

Determination of microscopic interaction constants by x-ray reflectivity measurements

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Abstract

The density profiles of liquid-gas interfaces of binary mixtures are determined by x-ray reflectivity measurements. The surface tension γ is calculated from the measured data in the framework of the capillary waves theory. It is demonstrated that gradient theory can be used to investigate the van der Waals interaction between the different constituents of the liquid. The determination of Lennard-Jones constants and mixing rules for molecule-molecule interactions leads to a microscopic understanding of the liquid-gas interface. The refinement of the gradient theory to the data shows very good agreement when a liquid-gas interface according to a capillary wave roughness is used.

Key words: Surface tension, X-ray reflectivity, Gradient theory

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1 INTRODUCTION

Liquid-gas interfaces are common in nature and technological applications. Many physical and chemical processes take place at these interfaces, for example catalytic reactions, adsorption of gas molecules on the liquid surface and solution of gas molecules in the liquid. These processes are determined by the surface morphology which is influenced by the surface tension. A microscopic understanding of a liquid's surface tension is a complicated problem. This is because the surface tension is generated by the interaction between

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the constituents of the liquid near the liquid surface. Thus, the access on the liquid's surface tension leads to an understanding of the particle interactions on microscopic length scales. In our work we demonstrate how Lennard-Jones constants of nonpolar binary mixtures can be determined using the x-ray reflectivity technique. Only a few experimental methods for the determination of Lennard-Jones parameters like solubility-, fluid viscosity measurements, and the analysis of virial coefficients are available leading to a large variance in experimental data of more than 20% for the Lennard-Jones diameter σ_{LJ} and more than 50% for the amplitude ϵ [1]. No direct microscopic access has been achieved so far.

2 THEORY

2.1 CALCULATION OF SURFACE TENSION

The surface tension can be calculated via the gradient theory, first published by Cahn and Hilliard [2]. It has been described extensively in the literature. For an overview see [2–4], applications of the theory can be found in [5–8]. The gradient theory provides good results for non-polar liquids. During the last years, several attempts to expand the gradient theory to polar liquids have been performed [9–11]. The gradient theory allows to calculate the surface tension by using the grand thermodynamic potential which is the usual ansatz described in literature. In this work, we show how the gradient theory can be used to extract Lennard-Jones constants by using an interfacial density profile. These interfacial density profiles can be determined with angstrom resolution using x-ray reflectivity measurements.

The surface tension γ of a nonpolar liquid is given by the gradient theory in two different forms [3]. In general, the grand thermodynamic potential Ω determines the surface tension via

$$\gamma = \sqrt{2c} \int_{n_v}^{n_l} \sqrt{\Delta\Omega(n)} dn. \quad (1)$$

Thus, γ is given by an integral over the particle density n from the density of the vapor phase n_v to the density of the liquid phase n_l . c is the so called influence parameter [4]. The term $\sqrt{\Delta\Omega(n)} = \sqrt{\Omega(n) - \Omega_0}$ (Ω_0 is equal to the negative equilibrium pressure $-p$ [5]) can be expressed by the density gradient perpendicular to the surface so that γ is given by

$$\gamma = \int_{-\infty}^{\infty} c \left(\frac{dn}{dz} \right)^2 dz. \quad (2)$$

The influence parameter can be calculated as [4]

$$c = -\frac{1}{6} \int r^2 U(r) C(r, n) d^3r, \quad (3)$$

where $C(r, n)$ denotes the direct correlation function of the homogeneous fluid at density n , and $U(r)$ is the interaction potential. As no correlation functions are available for the majority of systems, the calculation of c has to be modeled with simple parameters. Many empirical expressions for the influence parameter can be found in [5]. Alternatively, the correlation function can be approximated by [12]

$$C(r, n) = \begin{cases} 0 & , r < \sigma_{\text{LJ}} \\ 1 & , r \geq \sigma_{\text{LJ}} \end{cases} \quad (4)$$

where σ_{LJ} denotes the Lennard-Jones constant in the Lennard-Jones potential $U(r)$. Using this potential in Eq. (3) and the approximation in Eq. (4) yields

$$c = \frac{16}{7} \pi \epsilon \sigma_{\text{LJ}}^5 \quad (5)$$

for a homogeneous fluid with the amplitude of the Lennard-Jones potential ϵ . Thus, Eq. (2) can be used for the determination of the surface tension based on microscopic measurements of the profile dn/dz . Because of the existence of alternative, less complicated methods for the surface tension determination the more interesting case is the determination of the influence parameter c leading to a direct access to the interaction potentials. For this purpose the surface tension γ and the density profile are required.

