COMPUTATIONAL CHEMISTRY COLUMN

Column Editors:
Prof. Dr. J. Weber, University of Geneva
Prof. Dr. H. Huber, University of Basel
Dr. H. P. Weber, Sandoz AG, Basel
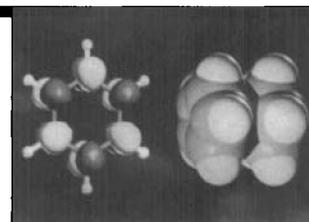
Bulk Properties of Liquids and Molecular Properties in Liquids from a Combination of Quantum Chemical Calculations and Classical Simulations

Hanspeter Huber*, **Elena Ermakova**, **Jan Solca**, and **Gerold Steinebrunner**

In the first Column of this series [1] we presented an introduction to the title subject including a historical background and some educational aspects. Here, we show how to calculate bulk properties of liquids without claiming to be comprehensive. The next Column will end the cycle with an introduction to the calculation of solvent effects on nuclear and molecular properties.

Part II. Bulk Properties

How to calculate them

We are going to describe in this section the 'straightforward' combination of quantum chemical calculations of pair potentials with standard classical simulation methods. The problems which arise and possible solutions will be discussed in the next section.

Fig. 1 displays a pictorial description of the method. First, quantum chemical calculations are performed for two particles (atoms or molecules) in many relative configurations yielding points on the intermolecular potential surface. For rare gases, where the only variable is the distance between atoms, about ten points are enough to give an accurate description of the potential curve. It is easy to find an analytical

ansatz, *i.e.* a parametrised potential which fits these points very accurately. For molecules, however, the intermolecular potential is in general six-dimensional. In addition, there are intramolecular degrees of freedom. The usual assumption is that intra- and intermolecular degrees of freedom are only weakly coupled and, therefore, can be treated independently. Intramolecular degrees can then be calculated easily in a harmonic approximation. To obtain the highly anharmonic six-dimensional intermolecular potential, typically from 50 up to more than thousand quantum chemical calculations (see, *e.g.*, the HF–HF potential surface by *Bunker et al.* [2]) are performed. The latter means quite an effort, but compared to the 10 points in the one-dimensional case (corresponding to 10^6 points in the general six-dimensional case), it is still a wide mesh. The quantum chemical calculations have not only to be performed with very large basis sets, but correlation has to be included at a high level, as dispersion energy is normally a significant part of the intermolecular in-

teraction. In addition, the so-called basis set superposition error (for a recent review see *van Duijneveldt et al.* [3]) has to be corrected for, which prohibits the use of gradient methods. Altogether, the expense of computer time is large enough that only the most simple molecules (and, hence, liquids) can be handled by this approach at the moment.

After one takes care of all the above details and obtains a large enough number of accurate points on the potential surface, they have to be fitted to an analytical ansatz. This is straightforward in the case of rare gases, but leads to severe problems for the multidimensional case (see below). The high accuracy of the quantum chemical calculations may be easily wasted here, if no adequate analytical form is found.

The analytical potential is then used in a Monte Carlo or molecular dynamics simulation program [4]. We restrict the discussion to the latter one and to a microcanonical ensemble (constant number of particles, volume and energy). The simulation program integrates the *Newton*ian equations of motion of the particles (typically a few hundred) numerically. The continuous time variable is divided into small finite time steps, typically of the order of 10^{-15} s. In each time step the total forces on all particles are calculated. For a specific particle it is obtained usually under the assumption that it is approximately equal to the sum of forces (*i.e.* the derivatives of the potential) between pairs, hence a loop over all other particles has to sum the forces between those and the specific particle. The consequence of neglecting many-body interactions will be discussed below. *Newton*'s law leads from the forces to the accelerations of the particles and hence the change of the velocities at this time step. The new velocities in turn lead to a change of the positions of the particles and to the begin of the next time step. At each time step we have the full information about the system, that is coordinates, velocities, and forces for all particles. If we like, we can store them on disk for later evaluation or we can immediately process them into a few accumulated values needed for a further statistical evaluation.

