„Quantenmechanische Berechnung der Dispersionsenergie in Fluiden Systemen und Anwendung in Zustandsgleichungen“

“Quantum Mechanical Computation of the Dispersion Energy in Fluid Systems and Application in Equations of State”

Von der Fakultät für Maschinenwesen der Rheinisch-Westfälischen Technischen Hochschule Aachen zur Erlangung des akademischen Grades eines Doktors der Ingenieurwissenschaften genehmigte Dissertation

vorgelegt von

Mahendra Singh

Berichter: Prof. Dr.-Ing. Klaus Lucas
Prof. Dr. Ulrich K. Deiters

Tag der mündlichen Prüfung: 23. Juli 2009

Berichte aus der Thermodynamik

Mahendra Singh

Quantenmechanische Berechnung der Dispersionsenergie in Fluiden Systemen und Anwendung in Zustandsgleichungen

Quantum Mechanical Computation of the Dispersion Energy in Fluid Systems and Application in Equations of State

Shaker Verlag
Aachen 2010

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at http://dnb.d-nb.de.

Zugl.: D 82 (Diss. RWTH Aachen University, 2009)

Copyright Shaker Verlag 2010
All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior permission of the publishers.

Printed in Germany.

ISBN 978-3-8322-9096-2
ISSN 0946-0829

Shaker Verlag GmbH • P.O. BOX 101818 • D-52018 Aachen
Phone: 0049/2407/9596-0 • Telefax: 0049/2407/9596-9
Internet: www.shaker.de • e-mail: info@shaker.de

Acknowledgments

This manuscript would have not been completed without the help of many people. I would like to express my sincere gratitude to the following persons for their contributions toward this thesis.

Firstly, I would like to thank my supervisor, Univ. Prof. Klaus Lucas, Chair of Technical Thermodynamics, RWTH Aachen, for giving me the opportunity to undertake this task. I am greatly indebted to him, whose expert knowledge in molecular thermodynamics provided the necessary depth for consistent timely input through the entire candidature. He was extremely patient with me as I struggled to understand some difficult theories about this research. Professor Lucas has also patiently read, corrected and given useful comments to the thesis. His guidance and encouragement have been the most generous and precious.

My special thanks are expressed to Dr. rer. nat. Kai Leonhard, Head of Molecular Thermodynamics group at Institute for Technical Thermodynamics, RWTH Aachen, to guide me very professionally through the project, given me room to do it my way, but always supported me. I owe great thanks to him for simulating me intellectually, and all the time and effort he has put on my PhD thesis. I doubt that I will ever be able to convey my appreciation fully, but I owe him my eternal gratitude.

I acknowledge kindness of Dr. rer. nat. Kai Leonhard and Dr. rer. nat. Van Nhu Nguyen and their permission to include original work from their publication in this thesis [1].

I would like to thank Prof. Ulrich Deiters for his thorough and very detailed proofreading of this thesis. I appreciate all his comments and suggestions.

Many thanks to Dipl.-Phys. Stefan Korden for providing useful suggestions and comments to improve the final thesis.

To my new friends in Germany: Mangesh Agarwal, Jaswinder Singh, Satish Patil, Sarvpreet Singh, Pankaj Bhatia, Irfan Patel, thank you for the good time, your support and encouragement, and for helping to make my stay in Germany more home-like.

I would like to extend my sincere thanks to Dipl.-Ing. Frank Henrich and Dr.-Ing. Ralf Giesen for providing initial indispensable values on the professional front.

Last, but not least, I reserve my deepest gratitude to my family for their constant source of love, support and encouragement during the entire candidature.

Declaration

I hereby declare that the thesis, entitled "Quantum Mechanical Computation of the Dispersion Energy in Fluid Systems and Application in Equations of State" submitted in fulfillment of the requirements for the degree of Doctor of Philosophy at the Institute for Technical Thermodynamics, RWTH Aachen, is my own work and that it contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text of the thesis. To the best of my knowledge and belief, it contains no material previously published or written by another person except where due reference is made in the text of the thesis.

Mahendra Singh
Aachen
7th April 2010

Abstract

Thermodynamic properties are the main requirements of phase equilibrium calculations for process development in the chemical industry. These properties can be obtained either from expensive experiments or by using a predictive thermodynamic model. One such model is the PCP-SAFT equation of state (EOS). This EOS is based on a theoretical foundation that describes it's parameters as a measure of the molecular interactions both for pure components and fluid mixtures. For mixtures, it requires combination rules that are necessary to determine the unlike-pair interaction parameters. These combination rules are often of empirical origin and therefore require at least one adjustable binary parameter that is usually incorporated into the dispersion parameter combination rule. The model is then no more predictive. In this study, it is shown how such EOS models can be made predictive by using a quantum mechanically derived dispersion combination rule. This rule uses static and dynamic polarizabilities and is based on well defined approximations for the dispersion interaction.