2.2 X-RAY REFLECTIVITY

The x-ray reflectivity of a liquid surface yields the lateral averaged dispersion profile $\delta(z) = \langle \delta(x, y, z) \rangle_{xy}$ perpendicular to the sample's surface. The dispersion δ is a function of the electron density ρ_e and is defined by $\delta = r_e \rho_e \lambda^2 / (2\pi)$, where r_e denotes the classical electron radius and λ the wavelength of the incident radiation. δ is directly proportional to the density n . The wave vector transfer has only one component perpendicular to the surface given by

$q_z = (4\pi/\lambda) \sin \theta$, where θ denotes the angle between the sample surface and the x-ray beam. The scattered intensity I is given by [13]

$$I(q_z) \propto \frac{1}{q_z^4} \left| \int \frac{\partial \rho_e(z)}{\partial z} e^{iq_z z} dz \right|^2. \quad (6)$$

The structure of liquid surfaces is dominated by thermally excited capillary wave fluctuations. They cause a surface roughness on the order of a few angstroms. The amplitude of these waves is determined by the surface tension. Thus, measuring the roughness σ of the liquid surface gives access to both, the surface tension γ and the density profile with angstrom resolution.

Based on capillary wave theory, σ can be calculated after the resolution of the reflectivity setup has been taken into account using [14–16]

$$\sigma^2 = \frac{k_B T}{2\pi\gamma} \ln \left(\frac{q_{uc}}{q_{lc}} \right) + \sigma_0^2, \quad (7)$$

with Boltzmann's constant k_B , the intrinsic width of the interface σ_0 , the upper wave-vector cutoff $q_{uc} = 2\pi/d$, the molecule diameter d and the lower wave-vector cutoff q_{lc} which is determined by the resolution of the diffractometer via $q_{lc} = q_z \Delta\alpha/2$. $\Delta\alpha$ denotes the angular acceptance of the detector [17, 18]. Values for the intrinsic roughness are about $\sigma_0 \approx 1 - 2 \text{ \AA}$ [14, 16]. The intrinsic roughness is difficult to measure due to the convolution with the capillary wave roughness. However, the question arises if only the intrinsic roughness σ_0 or the full capillary wave roughness has to be used for gradient theory calculations.

Using an error function electron density profile the reflectivity of a single surface is given by [19]

$$R(q_z) = R_F \exp(-\sigma^2 q_z^2) \frac{1}{\sqrt{\pi}} \Gamma(A, B), \quad (8)$$

where R_F is the Fresnel reflectivity of an ideally smooth surface, $\Gamma(A, B)$ is the incomplete Gamma function with $A = (1 - q_z^2 k_B T / (2\pi\gamma)) / 2$ and $B = 2\pi^2 (q_z \Delta\alpha / 2)^2 / q_{uc}^2$.

In this work, the gas-liquid interface of a polypropylene glycol 4000 (PPG4000) - isobutane mixture is investigated as a function of gas pressure by x-ray reflectivity measurements. The surface tension γ of the mixture is a function of isobutane molecules solved in the liquid. It will decrease with rising isobutane proportion, i.e. with rising isobutane pressure. Thus, for different gas pressures the surface tension can be determined and the interaction potential can be

obtained for van der Waals interactions between the different constituents isobutane-isobutane, PPG-PPG and isobutane-PPG.