Correspondence: Prof. Dr. H. Huber
Institut für Physikalische Chemie
der Universität Basel
Klingelbergstrasse 80
CH–4056 Basel

Finally, we have to evaluate the physical properties of the liquid. First a few thousand steps are disregarded until the system has reached equilibrium. Then the 'mill of statistical mechanics' starts to grind the raw data. From your physical chemistry courses you might remember an equation, which connects classical mechanics with thermodynamics: $^3/_2 kT = ^1/_2 mv^2$, where k is the *Boltzmann* constant. Knowing the mass m and the velocities v of all particles, we can immediately calculate an instantaneous temperature T or, over a longer time period, obtain the average temperature of the system in equilibrium. Similarly, there are other equations from statistical mechanics, mostly unknown to us due to a lack of education in this field, which yield all kind of interesting properties. To give just one further example, the molar heat capacity $C_{V,m}$ is obtained from the fluctuation of the kinetic energy $<\delta E^2_{kin}>$ (again accessible by time averaging) by the equation

$$C_{V,m} = {}^3/_2 R \cdot (1 - {}^2/_3 N < \delta E^2_{kin} > / (R<T>)^2)^{-1}$$

where R is the ideal gas constant, N the number of particles, and $<T>$ the time averaged temperature.

Now that a procedure to obtain bulk properties of liquids from quantum chemically calculated potentials applied in molecular simulations has been described, we should point out a few problems of this approach before discussing some of the results.

Problems

As the above method consists of three independent steps, the quantum chemical calculation, the fit of an analytical potential surface, and the molecular dynamics simulation, the problems are best discussed separately.

The results discussed below are obtained by quantum chemical calculations of the *ab initio* type. There are good reasons for this. The usual semiempirical methods like MNDO, AM1, *etc.* are not suitable for intermolecular calculations as they have been parametrised for intramolecular properties, utilise no diffuse basis orbitals and in general do not include correlation accurately enough to take care of the dispersion energy. The latter might not be of much importance for strongly hydrogen bonded systems as H_2O, but is significant in most other cases. Density functional theory might be applied, but a recent investigation of the quality of present functionals by *Pérez-Jordá* and *Becke* [5]
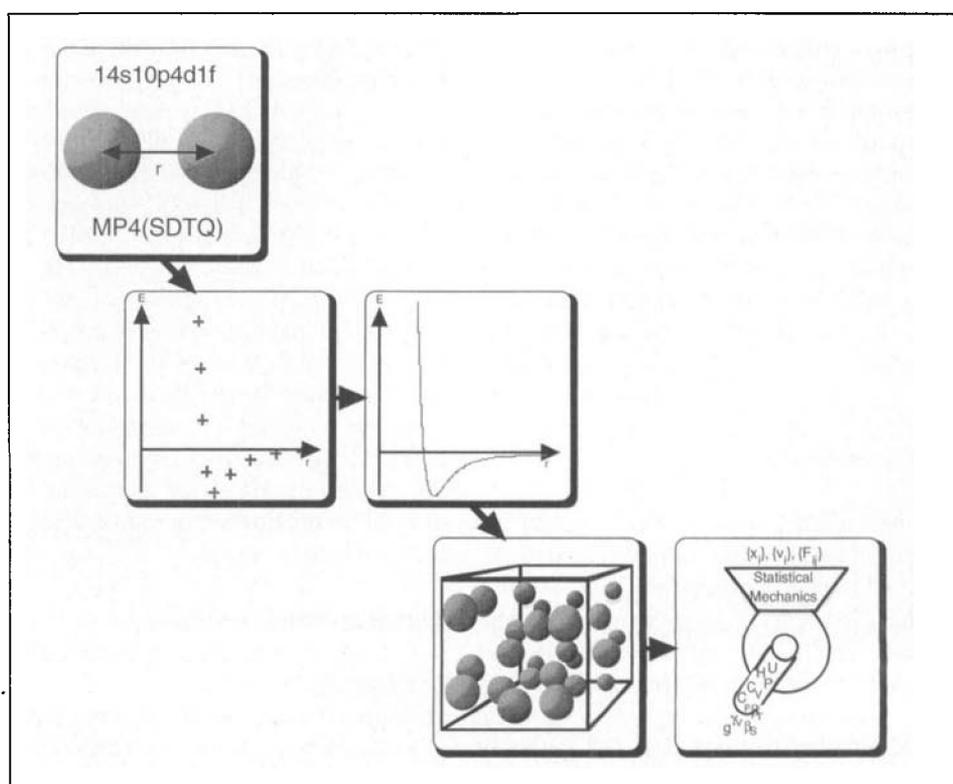
Fig. 1. *Graphical representation of the method discussed.* Quantum chemically calculated potentials are fitted to an analytical ansatz and used in classical molecular dynamics simulations.

for rare gas interactions showed rather poor results for such properties. Therefore, only hundreds or thousands of very sophisticated *ab initio* calculations can yield potential surfaces of adequate quality. The only exception are rare gases, where ten calculations might suffice; on the other hand, the accuracy has to be even higher due to the small interaction energy. A problem is that the interaction energies are obtained as the difference of the energy of the supersystem and the two subsystems. In the case of Ne this difference shows up at the seventh significant digit of the absolute energies! (This corresponds to the measurement of the weight of a chocolate by weighing an airbus with and without the chocolate and taking the difference.)

