

Flexible or rigid molecular models? - A study on vapour-liquid equilibrium properties of ammonia

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Abstract

The influence of the intramolecular degrees of freedom on the vapour-liquid equilibrium properties of ammonia is studied for vapour pressure, saturated densities and enthalpy of vaporisation. Molecular force fields with and without intramolecular degrees of freedom, keeping all other parameters unchanged, show significantly different phase envelopes. For ammonia, the angle potential is particularly important, because the hydrogen sites are more aligned in the liquid than in the vapour, leading to a significantly enhanced molecular dipole moment in the condensed phase. Based on a rigid force field for ammonia from prior work of our group [Eckl et al., *Mol. Phys.*, Vol. 106, p. 1039-1046, 2008], a new accurate force field with intramolecular degrees of freedom is developed.

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I. INTRODUCTION

Ammonia is a particularly important and widely used substance with numerous applications in modern society. Also for the development of theories on the behaviour of matter, it plays an important role, because of its simple molecular structure and its strong interactions.

In order to understand the thermo-physical behaviour of ammonia and mixtures containing ammonia, models on the molecular level are required. In the preceding three decades, much effort has been made to develop effective force field models for the molecular interactions to facilitate this task.¹⁻⁷ In comparison to quantum chemical approaches, such models require very little computational effort for their evaluation, e.g. by means of molecular dynamics or Monte-Carlo simulation. Through the progress in methodology and computational power, current effective force fields are much more accurate and allow for convincing predictions over a wide range of states.⁵⁻⁷

By modelling thermodynamic properties of small molecules like ammonia with force fields, it is commonly assumed that the intramolecular interactions are only of little importance. This is supported by the compact geometry of that molecule, exhibiting little conformational changes. The intramolecular interactions are thus usually frozen by defining rigid force fields. With respect to the thermodynamic properties of bulk fluid ammonia, it was shown that this simplification does not lead to serious errors.⁶

Recently, Shi and Maginn published a study on the solubility of ammonia in an ionic liquid,⁸ in which they have applied the ammonia force fields by Gao et al.⁴ and by Eckl et al.⁶ However, for technical reasons, they have subsequently introduced the intramolecular degrees of freedom on top of the parameterized rigid force fields. They utilized hybrid Monte Carlo moves, which require a reversible integrator that is much easier to implement for systems that have intramolecular degrees of freedom.⁸ Note that also for some molecular dynamics implementations, force fields with intramolecular degrees offer technical advantages. Despite anticipating some influence on the thermo-physical properties, Shi and Maginn obtained very unfavourable results with respect to the vapour-liquid equilibrium (VLE) of ammonia.

These findings stimulated the present work, where the influence of the intramolecular degrees of freedom on the VLE properties was studied. Based on the rigid model by Eckl et al.,⁶ an accurate new effective force field with intramolecular degrees of freedom was developed.

II. MOLECULAR MODEL

To describe the molecular interactions of ammonia, the nitrogen atom is typically modelled by one negatively charged Lennard-Jones (LJ) site and the three hydrogen atoms are each represented by a positive partial charge.³⁻⁷ This leads to the following functional form of the pairwise intermolecular interactions between two ammonia molecules i and j

$$u_{inter} = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right] + \sum_{a=1}^4 \sum_{b=1}^4 \frac{q_{ia}q_{jb}}{4\pi\epsilon_0 r_{ijab}}, \quad (1)$$

where a is the site index of the charges on the molecule i and b is the site index of the charges on the molecule j , respectively. The site-site distances between the molecules i and j are denoted by r_{ij} for the single LJ site and by r_{ijab} for the four charges. σ and ϵ are the LJ size and energy parameters, while q_{ia} and q_{jb} are the magnitudes of the charges a and b on the molecules i and j , respectively. Finally, ϵ_0 denotes the permittivity of the vacuum. Throughout the present study, the parameters for the equilibrium geometry were taken from Eckl et al.,⁶ which are based on quantum chemical calculations on the Møller-Plesset 2 level of theory.

The intramolecular interactions were taken into account by the following common potentials for the intramolecular interactions

$$u_{intra} = \sum_{bonds} k_b (r - r_0)^2 + \sum_{angles} k_\theta (\theta - \theta_0)^2. \quad (2)$$

Thereby, the molecules are described as harmonic oscillators, which may accurately reproduce the experimentally observed frequencies of the vibrational spectrum,¹⁰ where k_b and k_θ are the force constants. These two parameters can be determined by quantum chemical calculations⁸ or by adjustment to experimental IR spectra.¹¹ The equilibrium values of bond length and bond angle are denoted by r_0 and θ_0 , respectively.

