

„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
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tation

vorgelegt von

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Berichte aus der Thermodynamik

Mahendra Singh

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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
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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 its 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.

Zusammenfassung

Thermodynamische Eigenschaften sind die entscheidenden EingangsgröÙe 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 mittelgroÙe 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.

Contents

List of Figures	xiii
List of Tables	xv
List of Abbreviations and Nomenclature	xxi
Glossary	xxv
1 Introduction	1
2 Tools of Quantum Mechanics	3
2.1 The Born-Oppenheimer Approximation	4
2.2 Hartree-Fock Method	5
2.3 Post Hartree-Fock Methods	7
2.3.1 Perturbation Theory	8
2.3.2 Configurational Interaction	11
2.3.3 Coupled Cluster	12
2.4 Density Functional Theory	13
2.5 Basis Sets	16
2.5.1 Minimal Basis Sets	18
2.5.2 Split Valence Basis Sets	18
2.5.3 Polarized Basis Sets	18
2.5.4 Diffuse Basis Sets	18
2.5.5 Split Valence Basis Sets with Polarized and Diffuse Basis Functions	19
3 Dispersion Coefficients and Dispersion Interaction Energy	21
3.1 $C^{(6)}$ Coefficients from Dipole Oscillator Strength Distributions (DOSDs) and Pseudo DOSDs	24
3.2 $C^{(6)}$ Coefficients and Casimir-Polder Forces	26
3.3 $C^{(6)}$ Coefficients from Quantum Mechanics	27
3.3.1 Cartesian Tensor Expression	29
3.3.2 Spherical Harmonic Tensor Expression	35
3.4 $C^{(6)}$ Coefficients from London's Approximation	40
3.5 $C^{(6)}$ Coefficients from Scaling Methods	43

4	Equations of State	49
4.1	The Unlike Pair Interactions	50
4.2	Methods for Henry's Law Constant Calculations	53
4.2.1	Theory	53
5	Results and Discussion	61
5.1	Quantum Chemical Calculations	61
5.1.1	Static Polarizability	62
5.1.2	Pure Component Dispersion Coefficient	63
5.1.3	Binary Systems Dispersion Coefficient	64
5.1.4	Dispersion Coefficient Ratio	67
5.2	Prediction of Mixture Behavior	72
5.3	Henry's Law Constant	77
6	Summary	81
	Bibliography	83
A	Theory Supplements	92
A.1	Derivation of Frequency Dependent Dynamic Polarizability	92
A.2	Proof of the Identity Eq. (3.57)	93
B	Result Supplements	95
B.1	Code for the Calculation of the Dispersion Coefficient	95
B.2	32-point Gauss-Legendre Abscissas and Weights	100
B.3	Quantum Chemically Calculated Results	101
B.4	EOS Parameters	124

List of Figures

2.1	Comparison of basis sets with quantum chemical methods to yield an exact solution to Schrödinger equation.	20
3.1	Interaction geometry between molecule A of point charges q_a situated at the points $\mathbf{r}_a$ and molecule B of q_b at $\mathbf{r}_b$	28
3.2	Geometry of interaction for two linear molecules.	36
3.3	Frequency dependent dynamic polarizabilities of methane at imaginary frequencies computed with DOSD method.	43
3.4	Frequency dependent dynamic polarizabilities of methane at imaginary frequencies computed with DOSD and TDHF method.	47
4.1	The real contact distance of two elongated molecules (a) and the one arising when effective molecular diameters are used (b).	51
5.1	Vapor-liquid equilibrium of the system n-decane(1)-ethane(2).	72
5.2	Vapor-liquid equilibrium of the system ethane(1)-carbon dioxide(2) at 223.15 K.	73
5.3	Vapor-liquid equilibrium of the system ethane(1)-carbon dioxide(2) at 283.15 K.	74
5.4	Vapor-liquid equilibrium of the system octane(1)-carbon dioxide(2) at 298.2 K (squares), 333.2 K (diamonds) and 383.15 K (circles).	75
5.5	Vapor-liquid equilibrium of the system cyclohexane(1)-benzene(2) at 343.15 K.	76
5.6	Vapor-liquid equilibrium of the system propane(1)-R32(2) at 280.2 K (circles) and 340.1 K (squares).	77