For molecules it is generally not easy to find an analytical form of the parametrised potential simple enough so as to avoid introducing artifacts and to be used reliably in the simulations, while allowing a fit of good quality. There exists an infinite number of analytical forms, which one could try, but the chance to hit a good one is quite small, even if one uses 'physical knowledge' in its selection. *Suhm* [6] suggested to circumvent this problem using a discrete potential representation, in particular a *Voronoï* step representation. He applied the scheme in a Monte Carlo type calculation for fully anharmonic vibrational ground states, but it has not yet been extended to molecular dynamics sim-

ulations. *Collins* and coworkers [7][8] suggest a moving interpolation technique utilising the energies, gradients, and second derivatives of *ab initio* calculations. Recently, *Blank et al.* [9] trained a neural network with a set of points on a potential surface to predict interpolated forces in the simulation.

In molecular dynamics simulations, the errors due to a finite time step, a limited number of particles, *etc.*, which often are called technical errors, can be reduced using a suitable choice of parameters so as to become negligible. However, there remain two more fundamental error sources, the neglect of many-body interactions and, at low temperatures, of quantum effects. The latter are of no importance at room temperature, where most chemistry of interest takes place, and we will not discuss them further. Many-body interactions, however, are not negligible and the knowledge about their influence on different properties of interest is still very limited. Although some investigations of their influence in molecular liquids have been published, only partial results are available for rare gases as deduced from work with empirical [10] and *ab initio* potentials [11]. Many-body interactions could probably be included to a large extent by calculating a three-body potential and including it in the simulations, but this would lead to a significant increase in computer time. Some authors partially introduce this interaction by using polarisable potentials.

A method avoiding the pair-additivity approximation would obviously be the *Car-Parrinello* model [12]. However, such calculations involving a large enough number of particles to obtain bulk properties of liquids are not yet feasible. If the approach of *Lustig* [13–15], which allows one to obtain thermodynamic properties from simulations with relatively small numbers of particles, could be implemented in the *Car-Parrinello* method, the situation could change.

State-of-the-art

We will discuss now some results from the literature for structural, thermodynamic, and transport properties. Note that this is not intended to be a review, but we will mainly discuss two extreme cases, H_2O as a hydrogen bonded and Ar as an extremely unpolar system. These cases will show the accuracy one can obtain today for small systems. Only examples, where the potential was obtained from quantum chemical calculations (with no partial fit to experiment) are included.

Structure of Liquids

The structure of a liquid is usually described using pair distribution functions. *Fig. 2* shows experimental and calculated radial pair distribution functions for liquid Ar at 85 K. The simulations take care of quantum effects by applying *Wigner-Kirkwood* (WK) quantum effective potentials. The potential was obtained from high level *ab initio* calculations including electron correlation [16]. It was shown that an improvement of the pair potential would hardly influence the pair distribution function. The figure displays not only a quantitative agreement between experimental and quantitative curves, but confirms indirectly, that many-body effects on the pair distribution function of liquid Ar are negligible [17].
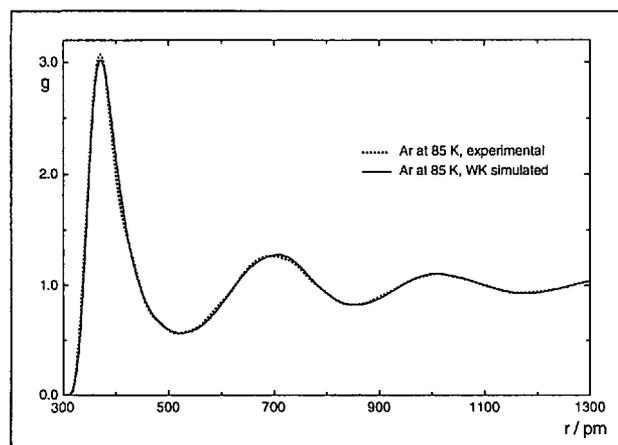
For H_2O, a molecular liquid, the structure might be described by three pair distribution functions, the g_{OO}, the g_{OH}, and the g_{HH} function. In *Fig. 3* the experimental curves by Soper et al. [18][19] are compared with curves obtained from a simulation using a flexible and polarisable *ab initio* potential (NCC (vib)) [20] and an older *ab initio* potential (MCYL) [21]. Although the agreement between experiment and simulation is not as perfect as for Ar, there exists a qualitative agreement and the shell radii are simulated pretty accurately. It should be pointed out that part of the disagreement might be due to the experimental curve, as it is difficult to obtain the separate g functions for a molecular liquid.

