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Christian Spickermann

Entropies of Condensed Phases and Complex Systems

A First Principles Approach

Doctoral Thesis accepted by
Wilhelm-Ostwald-Institute of
Physical and Theoretical Chemistry,
University of Leipzig, Germany

 Springer

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Supervisor's Foreword

Theoretical investigation of complicated systems should include the treatment of the condensed phase, because it is mainly the liquid state in which most chemical processes occur. Traditional methods usually applied to study chemical phenomena encompass molecular dynamics (MD) simulations based on force fields as well as static quantum chemical (QC) methods. While both these methods have matured to become powerful tools over several decades, they almost complementarily share advantages and disadvantages. MD is good in allowing for large samples of molecules as well as long simulation times to be treated, while QC provides an excellent insight into the electronic structure of molecules as well as into their intermolecular forces. The disadvantages are clear; whereas MD neglects cooperativity and nuclear quantum effects, QC treats isolated molecules at zero temperature. Alternatives to these methods are given by ab initio molecular dynamics (AIMD) simulations and the quantum cluster equilibrium (QCE) method which was developed by Frank Weinhold [Weinhold, F. J. Chem. Phys. 1998, 109, 367]. As a combination of quantum chemistry with simulations, ab initio molecular dynamics simulations have the advantage to describe spontaneous events and important intermolecular forces as cooperativity. However, simple electronic structure methods have to be applied in AIMD and due to that AIMD is only able to perform in a range of quality prescribed by the electronic structure method which is combined with it. That only middle-sized ensembles can be calculated together with the short simulation times is the downside of a method which on the other hand allows one to obtain the electronic structure on the fly. The quantum cluster equilibrium method treats many clusters in a mean field approach and via the rigid rotor harmonic oscillator (RRHO) model allows one to derive partition functions for different phase points from high level ab initio QC (Kirchner, B. J. Chem. Phys. 2005, 123, 204116). With the partition function, the simple QCE method opens the access to thermodynamic quantities for a wide range of temperatures and pressures. Whereas cooperativity and nuclear quantum effects can be accounted for, there is no dynamics in the method and all the approximations made within the RRHO model might worsen the results. Thus, it becomes apparent that for the study of the microscopic details of complex chemical processes in large

systems and in condensed phase, i.e. under conditions that closely resemble laboratory conditions, more accurate methods and at the same time faster methods are needed. An all-encompassing picture can be obtained only by scale-transferring concepts.

Theoretical investigation of complicated systems should also involve the calculation of quantities which can be compared to experimental findings. In seven chapters Christian Spickermann's thesis deals with the calculation of thermodynamic quantities in general and with entropy calculations especially. The manipulation of equations in order to arrive at the right form to be implemented in our computer programs (http://www.uni-leipzig.de/~quant/qce/pm_en.html) was one of the major goals of Christian Spickermann's thesis, next to the derivation of correction terms for the widely used equations to calculate thermodynamic quantities. Thereby important rules for the calculation of condensed phase thermodynamics from quantum chemistry have been established. However, the main reason for recommending his thesis for publication in this series is that Spickermann builds up the knowledge of theoretical possibilities from simple models to more complicated tools such as the QCE method in the most systematic and thus didactically effective way, from the treatment of isolated molecules to the one of the condensed phase. After a brief introduction, Spickermann explains each method from basics and discusses the approximations together with their advantages and disadvantages in order to allow the readers to derive their own conclusions. He carefully guides us through the methods and thereby makes it possible to gain from his experience which methods should be applied in which situation. This is followed by some case studies employing the simple RRHO model and the helpful discussion of the problems involved by using the example of the pseudorotaxane system as synthesized by Vögtle and Hunter [Hunter, C.A. J. Am. Chem. Soc. 1992, 114, 5303; Schalley et al. Acc. Chem. Res. 2001, 34, 465]. In the spirit of microsolvation, Christian Spickermann shows that simple but elegant concepts like describing a different kind of reaction (exchange with one solvent molecule instead of the basic association reaction) already leads to large improvements of the accuracy of calculated thermodynamic quantities. In two further chapters he offers insight into the outcome of QCE calculations based on different levels of quantum chemical accuracy and based on different levels of intercluster interaction. The associated liquids subject to his investigations are water and hydrogen fluoride, both complicated substances forming hydrogen bonds. He discusses cooperativity and its neglect as inherent in the pairwise additivity approximation of traditional molecular dynamics simulations. He shows that the thermodynamics of phase transitions is controlled by the stability of the clusters which rely on the accuracy of the chosen quantum chemical calculation. Error compensation as given by density functional theory in the standard formulation which is widely used in AIMD plays the same role in the liquid phase as in the gas phase. The influence of basis sets is analyzed. However, next to these important technical details, the choice of clusters plays a very important role. Distinct structural motives within the clusters are necessary in order to provide the best theoretically derived liquid phase. Given that these ingredients are chosen

