\epsilon = 0.449 mE_h = 1179 \text{ J/mol} = 141.8 \text{ K}$, the equilibrium distance $r_e = 7.134 a_0 = 377.5 \text{ pm}$ and the distance, where the potential is zero, $\sigma = 6.370 a_0 = 337.0 \text{ pm}$. These are pure theoretical data as are the bulk properties obtained from them in molecular dynamics simulations.

To keep calculations simple in this article, we make now the following approximations. The potential is approximated by a square well potential (see *Fig.*) with ϵ and σ taken from *Woon's* potential above. σ' is taken as $\sqrt{2}\sigma$, which might be interpreted just as an arbitrary approximation of the model or rationalized as the distance where the second shell begins in an face-centered cubic lattice (fcc). That argon crystallizes in an fcc lattice could again be shown with an approximative theory by *Max Born* and *Huang Kun* ('*Dynamical Theory of Crystal Lattice*', Clarendon, Oxford, 1954) utilizing the exact shape of the potential.



BOX 2

The Density of Condensed Argon

To calculate the density of crystalline argon, we need from the data in BOX 1 the equilibrium distance r_e and the fact that argon crystallizes in a fcc lattice. If we assume in our model that the potential is zero for the second and higher shell and that we can neglect many-body effects^{a)}, then r_e is also the equilibrium distance in the crystal. The side-length of the fcc cell, containing four argon atoms is $\sqrt{2}r_e$ and, therefore, the cell volume is $\sqrt{2} \cdot 2r_e^3$. With the molecular weight of argon $m = 39.95 \text{ g/mol}$ we obtain the density $d = 4 \cdot 39.95 / (N_A \cdot \sqrt{2} \cdot 2r_e^3) = 1.74 \text{ g/cm}^3$. This compares favorably with the experimental values at 1 bar, which lies between 1.79 g/cm^3 at 1 K and 1.62 g/cm^3 at the melting point (84 K).

If we assume, that due to the disorder in the liquid, the first shell contains only 10 atoms (a result, which could be obtained more accurately in a simulation) compared to 12 atoms in the solid, we obtain a density reduced by $10/12$, *i.e.* 1.45 g/cm^3 . This might be compared with the experimental value of 1.41 g/cm^3 for the liquid at its boiling point (86 K at 1 bar).

^{a)} In this context an atom is called a body. That is if we neglect many-body effects, we assume, that the interaction between particles is a simple sum of pair interactions.

BOX 3

The Heat of Vaporization and the Boiling Point of Argon

The energy needed per atom to separate it from all other argon atoms in our model potential consists just of the number of atoms in the first shell times the interaction energy (neglecting again many-body interactions; the higher shells do not contribute as the potential there is zero, due to the way we have chosen σ). To obtain the energy to separate all atoms of one mol completely, we have to multiply the above energy by the *Avogadro* constant and to divide by two (otherwise the energy would be counted twice, *i.e.*, for each atom of a pair). This energy might be identified as vaporization energy $\Delta_1^{\text{E}}U^*$, if we take the number of atoms in the first shell as above for the liquid as 10. $\Delta_1^{\text{E}}U^* = 10/2 \cdot 1179 \text{ J/mol} = 5895 \text{ J/mol}$. We might compare this in a first approximation with the experimental heat of vaporization (which is usually taken as $\Delta_1^{\text{E}}H^*$) or we can make the following further approximations.

Assuming that the liquid has a negligible volume and the vapor behaves as an ideal gas, we can replace in the relation $\Delta H = \Delta U + P\Delta V$ the latter term by RT , where T is the boiling temperature, *i.e.* $\Delta H = \Delta U + RT$. With $\Delta_1^{\text{E}}S^* = \Delta_1^{\text{E}}H^*/T$ we can replace T yielding $\Delta_1^{\text{E}}H^* = \Delta_1^{\text{E}}U^* + R \cdot \Delta_1^{\text{E}}H^*/\Delta_1^{\text{E}}S^*$, which might be rearranged to $\Delta_1^{\text{E}}H^* = \Delta_1^{\text{E}}U^*/(1 - R/\Delta_1^{\text{E}}S^*)$. Approximating $\Delta_1^{\text{E}}S^*$ with *Trouton's* rule as $85 \text{ JK}^{-1}\text{mol}^{-1}$ yields $\Delta_1^{\text{E}}H^* = 5895/(1 - 8.314/85) \text{ J/mol} = 6534 \text{ J/mol}$ in good agreement with the experimental value of **6506 J/mol**.