List of Tables

2.1	Descriptions of different Basis Sets.	20
3.1	Comparison of $C_{AB}^{(6)}$ coefficients calculated from London's approximation and Spackman's approach.	46
4.1	Calculated Henry's constant at different solute mole fractions by PC-SAFTP2 method with geometric mean CR for the system carbondioxide(1)-butane(2).	56
5.1	Data set of pure components for static polarizability and dispersion coefficient calculations.	62
5.2	Percentage averages and standard deviations of calculated static polarizabilities from experimental polarizabilities (DOSD), for the data set defined in Table 5.1.	62
5.3	Percentage averages and standard deviations of calculated pure component dispersion coefficients from experimental ones (DOSD), for the data set defined in Table 5.1. The first column indicates the method used to calculate the static polarizability. Dynamic polarizabilities of all the components are calculated with TDHF/aug-cc-pVDZ method.	63
5.4	Percentage averages and standard deviations of calculated pure component dispersion coefficients from experimental ones (DOSD), for the data set defined in Table 5.1. The first column indicates the method used to calculate the static polarizability. Dynamic polarizabilities of all the components are calculated with TDHF/aug-cc-pVTZ method.	63
5.5	Percentage averages and standard deviations of calculated pure component dispersion coefficients from experimental ones (DOSD), for the data set defined in Table 5.1. The first column indicates the method used to calculate the static polarizability. Dynamic polarizabilities of all the components are calculated with TDHF/aug-cc-pV5Z method.	64
5.6	Data set of binary components for dispersion coefficient and dispersion coefficient ratio calculations.	64

5.7	Percentage averages and standard deviations of the calculated binary systems dispersion coefficients from experimental ones (DOSD), for the data set defined in Table 5.6. The first column indicates the method used to calculate the static polarizability. QM: binary dispersion coefficient is obtained by Cybulski's approach with quantum mechanically calculated dynamic polarizabilities (TDHF/aug-cc-pVDZ).	65
5.8	Percentage averages and standard deviations of the calculated binary systems dispersion coefficients from experimental ones (DOSD), for the data set defined in Table 5.6. The first column indicates the method used to calculate the static polarizability. QM: binary dispersion coefficient is obtained by Cybulski's approach with quantum mechanically calculated dynamic polarizabilities (TDHF/aug-cc-pVTZ).	66
5.9	Percentage averages and standard deviations of the calculated binary systems dispersion coefficients from experimental ones (DOSD), for the data set defined in Table 5.6. The first column indicates the method used to calculate the static polarizability. QM: binary dispersion coefficient is obtained by Cybulski's approach with quantum mechanically calculated dynamic polarizabilities (TDHF/aug-cc-pV5Z).	66
5.10	Percentage averages and standard deviations of calculated dispersion coefficient ratios L_{AB} from experimental ones for the data set defined in Table 5.6. QM: pure and binary dispersion coefficients are obtained by Cybulski's approach with quantum mechanically calculated dynamic polarizabilities (TDHF/aug-cc-pVDZ).	68
5.11	Percentage averages and standard deviations of calculated dispersion coefficient ratios L_{AB} from experimental ones for the data set defined in Table 5.6. QM: pure and binary dispersion coefficients are obtained by Cybulski's approach with quantum mechanically calculated dynamic polarizabilities (TDHF/aug-cc-pVTZ).	69
5.12	Percentage averages and standard deviations of calculated dispersion coefficient ratios L_{AB} from experimental ones for the data set defined in Table 5.6. QM: pure and binary dispersion coefficients are obtained by Cybulski's approach with quantum mechanically calculated dynamic polarizabilities (TDHF/aug-cc-pV5Z).	69
5.13	$C^{(6)}$ dispersion coefficients and their ratios for the indicated species. All values in atomic units. For all the molecules dynamic polarizabilities at TDHF level are calculated with aug-cc-pVDZ basis set and static polarizabilities are calculated with MP2/aug-cc-pVDZ method.	70
5.14	$C^{(6)}$ dispersion coefficients and their ratios for the indicated species. All values in atomic units. For all the molecules dynamic polarizabilities at TDHF level are calculated with aug-cc-pVTZ basis set and static polarizabilities are calculated with MP2/aug-cc-pVDTZ method.	71

5.15	$C^{(6)}$ dispersion coefficients and their ratios for the indicated species. All values in atomic units. For all the molecules dynamic polarizabilities at TDHF level are calculated with aug-cc-pVTZ basis set and static polarizabilities are calculated with CCSD(T)/aug-cc-pVTZ method.	71
5.16	Henry's law constants of the indicated systems with COSMO-RS method. .	79
5.17	Henry's law constants of the indicated systems with VTPR-CRS, PC-SAFTP2 and PSRK methods.	80
B.1	32-point Gauss-Legendre Abscissas and Weights	100
B.2	Average static dipole polarizabilities of the indicated species. All values in atomic units. Reference values are based on DOSD data.	102
B.2	Average static dipole polarizabilities of the indicated species. All values in atomic units. Reference values are based on DOSD data (contd.)	103
B.3	Dipole dispersion coefficients ($C^{(6)}$) of the indicated pure species calculated quantum mechanically with Cybulski's approach (except TDHF and DFT). All values in atomic units. All dynamic polarizabilities at TDHF level are calculated with the aug-cc-pVDZ basis set.	104
B.3	Dipole dispersion coefficients ($C^{(6)}$) of the indicated pure species calculated quantum mechanically with Cybulski's approach (except TDHF and DFT). All values in atomic units. All dynamic polarizabilities at TDHF level are calculated with the aug-cc-pVDZ basis set (contd.).	105
B.4	Dipole dispersion coefficients ($C^{(6)}$) of the indicated pure species calculated quantum mechanically with Cybulski's approach. All values in atomic units. All dynamic polarizabilities at TDHF level are calculated with the aug-cc-pVTZ basis set.	106
B.5	Dipole dispersion coefficients ($C^{(6)}$) of the indicated pure species calculated quantum mechanically with Cybulski's approach. All values in atomic units. All dynamic polarizabilities at TDHF level are calculated with the aug-cc-pV5Z basis set.	107
B.6	Dipole dispersion coefficients of the indicated binary species calculated quantum mechanically with Cybulski's approach. All values in atomic units. All dynamic polarizabilities at TDHF level are calculated with aug-cc-pVDZ basis set.	108
B.7	Dipole dispersion coefficients of the indicated binary species calculated quantum mechanically with Cybulski's approach. All values in atomic units. All dynamic polarizabilities at TDHF level are calculated with aug-cc-pVTZ basis set.	109
B.8	Dipole dispersion coefficients of the indicated binary species calculated quantum mechanically with Cybulski's approach. All values in atomic units. All dynamic polarizabilities at TDHF level are calculated with aug-cc-pV5Z basis set.	110