correctly, the QCE method is able to provide densities within chemical accuracy. It is also a large improvement over the simple RRHO model. Entropies can be calculated within 10 J/(mol K) and the transition entropies deviate less than 10% from the experimental values. Therefore, the present book does not only document a successful thesis, but should, in addition to this, serve as a demonstration of how systematic improvement of the calculated thermodynamics is possible when using highly accurate quantum chemical data and applying models and methods ranging from the RRHO model to the QCE method without and with intercluster interaction. Critical discussion of the results here accompanies the data evaluation so that calculation of condensed phase thermodynamics is conducted based on the first-principles idea of quantum chemistry. The benefits from this ansatz are clear: If we know which approximation and improvement leads to which particular result, we learn more about the nature of these chemical systems.

Leipzig, September 2010

Barbara Kirchner

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Bochum, September 2010

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List of Abbreviations and Symbols

aug-cc-pVTZ	Dunning's augmented, correlation-consistent valence triple- ζ basis set with polarization functions
aug-cc-pVQZ	Dunning's augmented, correlation-consistent valence quadruple- ζ basis set with polarization functions
BP	Density functional
B3LYP	Becke's three parameter hybrid functional
cbs	Complete basis set limit
CCSD	Coupled cluster including single and double excitations
CCSD(T)	CCSD with perturbative treatment of triple excitations
cp	Counterpoise correction
dft	(Kohn-Sham) density functional theory
fep	Free energy perturbation
fpmD	First principles molecular dynamics
fvci	Full vibrational configuration interaction
md	Molecular dynamics
MP2	Second order Møller-Plesset perturbation theory
fpmD	First principles molecular dynamics
NPA	Natural population analysis
PBE	Density functional
qce	Quantum cluster equilibrium
QZVP	Ahlrichs quadruple- ζ basis set
rrho	Rigid rotor harmonic oscillator
scf	Self-consistent field
SEN	Shared electron number
TZVP	Ahlrichs triple- ζ basis set
TZVPP	Ahlrichs triple- ζ basis set with extra polarization functions
E	Energy of N -particle system
ϵ	Energy of single particle
h	Planck constant
\hbar	Reduced Planck constant

\mathcal{H}	Hamilton function
\hat{H}	N -particle Hamilton operator
\hat{h}	Single particle (molecular) Hamilton operator
i_j	Number of monomers in cluster j
k_B	Boltzmann's constant
\mathcal{K}	Kinetic energy function
\hat{K}	Kinetic energy operator
λ	Wavelength
m	Mass of particle or nuclei
N_A	Avogadro constant
n_j	Number of monomers in cluster j
ρ_n	Number density
∇	Nabla operator
p	Pressure
P	Probability
\mathbf{p}	Momentum vector for N -particle system
Q	N -particle partition function
q	Single particle (molecular) partition function
\mathbf{q}	Coordinate vector for N -particle system
R	Gas constant
S	Entropy
T	Absolute temperature
t	Time
U	Interaction potential
V	Volume
W	Work