3 EXPERIMENT

The x-ray reflectivity measurements were performed with a laboratory Bruker-AXS D8 Advanced diffractometer in theta-theta geometry. The radiation ($\lambda = 1.54 \text{ \AA}$) was produced by an x-ray tube with a copper anode and was parallelized by a Goebel mirror. The distance between sample stage and detector (NaI(Tl)) of approximately 300 mm leads to a resolution of $\Delta\alpha \approx 0.7 \text{ mrad}$. A sample cell designed for x-ray reflectivity experiments was used [20, 21]. Thus, a pressure accuracy of $\pm 0.02 \text{ bar}$ and temperature stability of $\pm 20 \text{ mK}$ during one measurement was achieved. The measurements were carried out at a temperature of 16°C . The condensation pressure of isobutane at this temperature is 2.67 bar [22]. Isobutane (C_4H_{10}) with a purity of 99.5% and PPG4000 ($\text{H}[\text{OC}(\text{CH}_3)\text{H}(\text{CH}_2)]_m\text{OH}$) with $m \approx 69$ purchased by Alfa Aesar (purity $\geq 99.9\%$) was used for all experiments. Before filling isobutane into the sample chamber a calibration reflectivity of the PPG nitrogen interface was recorded. The diffusely scattered intensity was measured and subtracted from the reflectivity data.

For determination of q_{uc} the shape of the bulk structure factor of PPG was measured at beamline BL9 of the synchrotron light source DELTA [23]. Detailed information about the beamline BL9 can be found in [24].

4 DATA ANALYSIS AND DISCUSSION

Fig. 1 shows x-ray reflectivities normalized to the Fresnel reflectivity measured at different gas pressures. The measurement at 1 bar nitrogen yields a surface roughness of the PPG4000 surface of $\sigma_{\text{PPG}_2} = (4.0 \pm 0.1) \text{ \AA}$. This is in good agreement with standard capillary wave theory using a surface tension of PPG4000 of $\gamma_{\text{PPG}} = 33.9 \text{ mN/m}$ [25]. With increasing gas pressure no isobutane layer formation was found, as can be seen in Fig. 1. The appearance of isobutane layers would become visible by deviations from the linearity in the $\log(R/R_{\text{F}})$ representation of the data as shown exemplarily by the dashed line in Fig. 1. The refined dispersion profiles corresponding to the data of Fig. 1 are shown in Fig. 2. The roughness increases with pressure from 4 \AA to 8 \AA . The absence of layer formation, solubility tests with PPG and pentane, and an observed pressure drop after each filling with isobutane confirm the assumption that isobutane solves almost perfectly in PPG4000. Therefore the

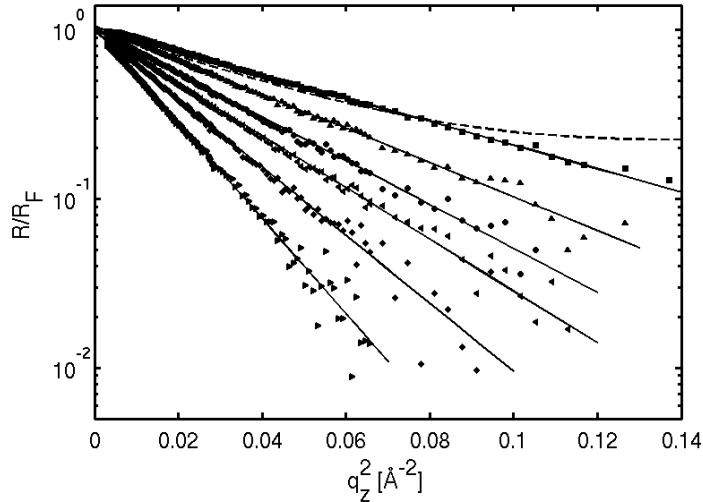


Figure 1. X-ray reflectivity data normalized by the Fresnel reflectivity for different gas pressures. N_2 ■; isobutane: $p = 1$ bar ▲, $p = 1.60$ bar ●, $p = 1.93$ bar ◀, $p = 2.22$ bar ◆, $p = 2.61$ bar ►. The dashed line represents a calculated reflectivity assuming a PPG4000 substrate with a monolayer of isobutane.

fraction of isobutane in the binary mixture was approximated to Raoult's law [26]

$$x_I = \frac{p}{p_0}, \quad (9)$$

where p_0 denotes the condensation pressure of isobutane and p the (partial) pressure of isobutane. The partial pressure of PPG can be set to 0, because of its low vapor pressure. The PPG fraction is then $x_P = 1 - p/p_0$.