Thermodynamic Properties

The most difficult property to obtain from simulations of liquids is probably the pressure. Together with the internal energy and related properties like the enthalpy it is strongly influenced not only by imperfect pair potentials, but also by many-body interactions. In addition, the pressure of a liquid depends to a large extent on density, hence small errors in density lead to large errors in pressure. Fortunately, many thermodynamic properties like molar heats, compressibilities, *etc.* are derivatives of the above properties and it turns out that in this case the errors cancel partially.

Corongiu [20] calculated with the NCC (vib) potential for H_2O at standard conditions (or more accurately at a density of 0.997 g/cm^3 and a temperature of 305.5 K) a pressure of –2150 atm instead of the expected +1 atm. For liquid Ar at 145 K, where quantum effects are expected to be small, at a density of 0.890 g/cm^3 the experimental pressure is 44.5 atm and the calculated one 125 atm. This is not a satisfactory result, but at least it displays the right sign and order of magnitude. Although a better potential might give

some improvement, it was shown that a correct result could only be obtained by inclusion of many-body effects. Better results for Ar were obtained over a wide range of states in the supercritical phase at higher temperatures, where the pressure was usually in error by less than 15%.

Corongiu compares an estimated vaporisation energy of –41.4 kJ/mol from the calculation with an experimental value of –41.8 kJ/mol. No other energetic or derived properties were published for H_2O to our knowledge. *Ermakova et al.* [11] obtained for liquid and supercritical Ar at temperatures between 95 and 600 K and pressures between 2 and 1000 MPa an internal energy with an accuracy between 0.2 and 0.8 kJ/mol.

For CH_4, *Gay et al.* [22] obtained virial coefficients within 3% of the experimental values between 110 and 623 K. From a Monte Carlo simulation they deduced for one state point an excess internal energy of –7.30 kJ/mol compared to an experimental value of –7.12 kJ/mol, but did not calculate any derived properties.

Böhm and *Ahlrichs* [23] published a decade ago a few data for N_2 obtained from a pure *ab initio* potential. At a temperature of 77 K and a density of 0.808 g/cm^3 they obtained an internal energy of –4.20 kJ/mol (experimental –4.94 kJ/mol) and a compression factor of 5.1 (experimental $\approx$ 0). They could improve their results significantly, when they fitted the attractive dispersion to experimental values. This is indeed a procedure adopted by many groups since then, which, however, leads to an immediate loss of the *ab initio* character of the work and no longer allows to draw conclusions, *e.g.*, about the influence of many-body interactions.

As mentioned above we might expect a higher accuracy for properties which are derivatives of pressure and energy. But we cannot expect to obtain reasonable values if the equation of state is off by several orders of magnitude. For liquid Ar at 130 K and 4.5 MPa, calculated molar heats $C_{V,m}$ of 18.2 J mol^{-1} K^{-1} and $C_{p,m}$ of 58.1 J mol^{-1} K^{-1} correspond to experimental values of 17.8 J mol^{-1} K^{-1} and 56.3 J mol^{-1} K^{-1}, respectively. A calculated sound velocity of 564 m/s compares with an experimental value of 536 m/s at the same conditions. There are no experimental compressibilities β and pressure factors γ available for liquid Ar. For a supercritical state at a high density (1.766 g/cm^3, corresponding to an experimental pressure of 1000 MPa; 300 K) calculated values of $\beta_S = 0.15$ GPa^{-1}, $\beta_T = 0.21$ GPa^{-1}, and $\gamma_V = 2.47$ MPa K^{-1}, compare with experimental values of $\beta_S = 0.16$ GPa^{-1}, $\beta_T =$

Fig. 2. *Radial pair distribution function of liquid Ar at 85 K.* The experimental curve shows a nearly perfect agreement with the one obtained from the simulation with the *Wigner-Kirkwood* quantum effective potential.

0.22 GPa⁻¹, and γ_V = 2.50 MPa K⁻¹. Hence a reasonable accuracy is obtained for these derived properties. Similar results were reported over a wide pressure and temperature range.