For ammonia, force constants for the bond lengths $k_b = 1896.6 \text{ kJ}/(\text{mol } \text{Å}^2)$ and for the bond angles $k_\theta = 123.5 \text{ kJ}/(\text{molrad}^2)$ were recently published by Shi and Maginn⁸ who derived these data from quantum chemical calculations. A normal mode analysis based on these parameters was carried out in the present work that yields the wave numbers listed in Table I. Taking into account the simplicity of the present description of the intramolecular degrees of freedom the agreement with experimental data¹² is good. The simple model with the parameters of Shi and Maginn was therefore used throughout the present study.

III. RESULTS AND DISCUSSION

A. Influence of the intramolecular degrees of freedom on vapour-liquid properties

The introduction of the intramolecular interactions on the basis of the harmonic potentials in Equation (2) with the force constants by Shi and Maginn⁸ into the originally rigid ammonia force field by Eckl et al.⁶ has a strong influence on the VLE properties. Figure 1 shows this effect over a temperature range of $0.65 \leq T/T_c \leq 0.95$, where T_c is the critical temperature. On average, the vapor pressure p is decreased by 38 %, the saturated liquid density ρ^{liq} is increased by 11 % and the enthalpy of vaporisation Δh_v is increased by 31 %. As usual, the saturated vapour density follows the trend of the vapour pressure.

The reasons for these discrepancies were studied in detail using the the vapor-liquid equilibrium at 347.5 K as an example. Results are presented in Figure 2 and Table II. These major changes result from the significant change in the molecular geometry of the flexible molecule in the liquid phase. Due to the intermolecular interactions, in the liquid, the flexible molecules oscillate around an average bond angle of 103.2° , instead of 106° in case of the equilibrium structure, which is adopted for the rigid model. The three partial dipoles, each constituted by the nitrogen atom and one hydrogen atom, are thus more aligned so that the overall dipole moment distribution has an average value of $\bar{\mu}^{liq} = 2.06$ D, which is 10 % higher than the equilibrium value of $\mu = 1.88$ D, which is also the one of the rigid model, cf. Figure 2 (top). In the vapour phase, the dipole distribution exhibits an average value of $\bar{\mu}^{vap} = 1.92$ D, which is only negligibly higher than that of the equilibrium structure, cf. Figure 2 (bottom). This shows that as expected for the studied condition the molecules in the vapour state oscillate around a geometry that is only marginally different from the equilibrium structure. The slight differences for the gas phase can be caused by the influence of the rotation on the geometry. To sum up: the strong intermolecular interactions in the liquid phase lead to changes of the flexible molecule’s structure that significantly influence the thermodynamic properties of the ensemble, whereas in the gas phase, only minor changes are observed.

Results from a detailed study on the influence of the various intramolecular degrees of freedom on the VLE properties of ammonia that was carried out for the temperature 347.5 K are summarized. In the "Rigid" model, both the bond length and the bond angle were kept fixed. In the "Bond length" model, the bond angle was fixed, whereas the bond length was allowed to vary. In the "Bond angle" model, the bond length was fixed, whereas the bond angle was allowed to vary. In the "Flexible" model, both the bond length and the

bond angle were allowed to vary. It can be seen that the bond angle potential is crucial, whereas the bond length potential has hardly any effect on the VLE properties of ammonia.

The observed changes of the VLE properties can be explained by the increase of the attractive molecular interactions due to the increased average dipole moment in the liquid phase. The average potential energy between two dipoles¹³ is

$$u_{\mu\mu}(r) = -\frac{2}{3} \frac{\mu_i^2 \mu_j^2}{k_B T r^6}, \quad (3)$$

which indicates that the dipole-dipole potential energy depends on the fourth power of the dipole moment. The dipole-dipole interaction yields on average an attractive contribution so that a relative increase of $\Delta\mu/\mu_0$ of the dipole moment leads to a relative increase in the total potential energy of $\Delta u_{\mu\mu}/u_{\mu\mu}^0 \geq 4\Delta\mu/\mu_0$. The charge distribution of ammonia has a quadrupole moment as well, however, the dipole moment is dominant. There is also an additional cooperative effect resulting from the configuration of the molecules, because intramolecular degrees of freedom enhance the ability of the molecules to avoid highly repulsive configurations.