Surface tensions of the different mixtures are accessible using Eq.(7) and the surface roughness obtained by the refinement of the reflectivity data. For a binary mixture we use the expression $q_{uc} = 2\pi/(x_I d_I + x_P d_P)$ as the upper wavevector cutoff, where d_I, d_P denote the diameter of an isobutane and a PPG molecule, respectively. For PPG an effective diameter of 6 \AA was assumed. This is supported by the structure factor measurements. At $q \approx 1.0 \text{ \AA}^{-1}$ the rising structure factor peak becomes clearly visible, so that no capillary waves are expected for $q \gtrsim 1.0 \text{ \AA}^{-1} = q_{uc}$. The molecule diameter of isobutane is $d_I = 6.5 \text{ \AA}$ [27]. A linear dependence of the sample's surface tension with gas pressure was found as shown in Fig. 3.

In order to apply the gradient theory, an equation of state (EOS), e.g. the Peng-Robinson-EOS [28], is usually computed via the critical constants. Accordingly, a grand canonical potential can be developed. As no critical data for PPG4000 are directly available, parameters of the EOS can only be obtained by a refinement. To avoid this approach, in contrast to the conventional pro-

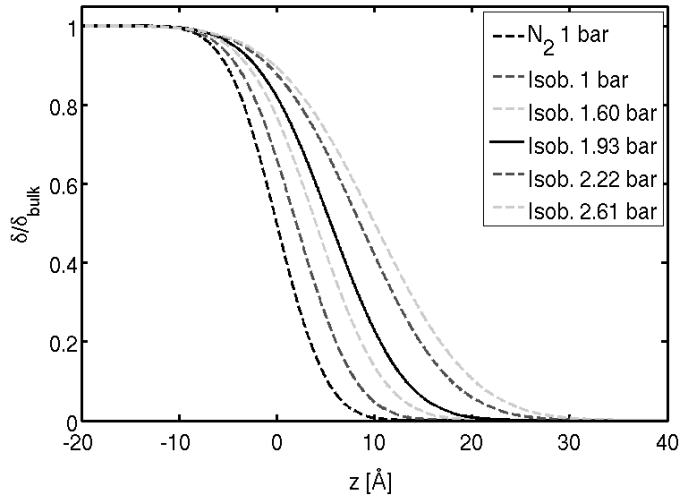


Figure 2. Normalized dispersion profiles for different isobutane pressures. The dispersion is proportional to the electron density ρ_e . The position of the interface is at $z = 0$.

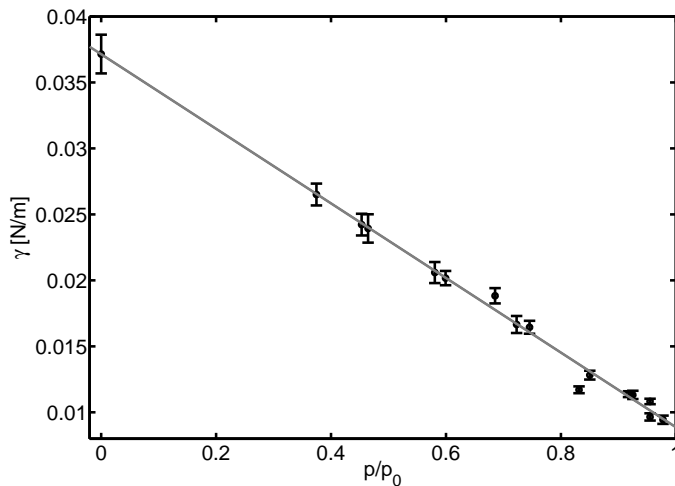


Figure 3. Surface tension of the PPG-isobutane mixtures obtained from fits of the x-ray reflectivity data. Gray line: linear fit to the data.