Applying once more *Trouton's* rule we obtain a boiling point of $T = \Delta_1^{\text{E}}H^*/\Delta_1^{\text{E}}S^* = 6534/85 \text{ K} = 77 \text{ K}$, which is a little lower than the experimental value of **87 K**. (It should be pointed out, that the empirical relation of *Trouton* is only needed due to the simplifications, we made; in molecular dynamic simulations the above properties could all be obtained from the potential itself.)

BOX 4

The Second Virial Coefficient

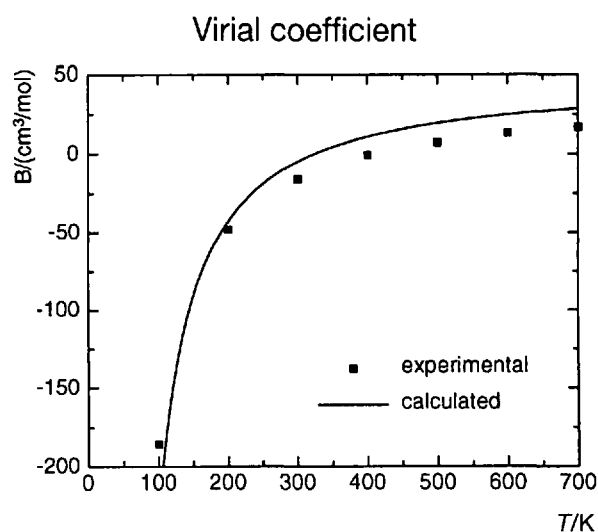
Although not a property of the condensed phase, the second virial coefficient is of interest here as it is a macroscopic property amenable to experiment, which is determined by the microscopic intermolecular interaction. The second virial coefficient is directly related to the potential by the following equation:

$$B = -2\pi N_A \int_0^\infty (e^{-V(r)/kT} - 1)r^2 dr, \text{ where the integral is taken from } r = 0 \text{ to } r = \infty.$$

With our model potential, we can easily calculate this integral:

$$\begin{aligned} B &= -2\pi N_A \cdot \left[\int_0^\sigma (e^{-\infty} - 1)r^2 dr + \int_\sigma^\sigma (e^{e/kT} - 1)r^2 dr + \int_\sigma^\infty (e^0 - 1)r^2 dr \right] \\ &= -2\pi N_A \cdot \left\{ [-r^3/3]_\sigma^\sigma + (e^{e/kT} - 1)[r^3/3]_\sigma^\sigma + 0 \right\} = -2/3\pi N_A \cdot \left\{ -\sigma^3 + \sigma^3 - \sigma^3 + e^{e/kT}(\sigma^3 - \sigma^3) \right\} \\ &= 2/3\pi N_A \cdot \left\{ \sqrt{2} \cdot 2 \cdot \sigma^3 - e^{e/kT}(\sqrt{2} \cdot 2 \cdot \sigma^3 - \sigma^3) \right\} \\ &= 2/3\pi N_A \cdot \sigma^3 \cdot \left\{ \sqrt{2} \cdot 2 - e^{e/kT}(\sqrt{2} \cdot 2 - 1) \right\} \\ &= 2/3\pi N_A \cdot (337 \text{ pm})^3 \cdot \left\{ \sqrt{2} \cdot 2 - e^{141.8 \text{ K}/T}(\sqrt{2} \cdot 2 - 1) \right\} \\ &= 48.27 \cdot (2.828 - 1.828 \cdot e^{141.8 \text{ K}/T}) \text{ cm}^3/\text{mol} \end{aligned}$$

This gives the curve in the following figure in fair agreement with experimental data:



molecules in liquids from microscopic features, it also becomes important to introduce new subjects into the chemical curriculum. This must be done now, as today's students are the chemists of tomorrow. A few simple examples how to connect microscopic with macroscopic properties are given in the *boxes*. A pair potential between two argon atoms obtained from quantum chemical *ab initio* calculations, is used to obtain several macroscopic properties as density, boiling temperature, *etc.* Here we restrict ourselves to examples, which are approximated by simple models to be solved in a few lines with paper and pencil. However, to do more accurate calculations and to obtain other properties like molar heats, viscosities, sound velocities, *etc.* we have to teach the students statistical mechanics. Whereas in the Anglo-Saxon countries statistical mechanics and statistical thermodynamics are important parts of physical chemistry education, in our country education in the field is usually limited to a very rudimentary introduction to statistical thermodynamics. This needs to be changed and in addition at least an introduction to simulation techniques must be given (working with more realistic potentials than the example used in the *boxes*).