B. Optimisation of an ammonia model with intramolecular degrees of freedom

Considering the discussion above, a subsequent introduction of intramolecular degrees of freedom into existing rigid force fields requires a re-parameterisation, if the quality of the models is to be maintained. Taking the rigid ammonia force field by Eckl et al.⁶ as a starting point, the intramolecular interactions were introduced as given by Equation (2), using the force constants for the bond lengths and the bond angles by Shi and Maginn.⁸ All geometric parameters of the equilibrium structure were kept as given by Eckl et al.⁶ Applying the optimisation method as described by Eckl et al.,⁶ the intermolecular interaction parameters were fitted in the present work to correlations of experimental data for vapour pressure and saturated liquid density.¹⁴ The results are presented in Table III. The results for VLE of ammonia obtained with the new flexible model are compared to those from the original model of Eckl et al and experimental data in Figure 1 and the deviation plot in Figure 3. The numerical data is given in Table IV, the average deviations between the flexible model and the experimental data for the saturated liquid density are below 0.5 %, for the vapour pressure below 5 % and for the enthalpy of vaporisation below 5 %. The accuracies of the original rigid model and new flexible model are similar.

IV. CONCLUSION

Even for very small molecules like ammonia, the introduction of intramolecular degrees of freedom has a significant influence on VLE properties. Using realistic potentials and force constants for the bond lengths and the bond angles, the average saturated liquid density can differ by up to 11 % and the average vapour pressure by up to 38 %. Therefore, introducing intramolecular degrees of freedom, in a originally rigid molecular model requires a re-parameterisation of the intermolecular potential, if the accuracy with respect to thermodynamic properties is to be conserved. The strong influence of the intramolecular degrees of freedom of ammonia on its VLE properties that was observed in the present study is mainly caused by the change in the dipole moment, which is significantly increased in the liquid phase, but retains its equilibrium magnitude in the vapour phase. The increased dipole moment leads to a stronger average attraction in the liquid, which results in a higher saturated liquid density, a lower vapour pressure and a higher enthalpy of vaporisation. Fuller and Rowley also observed an influence of the intramolecular degrees of freedom on the shear viscosity of polar fluids, induced by geometry changes that lead to an increased dipole moment.¹⁵ A force field with intramolecular degrees for freedom for ammonia based on the rigid force field by Eckl et al.⁶ was developed. The deviations from correlations of experimental data for saturated liquid density are below 0.5 %, for vapour pressure below 5 % and for enthalpy of vaporisation below 5 % over the temperature range of $0.65 \leq T/T_c \leq 0.95$.

APPENDIX: SIMULATION DETAILS

The present VLE results were obtained with two freely available Gibbs Ensemble Monte Carlo (GEMC)¹⁶ simulation tools: the Errington code¹⁷ and TOWHEE.¹⁸ The total number of particles in the coexisting phases was 1000. The systems were equilibrated for $2 \cdot 10^7$ MC steps and the number of production steps was $5 \cdot 10^7$ or 10^8 for temperatures below 300 K. In each step, one MC move was attempted, such as translation, rotation, volume change or exchange of particles between the phases. For the exchange of molecules, the configurational biased growth method¹⁹ was used. The moves were randomly selected with a fixed probability, which was specified as 75:1:12:12 for translation/rotation:volume change:transfer:regrowth. Translation and rotation were equally sampled. The electrostatic long range contributions were calculated with the Ewald summation method.²⁰ The cut-off radius corresponded to half of the respective edge length of the simulation volume and the usual LJ long-range corrections for the energy and the pressure were applied.