Quantum chemical calculations are performed to determine static as well as dynamic polarizabilities and further to calculate the dispersion coefficients for a set of molecules used in equation of state applications. The effect of the basis sets and quantum chemical levels on the accuracy of the computed properties is thus studied. The main focus is to find methods that provide a reasonable compromise between accuracy and efforts for medium sized molecules which are typical for equation of state applications. Various different methods used to calculate the dispersion coefficients are compared. Finally, the accuracy of a recent extrapolation method by Cybulski and Haley is assessed for the dispersion coefficient in combination with medium sized basis sets to make it applicable for the targeted molecules. This approach is also applied to compute the deviation of the unlike dispersion-interaction coefficient from the geometric mean combination rule which we call "dispersion non-ideality". It is found that due to cancellations of errors, the accuracy of the "dispersion non-ideality" is much higher than the calculation of absolute dispersion coefficients.

The predictive performance of the PCP-SAFT EOS with quantum mechanically determined pure compound properties (multipole moments and polarizability) along with the newly derived combination rule is checked by calculating phase equilibrium behavior. Further, the predictive performance of four methods: a slightly modified PCP-SAFT (PC-SAFTP2), VTPR4P-CRS, PSRK and COSMO-RS, is also checked by calculating Henry's constant.

Copyright © 2008 Mahendra Singh

Zusammenfassung

Thermodynamische Eigenschaften sind die entscheidenden Eingangsgröße in der Phasengleichgewichtsthermodynamik die für die Prozessentwicklung in der chemischen Industrie bedeutsam ist. Diese Eigenschaften können entweder durch kostspielige Experimente oder durch Nutzung eines prädiktiven thermodynamischen Modells erhalten werden. Ein solches Modell ist die PCP-SAFT Zustandsgleichung, die auf einer theoretischen Grundlage basiert, deren Parameter ein Maß der molekularen Interaktionen für Reinstoffe und flüssige Mischungen bilden. Für Mischungen sind Kombinationsregeln erforderlich, um die binären Interaktionsparameter festzulegen. Diese Kombinationsregeln haben häufig einen empirischen Ursprung und erfordern folglich mindestens einen anpassbaren binären Parameter, der normalerweise in die Dispersionsparameter-Kombinationsregel einfließt. Das Modell ist dann nicht prädiktiv. In dieser Studie wird gezeigt, wie solche Zustandsgleichungsmodelle prädiktiv gemacht werden können, indem man eine quantenmechanisch abgeleitete Dispersions-Kombinationsregel verwendet, die statische und dynamische Polarisierbarkeiten nutzt und auf genau definierten Näherungen für die Dispersionsinteraktion basiert.

Es werden quantenchemische Berechnungen durchgeführt, um die statischen sowie dynamischen Polarisierbarkeiten und die Dispersions-Koeffizienten für eine Reihe von Molekülen zu berechnen, die in der Zustandsgleichung benutzt werden. Die Effekte des gewählten Basissatzes und des quantenmechanischen Modells auf die Genauigkeit der berechneten Eigenschaften werden studiert. Der Hauptfokus soll dabei auf dem Auffinden von Methoden liegen, die einen angemessenen Kompromiss zwischen Genauigkeit und Aufwand für mittelgrosse Moleküle zur Verfügung stellen, die für die Zustandsgleichung-Anwendungen typisch sind. Unterschiedliche Methoden zur Berechnung der Dispersionskoeffizienten werden verglichen. Anschließend wird die Genauigkeit einer neuen Extrapolationmethode von Cybulski und Haley für den Dispersionskoeffizienten für mittelgroße quantenmechanische Basissätzen ermittelt und diese Methode auf die hier interessierenden Moleküle angewendet. Die gleiche Näherung wird auch angewendet, um die Abweichung des Dispersionskoeffizienten der Gemische von der ansonsten gebrauchten Kombinationsregel, die wir „Dispersions–Nicht-Idealität“ nennen, zu berechnen. Dabei wird beobachtet, dass wegen der gegenseitigen Aufhebung von Fehlern, die Genauigkeit der „Dispersion–Nicht-Idealität“ viel höher als die des berechneten absoluten Dispersionskoeffizienten ist.

Die Vorhersagen, basierend auf quantenmechanischen Berechnungen von Reinstoffeigenschaften zusammen mit der neuen Kombinationsregel, stellen eine bedeutende Verbesserung der ursprünglichen PCP-SAFT Kombinationsregel dar. Anschließend wurde die Güte der Vorhersage von Henry-Konstanten von vier Methoden, eine leicht modifizierte PCP-SAFT (PC-SAFTP2), VTPR4P-CRS, PSRK und COSMO-RS, überprüft. Die PSRK-Methode liefert die besten Ergebnisse im Vergleich zu allen anderen Methoden. Aber, diese Methode benötigt Gruppe-Interaktion parameter die nicht für alle Systeme verfügbar sind. In diesem fällen, ist die PC-SAFTP2 Methode wird für die Berechnung der Henry-Konstante zu bevorzugen.