At the moment it is often left to the physicists in our universities to deal with statistical mechanics. Usually they have quite different goals from chemists. They often try to improve the theory of liquids in the 'classical' form. This means, they start from simple model potentials and try to find equations in closed forms or at least in form of series expansions *etc.* Then they make improvements by introducing perturbations into their potentials which they can treat again by algebra. To check the quality of their approximated equations, they use simulations with the improved potential. Their simulations are, therefore, computational experiments, used to calibrate their theories. In contrast chemists want to use simulations with potentials which are as exact as possible in order to simulate the experiment, *i.e.* nature.

Outlook

There is no doubt, that understanding fluids is an important step in theoretical chemistry. Not only most reactions, but also most important peripheral techniques like chromatographies take place in fluids. The rapid development of computers in the last decades has opened up new possibilities, undreamt of two decades ago. Presently many parts of the field are still in an experimental phase, but there is little doubt, that many new techniques will be

BOX 5

The Joule-Thomson Coefficient

Related to the second virial coefficient is the *Joule-Thomson* effect in the zero pressure limit. It is in general given by

$$\mu_{JT} = (T \cdot (\partial V / \partial T)_P - V) / C_P$$

In the zero pressure limit we obtain from the virial equation of state

$$\mu_{JT} = (T \cdot (\partial B / \partial T)_P - B) / C_P$$

and inserting C_P for an ideal atomic gas we get

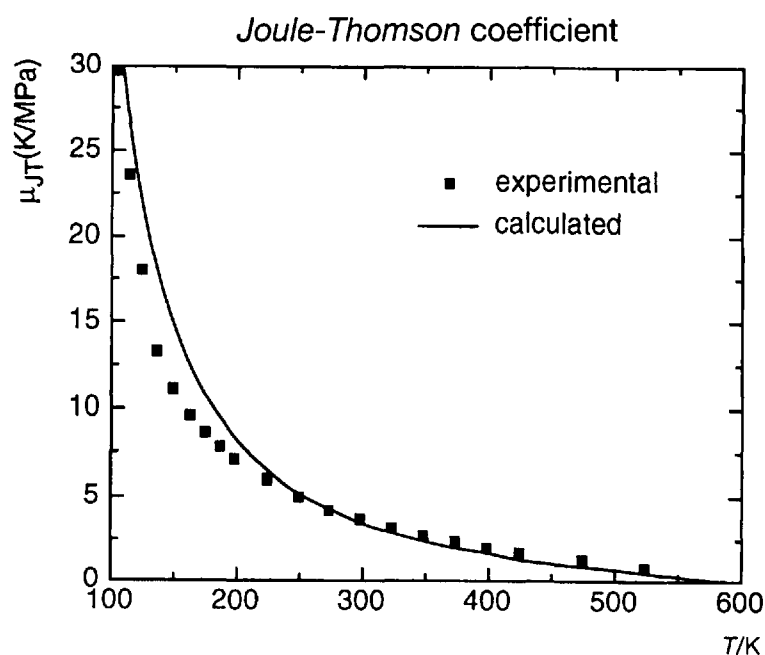
$$\mu_{JT} = \frac{2}{5k} (T \cdot (\partial B / \partial T)_P - B)$$

(We follow here a recent article by *M.P. Hanson* (*J. Chem. Educ.* **1995**, *72*, 315).)

Inserting now $B = \frac{2}{3} \pi N_A \cdot \sigma^3 \cdot \{\sqrt{2} \cdot 2 - e^{e/kT} (\sqrt{2} \cdot 2 - 1)\}$, as obtained above, we obtain

$$\mu_{JT} = 4.244 \cdot \{e^{141.8K/T} \cdot (141.8K + T) / T - 1.547\}$$

This gives the curve in the following figure in fair agreement with experimental data:



transferred to industrial praxis within the next decades. If computer performance continues to improve at the current rate for two more decades, super-computer simulations will arrive at your desk.

You might ask why one should calculate molar heats or solubilities on a computer, if you can just as well measure them. The answer is threefold: economy, ecology, and safety. Experiments require chemicals, technical equipment, and manpower. With costs growing each year, about the only thing getting cheaper is computer power making it the cost effective choice of the future. In addition, computational chemistry will help industry in its efforts to decrease chemical waste. If you need data on dangerous chemicals or at high pressure, it is much safer to do a computer simulation than an experiment. Synthesis and extractions will still take

place in real world and not in the computer, but optimizations of the reaction conditions will more and more be simulated.

This is probably an enthusiastic outlook. Perhaps the train will not be as fast as promised, may be there will be obstacles on the rails. But be sure – if we miss the educational train now, we will not arrive at 'Innovation City'.

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