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TABLE I: Results of the normal mode analysis based on the force constants by Shi and Maginn⁸ in comparison with experimental data.¹²

Mode	Calc. / cm ⁻¹	Exp. / cm ⁻¹
Symmetrical stretching	3323	3337
Symmetrical deformation	994	950
Degenerate stretching	3417	3444
Degenerate deformation	1308	1627

TABLE II: Influence of the intramolecular degrees of freedom on the vapour-liquid equilibrium of ammonia at 347.5 K for different models with constant intermolecular interaction potential parameters as given by Eckl et al.⁶ In the "Rigid" model, both the bond length and the bond angle were kept fixed. In the "Bond length" model, the bond angle was fixed, whereas the bond length was allowed to vary. In the "Bond angle" model, the bond length was fixed, whereas the bond angle was allowed to vary. In the "Flexible" model, both the bond length and the bond angle were allowed to vary. The force constants by Shi and Maginn⁸ were used in those cases where the intramolecular degrees of freedom were introduced. "Exp." are reference data determined using correlations taken from the NIST Chemistry Webbook.¹⁴

Model	ρ^{liq} / mol l ⁻¹	ρ^{vap} / mol l ⁻¹	p / MPa	Δh_v / kJ mol ⁻¹	$\bar{\mu}^{liq}$ / D	$\bar{\mu}^{vap}$ / D
Rigid	30.3 (1)	1.73 (3)	3.69 (7)	15.9 (4)	1.88 ^a	1.88
Bond length	30.5 (1)	1.69 (3)	3.67 (5)	16.1 (4)	1.88	1.88
Bond angle	33.0 (2)	1.05 (8)	2.5 (1)	19.3 (5)	2.05	1.89
Flexible	33.3 (2)	0.98 (5)	2.36 (5)	19.6 (6)	2.06	1.92
Exp.	30.4	1.73	3.66	15.5		1.47

^aEckl et al.⁶ mistakenly reported a resulting dipole moment of 1.94 D.

TABLE III: Parameters of the Lennard-Jones site and the partial charges of the rigid ammonia force field by Eckl et al.⁶ and the present ammonia force field with intramolecular degrees of freedom, using the force constants by Shi and Maginn.⁸ Note that the equilibrium structures are identical.

Model	Interaction site	$x / \text{\AA}$	$y / \text{\AA}$	$z / \text{\AA}$	$\sigma / \text{\AA}$	$(\epsilon/k_B) / \text{K}$	q / e
Rigid	N	0	0	0.0757	3.376	182.9	-0.9993
	H(1)	0.9347	0	-0.3164	-	-	+0.3331
	H(2)	-0.4673	0.8095	-0.3164	-	-	+0.3331
	H(3)	-0.4673	-0.8095	-0.3164	-	-	+0.3331
Flexible	N	0	0	0.0757	3.3971	167.96	-0.98586
	H(1)	0.9347	0	-0.3164	-	-	+0.32862
	H(2)	-0.4673	0.8095	-0.3164	-	-	+0.32862
	H(3)	-0.4673	-0.8095	-0.3164	-	-	+0.32862

TABLE IV: Vapour-liquid equilibrium properties of the present ammonia force field with intramolecular degrees of freedom obtained with the GEMC code by Errington¹⁷ and Towhee.¹⁸ Experimental data were determined by correlations.¹⁴

	T / K	$\rho^{liq} / \text{mol l}^{-1}$	$\rho^{vap} / \text{mol l}^{-1}$	p / MPa	$\Delta h_v / \text{kJ mol}^{-1}$
Errington	260	38.7 (1)	0.11 (1)	0.24 (1)	23.3 (5)
Exp.	260	38.5	0.12	0.26	22.3
Errington	280	37.0 (1)	0.24 (1)	0.53 (1)	22.0 (4)
Towhee	280	37.1 (3)	0.25 (4)	0.54 (8)	22.0 (4)
Exp.	280	36.9	0.26	0.55	21.1
Errington	315	34.0 (1)	0.72 (2)	1.63 (3)	19.4 (5)
Towhee	315	33.6 (4)	0.69 (8)	1.6 (2)	19.6 (3)
Exp.	315	33.8	0.74	1.64	18.6
Errington	330	32.3 (2)	1.08 (6)	2.41 (9)	18 (1)
Towhee	330	32.5 (4)	1.2 (2)	2.6 (3)	17.9 (4)
Exp.	330	32.4	1.11	2.42	17.3
Errington	345	30.6 (1)	1.61 (5)	3.50 (6)	16.5 (5)
Towhee	345	30.6 (4)	1.7 (2)	3.6 (4)	16.4 (5)
Exp.	345	30.7	1.62	3.46	15.8
Errington	363	28.0 (1)	2.51 (5)	5.17 (6)	14.2 (5)
Towhee	363	27.8 (5)	2.6 (3)	5.3 (4)	14.0 (5)
Exp.	363	28.4	2.54	5.10	13.7
Errington	375	26.4 (1)	3.4 (1)	6.6 (1)	12.5 (6)
Towhee	375	26.1 (6)	3.6 (4)	6.8 (4)	12.3 (3)
Exp.	375	26.5	3.46	6.49	11.9
Errington	385	24.7 (3)	4.6 (3)	8.2 (3)	10.5 (8)
Towhee	385	24.9 (6)	5.4 (5)	8.9 (8)	10.1 (7)
Exp.	385	24.6	4.55	7.85	10.1

