# Reorientation relaxation in supercritical ammonia

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## ARTICLE INFO

## ABSTRACT

In the present study, we investigate the reorientation and rotation relaxations of ammonia along the 135 bar isobar and in a range of density between 0.666 g cm$^{-3}$ and 0.074 g cm$^{-3}$. One of our primary interests is in clarifying the changes in the intermediate time behavior of the reorientation correlation, which connects the inertial motion at short time and the diffusive one at long time. Our results show that at low temperatures far from the critical one, the intermediate time behavior of the reorientation correlation of the dipole axis is connected to the anisotropy of the angular velocity correlation around the principal molecular axes. Indeed, at these temperatures, the hydrogen bond interactions are strong enough to affect the angular velocity correlation which is less hindered around the dipole axis than that around its perpendicular one. As a consequence, the intermediate time behavior of the reorientation of the dipole axis is characterized by an occurrence of a kink. At higher temperatures than the critical one, the intermediate time behavior of reorientation of the dipole axis has a free rotor characteristic (a sudden increase of the correlation) and this was associated with the fact that the angular velocity along the molecular axes becomes almost free as a consequence of the weakening of hydrogen bonding.

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## 1. Introduction

Ammonia is an important compound with many industrial applications e.g., uses such as in the manufactures of fertilizers, explosives and pharmaceuticals [1]. Moreover, liquid ammonia is an important solvent and special interest exists in the solutions of solvated electron [2]. As liquid ammonia is an important example of weak hydrogen bond system, the properties of ammonia in supercritical conditions are of fundamental interest. Indeed, a number of experimental investigations have been performed using X-rays [3,4], neutron scattering [5,6], infrared [7], Raman scattering [8–10] and more recently non linear transient spectroscopy [11] as well as theoretical simulations [12–19]. This paper has two main goals. Firstly, it concerns the analysis of the time behavior of the reorientation and the angular velocity correlation functions of ammonia and secondly it is an investigation of the relationship between this time behavior and the changes in the local structure particularly while approaching the critical regime. Indeed, the molecule reorientation should be affected by an effective friction arising from the intermolecular interactions. Therefore, the reorientation correlation should be sensitive to the local density fluctuations on molecular level and particularly to the density inhomogeneities near the critical regime. To some extent, the reorientation dynamics may be described as an interplay between two extreme regimes: one is the

Debye diffusion describing the molecular reorientation at long time which is associated with an exponential time behavior [20]. The other one occurs at short time and is associated with inertial motion. The analysis of the intermediate time behavior of the reorientation correlation, which connects the inertial and the diffusive situations, is of particular interest, since it is directly connected to the change in the local structure. We then carried out molecular dynamics simulations of neat NH$_3$ over wide range densities, along the 135 bar isobar as a function of temperature and in a wide density range between 0.666 g cm$^{-3}$ and 0.074 g cm$^{-3}$.

## 2. Simulations methodology

Molecular dynamics (MD) simulations of the NH$_3$ system have been performed in the isothermal-isobaric ($N,p,T$) ensemble on cubic basic simulation boxes containing 864 molecules. Standard periodic boundary conditions have been applied. The force field used in our simulation was consisting of Lennard–Jones (LJ) and charge–charge Coulombic interactions and the corresponding parameters are given in Table 1. The total potential is written as follow:

$$U = \sum_{i\alpha} \sum_{j\beta} \left[ U^{LJ}\left(r_{i\alpha\beta j}\right) + U^{EL}\left(r_{i\alpha\beta j}\right) \right] \tag{1}$$

$$= \sum_{i\alpha} \sum_{j\beta} \left[ 4\varepsilon_{i\alpha j\alpha} \left( \left(\frac{\sigma_{i\alpha\beta j}}{r_{i\alpha\beta j}}\right)^{12} - \left(\frac{\sigma_{i\alpha\beta j}}{r_{i\alpha\beta j}}\right)^{6} \right) + \frac{q_{i\alpha} q_{j\beta}}{r_{i\alpha\beta j}} \right],$$

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**Table 1**
Parameters of the molecular potential model of ammonia. $r_{NH}$ is the distance between nitrogen and hydrogen atom. ∠HNH is the angle between H–N and N–H axes. µ is the molecular dipole moment.

| Site | ε(kcal) | σ(Å) | q(e) | $r_{NH}$(2Å) | ∠HNH (degree) | µ(D) |
|------|---------|------|------|------|------|------|
| N | 0.338 | 3.385 | −1.035 | 1.0124 | 106.7 | 1.90 |
| H | 0 | 0 | 0.345 | | | |