Copyright © 2008 Mahendra Singh

Contents

List of Figures

List of Tables

List of Abbreviations and Nomenclature

Abbreviations

BACK	Boublík–Alder–Chen–Kreglewski
BACKPF	Boublík–Alder–Chen–Kreglewski–Polar–Flexible
CCSD	coupled cluster, singles and doubles
CCSD(T)	coupled cluster, singles and doubles with approximate triples
COSMO	conductor-like screening model
COSMO-RS	COSMO–real solvent
CP	Casimir-Polder
CR	combination rule
CRS	COSMO-RS
DFT	density functional theory
DOSD	dipole oscillator strength distribution
Dr.-Ing.	*German* 'Doktor der Ingenieurwissenschaften' — i.e. M.Sc. Ph.D.
Dr. rer. nat.	*German* 'Doktor der Naturwissenschaften' — i.e. Ph.D.
e.g.	*Latin* 'exempli gratia' — i.e. for example
et.al.	*Latin* 'et alia,' 'et aliae', 'et alii' — i.e. and others
EOS	equation of state
EOSs	equations of state
HF	Hartree-Fock
i.e.	*Latin* 'id est' — i.e. that is
LJ-SAFT	Lennard Jones-SAFT
LLE	liquid-liquid equilibrium
M.Tech.	Master of Technology
mod (UNIFAC)	modified UNIFAC
MP	Møller-Plesset perturbation theory
PC-SAFT	perturbed-chain SAFT
PCP-SAFT	perturbed-chain polar SAFT
pDOSD	pseudo-spectral DOSD
PSRK	predictive Soave-Redlich-Kwong
QM	quantum mechanics

RWTH	*German* 'Rheinisch-Westfälische Technische Hochschule' — i.e. the Aachen University
SAFT	statistical associating fluid theory
SAFT-VR	SAFT for potentials of variable attractive range
TDHF	time-dependent Hartree-Fock
TF	Thomas-Fermi theory
TPT	thermodynamic perturbation theory
UNIFAC	universal quasichemical functional group activity coefficients
UNIQUAC	universal quasi-chemical
Univ.-Prof.	*German* 'Universitätsprofessor' — i.e. university professor
vdW	van der Waals
VLE	vapor-liquid equilibrium
VTPR4P	volume-translated Peng-Robinson 4 parameter

Symbols

A	Helmholtz free energy
a_0	bohr radius
c	speed of light
$C^{(6)}$	dipole-dipole dispersion coefficient
e	Euler's number, elementary charge
E	total energy
E_H	atomic unit of energy (Hartree)
exp	exponential function
f'	differential dipole oscillator strength
$\hat{F}$	Fock Operator
$\hbar$	reduced Planck constant or Dirac's constant
H	Henry's Law constant
$\hat{H}$	Hamilton Operator, Hamiltonian
$\hat{H}^0$	unperturbed Hamiltonian
$\hat{H}^{(1)}$	perturbing Hamiltonian
I	average excitation energy
k_B	Boltzmann's constant
k_{ij}	binary interaction parameter
L_AB	dispersion coefficient ratio $C^{(6)}_\mathrm{AB}/\sqrt{C^{(6)}_\mathrm{AA} * C^{(6)}_\mathrm{BB}}$
m	number of segments
N	number of electrons
N_A	the Avogadro number
$\boldsymbol{P}$	polarization
q	charge
R	intermolecular distance

T	Tensor
$\hat{T}$	kinetic energy operator
$\hat{V}$	potential energy operator
∇	Laplacian operator
ρ	particle density
ω	frequency
α	dipole-dipole polarizability
μ	dipole moment
$\delta_{\alpha\beta}$	Kronecker delta
ψ	wavefunction
ϵ	segment-energy parameter (K)
σ	segment diameter
ζ	electrical field strength
x, y, z	coordinates
$\alpha_{\alpha\beta}$	Cartesian component ($\alpha, \beta = x, y, z$) of the dipole-dipole polarizability

Indices, Suffices

assoc	association
A,B	molecules
calc.	calculated
disp	dispersion
ee	electron-electron
eff	effective
elec	electronic
exp.	experimental
ext	external
ig	ideal gas
ind	induced
int	interacting
LDA	local density approximation
MM	multipole-multipole
ne	nuclei-electron
occ	occupied
res	residual
s	single particle
tot	total
virt	virtual
XC	exchange–correlational