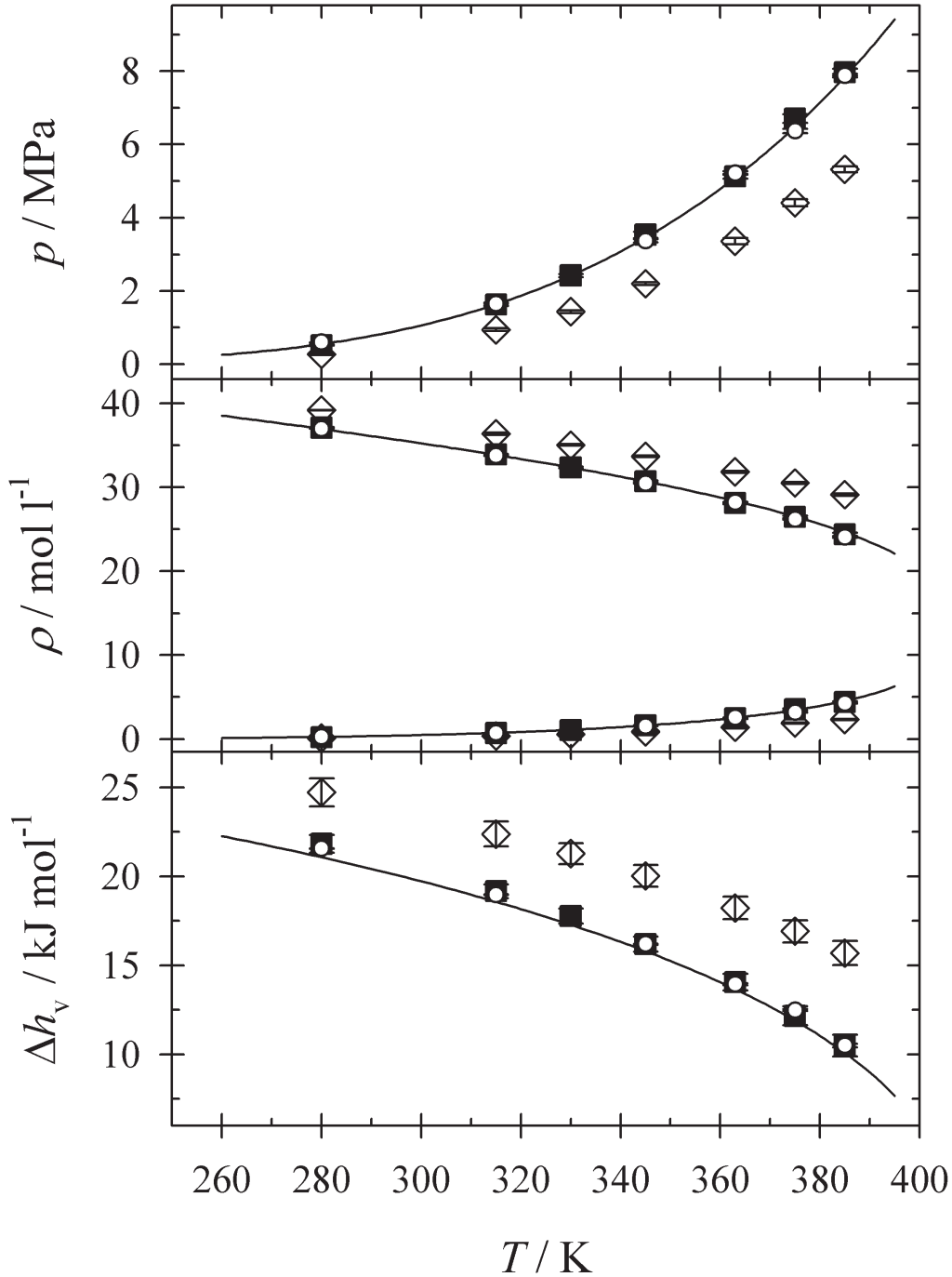


FIG. 1: Vapour-liquid equilibrium properties of the ammonia force field by Eckl et al.⁶ without and with intramolecular degrees of freedom, using the force constants by Shi and Maginn.⁸ The present simulation results, calculated with the Errington code¹⁷ without (full squares) and with intramolecular degrees of freedom (empty diamonds), are compared with the original simulation data by Eckl et al.⁶ (empty circles) and correlations of experimental data¹⁴ (lines). The error bars are often within the symbol size. Top: vapour pressure, center: saturated densities, bottom: enthalpy of vaporisation.