where $r_{i\alpha\beta j}$ is the distance between a site α on molecule i and a site β on molecule j, $q_{i\beta}$ is the charge on site β on molecule i, $q_{j\alpha}$ is the charge on site α on molecule j. ε and σ are the LJ parameters. The potential model used in this analysis was proposed by Kristof et al. [21] The calculated critical temperature, $T_c$, and the critical density, $\rho_c$ of this model are $T_c = 400$ K, $\rho_c = 0.218$ g cm$^{-3}$ which are quite close to the experimental values $T_c = 405.4$ K, $\rho_c = 0.225$ g cm$^{-3}$ [22]. The simulations have been performed using the DL_POLY program [23]. The temperature and pressure of the system have been kept constant by means of the weak coupling algorithms of Berendsen, using the coupling parameter values of 0.1 ps (temperature) and 0.5 ps (pressure). The van der Waals interactions have been truncated to zero beyond the center–center cut-off distance of 14 Å. And the long range part of the electrostatic interactions has been accounted for using the Ewald summation method. The equations of motion have been integrated using the leap-frog algorithm using a time step of 1.0 fs. The systems have been equilibrated by generating 5 ns long trajectories for each thermodynamic point.
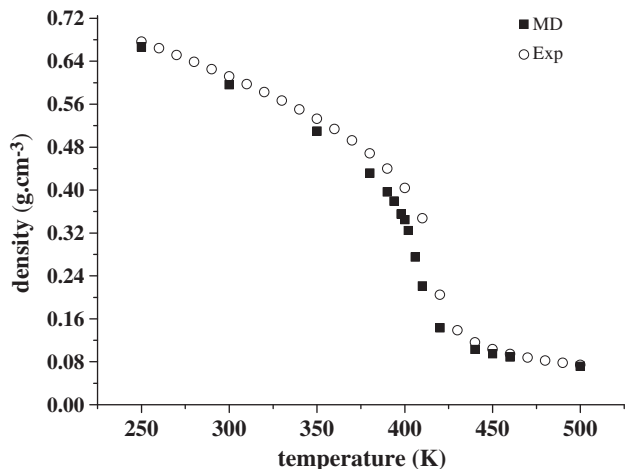
A good agreement was found between the experimental and calculated values for quantities such as the heat of vaporization, the structure, the liquid–gas coexistence curve [21], the density [22] (see Fig. 1), the thermal expansion [22] (see Fig. 2) and the diffusion coefficient [24,25] (see Fig. 3).

The relevant dynamical quantities computed in this work are the reorientation correlation function, $C_\ell^u(t)$ and the angular velocity correlation function $\Omega(t)$ which are defined as follow:
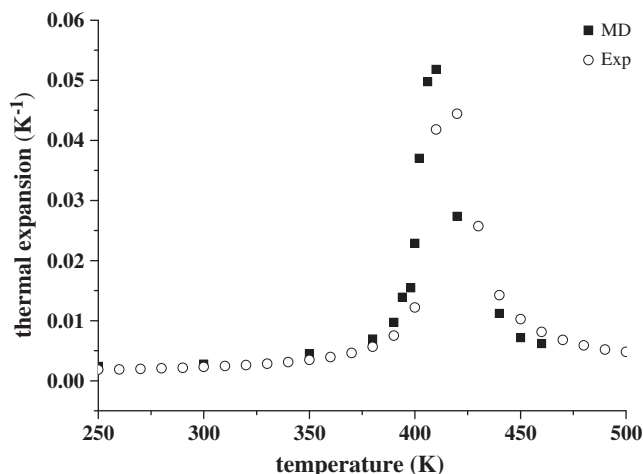
$$C_\ell^u(t) = \langle P_\ell(\mathbf{u}(t).\mathbf{u}(0)) \rangle \tag{2}$$

$$\Omega(t) = \langle \omega(t).\omega(0) \rangle \tag{3}$$

$\mathbf{u}$ is a unit vector along one of the principal axes of the molecule (see Fig. 4), $\omega(t)$ is the angular velocity and P is the Legendre Polynomial with order $\ell$. As the x and y axes are equivalent by symmetry, we will discuss only the reorientation correlation of the x and z axes as well as the angular velocity around these axes (see below). The order $\ell$ of the

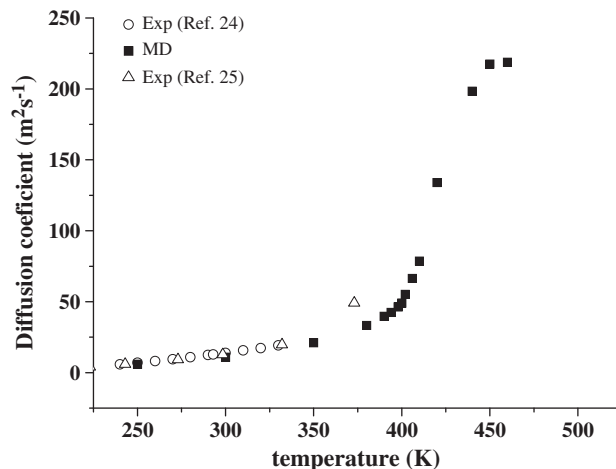**Fig. 2.** Comparison between the calculated and experimental thermal expansion [22].

Legendre polynomial being 1 if the MD results are compared with those obtained by infrared absorption experiment and being 2 if the comparison is done with those obtained by Raman scattering, NMR or fluorescence depolarization experiments. For a molecule having a permanent dipole moment, it is usually appropriate that $\mathbf{u}$ be taken in the direction of the principal axis of symmetry (here is the z axis). To quantify the reorientation dynamics of ammonia molecule, the reorientation correlation time $\tau_\ell^u$ (u = x,z) of the x and z axes were calculated as follow:

$$\tau_\ell^u = \int_0^{+\infty} C_\ell^u(t)dt \tag{4}$$

## 3. Results

### 3.1. Reorientation

The behavior of the reorientation correlation functions $C_\ell^u(t)$ (u = x,z) of the z and x molecular axes are given in Fig. 5A and B, respectively. One sees that upon a density decrease, it takes progressively smaller time for a reorienting principal axes to move to any particular displacement angle and thus the reorientation correlation function will decay on a smaller time. This is confirmed by

**Fig. 1.** Comparison between the calculated and experimental densities along the isobar 135 bar [22].

**Fig. 3.** Comparison between the calculated and experimental diffusion coefficient [24,25].