Transport Properties

Transport properties depend mainly on the repulsive part of the potential. It is well known, that the repulsive part is obtained quite accurately even with *ab initio* SCF calculations. Therefore, one might expect quite accurate transport properties, provided many-body and quantum effects are of minor importance. For liquid Ar this seems to be the case (recently, it was suggested to use *ab initio* calculated transport properties for dilute He gas to calibrate experimental devices [24]). At the state point at 130 K and 4.5 MPa of Ar a calculated thermal conductivity of 72 mW m⁻¹ K⁻¹ corresponds to experimental values of 72 mW m⁻¹ K⁻¹ and 76 mW m⁻¹ K⁻¹, respectively, whereas a calculated viscosity of 99 μPa s may be compared with experimental values of 91 μPa s and 94 μPa s. *Corongiu* calculated for H₂O self-diffusion coefficients of 2.4 · 10⁻⁵ cm²/s and 2.5 · 10⁻⁵ cm²/s for O and H, respectively. This is in good agreement with an experimental value of 2.4 · 10⁻⁵ cm²/s.

Therefore, we may conclude that with the calculations feasible today, we are approaching quantitative results of bulk properties of fluids for small systems. But it may still need one or more decades for improvements in the quality and for extensions to larger systems.

Fig.3. g_{OO}, g_{OH}, and g_{HH} radial pair distribution functions of liquid H₂O from experiment and from simulations using two different *ab initio* potentials [20]

[1] H. Huber, *Chimia* **1995**, *49*, 404.
[2] P.R. Bunker, P. Jensen, A. Karpfen, M. Kofranek, H. Lischka, *J. Chem. Phys.* **1990**, *92*, 7432.
[3] F.B. van Duijneveldt, J.G.C.M. van Duijneveldt – van de Rijdt, J.H. van Lenthe, *Chem. Rev.* **1994**, *94*, 1873.
[4] M.P. Allen, D.J. Tildesley 'Computer Simulation of Liquids', Clarendon Press, Oxford, 1987.
[5] J.M. Pérez-Jordá, A.D. Becke, *Chem. Phys. Lett.* **1995**, *233*, 134.
[6] M.A. Suhm, *Chem. Phys. Lett.* **1993**, *214*, 373.
[7] J. Ischtwan, M.A. Collins, *J. Chem. Phys.* **1994**, *100*, 8080.
[8] M.J.T. Jordan, K.C. Thompson, M.A. Collins, *J. Chem. Phys.* **1995**, *102*, 5647.
[9] T.B. Blank, S.D. Brown, A.W. Calhoun, D.J. Doren, *J. Chem. Phys.* **1995**, *103*, 4129.
[10] J.A. Barker, *NATO ASI Ser., Ser. B* **1989**, *186*, 341.
[11] E. Ermakova, J. Solca, H. Huber, M. Welker, *J. Chem. Phys.* **1995**, *102*, 4942.
[12] G. Galli, A. Selloni, R. Car, *Chimia* **1993**, *47*, 313.
[13] F. Lustig, *J. Chem. Phys.* **1994**, *100*, 3048.
[14] F. Lustig, *J. Chem. Phys.* **1994**, *100*, 3060.
[15] F. Lustig, *J. Chem. Phys.* **1994**, *100*, 3068.
[16] D.E. Woon, *Chem. Phys. Lett.* **1993**, *204*, 29.
[17] E. Ermakova, J. Solca, H. Huber, D. Marx, *Chem. Phys. Lett.*, in press.
[18] A.K. Soper, R.N. Silver, *Phys. Rev. Lett.* **1982**, *49*, 471.
[19] A.K. Soper, M.G. Phillips, *Chem. Phys.* **1986**, *107*, 47.
[20] G. Corongiu, *Int. J. Quantum Chem.* **1992**, *42*, 1209.
[21] G.C. Lie, E. Clementi, *Phys. Rev. A* **1986**, *33*, 2679.
[22] D.H. Gay, H. Dai, D.R. Beck, *J. Chem. Phys.* **1991**, *95*, 9106.
[23] H.-J. Böhm, R. Ahlrichs, *Mol. Phys.* **1985**, *55*, 1159.
[24] R.A. Aziz, A.R. Janzen, M.R. Moldover, *Phys. Rev. Lett.* **1995**, *74*, 1586.

Announcement

The Group of Swiss Computational Chemists (GSCC) presents information about its activities on the 'World Wide Web' under the following address:

http://www.unil.ch/gscc/