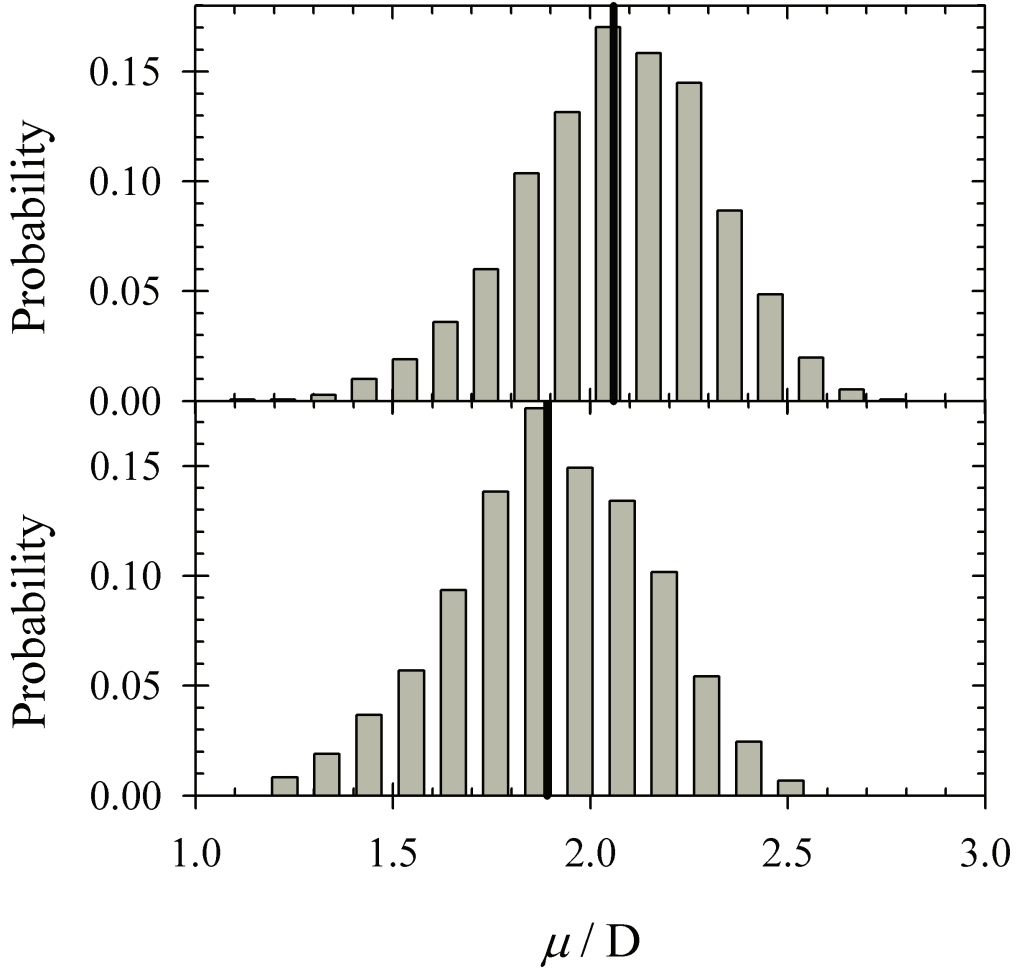


FIG. 2: Distribution of the dipole moment in the saturated liquid (top) and saturated vapour (bottom) at 347.5 K of the originally rigid ammonia force field by Eckl et al.⁶ with intramolecular degrees of freedom, using the force constants by Shi and Maginn.⁸ The data were sampled from six uncorrelated configurations. The vertical lines indicate the average molecular dipole moments $\bar{\mu}^{liq} = 2.06$ D and $\bar{\mu}^{vap} = 1.92$ D in the coexisting phases.