cedure [3, 4], Eq. (2) is used for calculation of the influence parameters instead of Eq. (1). The x-ray reflectivity technique allows to determine a density profile of the liquid's interface as presented in Fig. 2. Assuming a homogeneous mixture of both constituents and an influence factor that does not depend on the density [12] the surface tension can be calculated using Eq. (2) with an effective influence factor c_{eff} which is a function of the fraction of both components. The Lennard-Jones constants in Eq. (5) are replaced by effective constants $\sigma_{\text{LJ,eff}}$ and ϵ_{eff} of the mixtures to calculate c_{eff} . They are composed of the constants of the pure components via

$$\sigma_{\text{LJ,eff}} = f(x)\sigma_{\text{LJ,Isob.}} + g(x)\sigma_{\text{LJ,PPG}} + h(x)\frac{1}{2}(\sigma_{\text{LJ,PPG}} + \sigma_{\text{LJ,Isob.}}) \quad (10)$$

$$\epsilon_{\text{eff}} = f(x)\epsilon_{\text{Isob.}} + g(x)\epsilon_{\text{PPG}} + h(x)\sqrt{\epsilon_{\text{PPG}}\epsilon_{\text{Isob.}}} \quad (11)$$

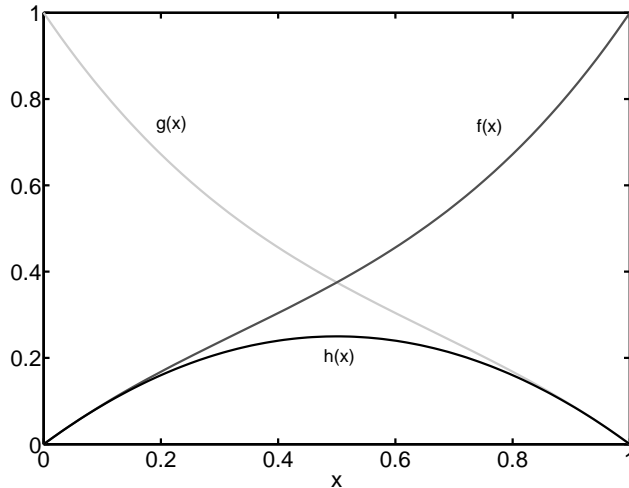


Figure 4. Mixing rules for different PPG isobutane mixtures.

The first term describes the isobutane-isobutane interaction, the second the PPG-PPG interaction and the third the PPG-isobutane interaction. Rules for mixing of the different constants for binary liquids can be found in [29]. The functions f, g, h represent the fraction of the regarding interaction, so that $f + g + h = 1$ for all isobutane fractions x . The functions f and g should fulfill the rule $f(x) = g(1 - x)$ and the boundary conditions $f(0) = g(1) = 0$, $f(1) = g(0) = 1$. The best results yield third order polynomials for f, g and a second order polynomial for h with a maximum at $x = 0.5$. Here $h(0.5) = 0.25$ is the best adaption. The functions f, g and h are shown in Fig. 4. With these functions and the known Lennard-Jones constants of isobutane $\sigma_{\text{LJ,Isob.}} = 5.278 \text{ \AA}$ and $\epsilon_{\text{Isob.}} = 330.1 \text{ K} \cdot k_{\text{B}}$ [30] the Lennard-Jones constants of PPG4000 can be computed via Eq. (5) and a fitting curve can be adapted.

$\epsilon\sigma_{\text{LJ}}^5$ derived from the experimental data using the surface tension and dispersion profiles inserted in Eq. (2) are shown in Fig. 5. The result of the refinement is also shown in Fig. 5 as a black line. ϵ_{PPG} and $\sigma_{\text{LJ,PPG}}$ are determined as $\sigma_{\text{LJ,PPG}} = (36.7 \pm 0.2) \text{ \AA}$, $\epsilon_{\text{PPG}} = (52.8 \pm 0.5) \text{ K} \cdot k_{\text{B}}$. A very good agreement between experimental data and refinement is achieved. For $x \rightarrow 1$ the experimental values of $\sigma_{\text{LJ,eff}}$ and ϵ_{eff} approach the literature values for isobutane which verifies the presented method for determination of Lennard-Jones constants.