B.9	Dipole dispersion coefficients of the indicated binary species calculated with London's approximation. All values in atomic units. Pure components static polarizabilities, and dipole dispersion coefficients are taken from Table B.2 and B.3 respectively with the same column headings used in this table. . .	111
B.10	Dipole dispersion coefficients of the indicated binary species calculated with London's approximation. All values in atomic units. Pure components static polarizabilities, and dipole dispersion coefficients are taken from Table B.2 and B.4 respectively with the same column headings used in this table. . .	112
B.11	Dipole dispersion coefficients of the indicated binary species calculated with London's approximation. All values in atomic units. Pure components static polarizabilities, and dipole dispersion coefficients are taken from Table B.2 and B.5 respectively with the same column headings used in this table. . .	113
B.12	L_{AB} ratio of the indicated binary species (Cybulski's approach). Pure and Binary dipole dispersion coefficients for this ratio are taken from Table B.3 and B.6 respectively with the same column headings given in this table. . .	114
B.13	L_{AB} ratio of the indicated binary species (Cybulski's approach). Pure and Binary dipole dispersion coefficients for this ratio are taken from Table B.4 and B.7 respectively with the same column headings given in this table. . .	115
B.14	L_{AB} ratio of the indicated binary species (Cybulski's approach). Pure and Binary dipole dispersion coefficients for this ratio are taken from Table B.5 and B.8 respectively with the same column headings given in this table. . .	116
B.15	L_{AB} ratio of the indicated binary species (London's Approximation). Pure and Binary dipole dispersion coefficients for this ratio are taken from Table B.3 and B.9 respectively with the same column headings given in this table.	117
B.16	L_{AB} ratio of the indicated binary species (London's Approximation). Pure and Binary dipole dispersion coefficients for this ratio are taken from Table B.4 and B.10 respectively with the same column headings given in this table.	118
B.17	L_{AB} ratio of the indicated binary species (London's Approximation). Pure and Binary dipole dispersion coefficients for this ratio are taken from Table B.5 and B.11 respectively with the same column headings given in this table.	119
B.18	Dipole dispersion coefficients of the indicated binary species calculated with London's approximation with pure component's DOSD polarizabilities and DOSD dispersion coefficients. All values in atomic units. Reference values are based on DOSD data.	120
B.19	Average static dipole polarizabilities of the indicated species for which the DOSD data is not available.	121
B.20	Dipole dispersion coefficients of the indicated pure species calculated quantum mechanically with Cybulski's approach for which DOSD data is not available.	122

B.21 Dipole dispersion coefficients of the indicated binary species calculated with Cybulski's approach and London's approximation for which DOSD data is not available.	123
B.22 Generalized Twu-Bluck-Cunningham-Coon α parameters for VTPR4P-CRS EOS used in the calculation of Henry's constant	124
B.23 Mathias-Copeman parameters for PSRK EOS used in the calculation of Henry's constant	124
B.24 Pure component parameters for PC-SAFTP2 EOS used in the calculation of Henry's constant	125
B.25 Binary mixture parameters for PC-SAFTP2 EOS used in the calculation of Henry's constant	126

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.	<i>German</i> ‘Doktor der Ingenieurwissenschaften’ — i.e. M.Sc. Ph.D.
Dr. rer. nat.	<i>German</i> ‘Doktor der Naturwissenschaften’ — i.e. Ph.D.
e.g.	<i>Latin</i> ‘exempli gratia’ — i.e. for example
et.al.	<i>Latin</i> ‘et alia,’ ‘et aliae,’ ‘et alii’ — i.e. and others
EOS	equation of state
EOSs	equations of state
HF	Hartree–Fock
i.e.	<i>Latin</i> ‘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	<i>German</i> ‘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.	<i>German</i> ‘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 $C_{AB}^{(6)}/\sqrt{C_{AA}^{(6)} * C_{BB}^{(6)}}$
m	number of segments
N	number of electrons
N_A	the Avogadro number
$\mathbf{P}$	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