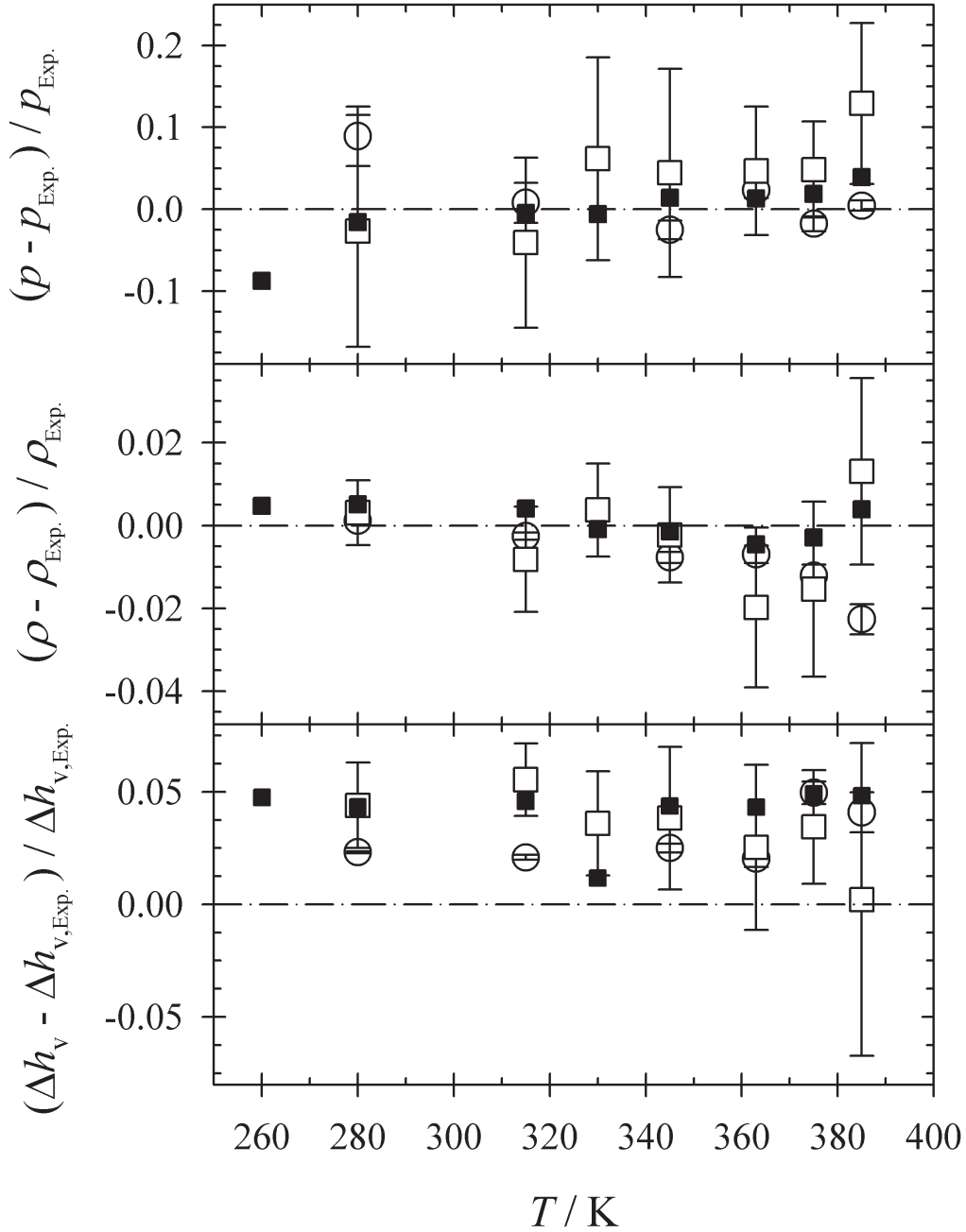


FIG. 3: Relative deviations of the vapour-liquid equilibrium properties of the present ammonia force field with intramolecular degrees of freedom and the rigid ammonia force field by Eckl et al.⁶ (circles) from correlations of experimental data.¹⁴ The present simulations were carried out with two different GEMC simulation tools: the Errington code¹⁷ (full squares) and Towhee¹⁸ (empty squares). For clarity, some error bars were omitted. Top: vapour pressure, center: saturated liquid density, bottom: enthalpy of vaporisation.