Besides, a fit assuming an intrinsic profile of the surface with a roughness of about 1.5 \AA is presented in Fig. 5 as a dashed line and crosses. For large

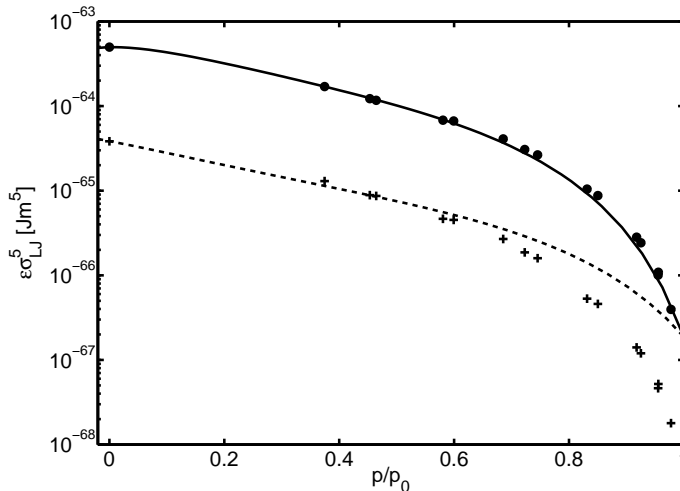


Figure 5. $\epsilon\sigma_{LJ}^5$ against isobutane fraction. c is proportional to $\epsilon\sigma_{LJ}^5$, see Eq. (5). The computed values via a capillary waves roughness: ● and solid line; the assumed intrinsic roughness: + and dashed line. The error bars are in the order of magnitude of the symbol size.

isobutane fractions the curve does not fit the experimental data. Therefore an intrinsic profile is not appropriate for using the gradient theory and capillary wave roughness has to be used. In the literature, the model of the interfacial width used for gradient theory calculations is frequently an intrinsic interface [31], whereas this is not specified in other publications [3–5]. The profiles shown there seem to be calculated with a capillary-wave-like roughness of about $\sigma = 3.5 \text{ \AA} - 12 \text{ \AA}$ which is in agreement with the results of this work.

5 SUMMARY

In summary, the influence parameter was determined for each solution of PPG and isobutane and was compared with a model for the influence parameter based on the gradient theory. A refinement of the PPG-Lennard-Jones constants including all possible combinations of van der Waals interactions between the different constituents of the mixture leads to very good agreement between theory and experiment. The Lennard-Jones constants of PPG4000 were refined to be $\sigma_{LJ,PPG} = (36.7 \pm 0.2) \text{ \AA}$ and $\epsilon_{PPG} = (52.8 \pm 0.5) K \cdot k_B$. The contribution of every particle-particle van der Waals interaction was quantified by deriving the mixing rules. Additionally we were able to deduce that the capillary wave roughness has to be used for the gradient theory. An intrinsic roughness underestimates the surface tensions of the mixtures and a good agreement with the measured data cannot be achieved. Thus, the combination of x-ray reflectivity technique and gradient theory gives the opportunity to investigate interactions within a liquid on a molecular length scale.

List of symbols

c	influence parameter
$C(r, n)$	direct correlation function
d	molecule diameter
f, g, h	interaction functions
i	imaginary unit
I	scattered intensity
k_B	Boltzmann's constant
n	particle density
p	pressure
p_0	condensation pressure
q	wave-vector transfer
q_c	lower wave-vector cutoff
q_{uc}	upper wave-vector cutoff
q_z	component of wave-vector transfer normal to the surface
r	radial component of spherical coordinates
r_e	classical electron radius
$R, R(q_z)$	reflectivity, reflected intensity
R_F	Fresnel reflectivity
T	temperature
$U(r)$	interaction potential
x, y, z	Cartesian coordinates
x_j	fraction of component j

Greek symbols

γ	surface tension
$\Gamma(A, B)$	incomplete gamma function
$\delta, \delta(z)$	dispersion
$\Delta\alpha$	angular acceptance of the detector
ϵ	Lennard-Jones constant, amplitude of the Lennard-Jones-Potential
θ	angle between sample surface and incident radiation
λ	wavelength
ρ_e	electron density
σ	surface roughness
σ_0	intrinsic surface roughness
σ_{LJ}	Lennard-Jones constant, Lennard-Jones diameter
Ω	grand thermodynamic potential
Ω_0	negative equilibrium pressure

Subscripts

eff	effective
$I, \text{Isob.}$	isobutane
l	liquid phase
P, PPG	PPG4000

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