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Time correlation functions of the vibrational frequency of nitrogen and of nitrogen in helium

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It is known from experimental evidence that, at ambient temperature and under high pressures, the linewidth of the Raman Q branch of nitrogen diluted in helium is considerably less than that of pure nitrogen. Molecular dynamics simulations have been used to explore this phenomenon. For that purpose, a detailed investigation has been made of the various contributions to the vibrational spectrum, and in particular of the time correlations of each of those parts. The results are not only in conformity with the experimental data, but also reveal which molecular properties are responsible for the evident differences between the Raman spectra of the two systems. A strong conclusion is that in the dilute mixture the linewidth is related primarily to the properties of the diluent and to a much lesser extent to the interactions between nitrogen and helium molecules. In fact, a vibrating nitrogen molecule in an environment of helium acts as a probe, signalling intrinsic dynamic behaviour of the helium system. The oscillation in the correlation function of the vibration frequency turns out to be due to a vibration in the mutual forces acting between the atoms and does not arise from the N₂-He interaction.

1. Introduction

In the past two decades, various investigators [1–17] have tried to calculate the linewidth and line-shift of Raman spectra of simple fluids, either by analytical methods or by computer simulations. Several models used are rather simple and schematic; sometimes *ad hoc* adjustments had to be made to provide for some agreement with experimental data. Presumably, the first sophisticated attempt using a numerical approach is that reported by Levesque *et al.* [7], who performed dynamic computer simulations of nitrogen, just above the boiling point. These authors investigated the various contributions to the vibration frequency and the self- and cross-correlations of these contributions separately. Due to an impractical, although still significant, definition of correlation times, the results concerning the effect on the linewidth are somewhat confusing. The first numerical investigation of the density dependence of dephasing time has been carried out by Chesnoy and Weis [10] but by the use of a spherical symmetric model for the intermolecular potential the rotational degrees of freedom had been excluded.

In previous papers [15, 17] we reported experimental studies as well as computer simulations performed on nitrogen and mixtures with nitrogen, in order to study the Raman Q branch in the fluid phase within a large pressure range. One of the marked results is a large difference between the linewidth in pure nitrogen and

in nitrogen diluted in helium, behaviour that has been found in the simulations as well. It turned out from these simulations that this difference is, for the greater part, due to the difference in the total correlation time of the vibration frequency. Another striking feature that is seen in both systems is the increase in the linewidth with pressure after passing through a minimum. Further, some very different behaviour is seen for the autocorrelation function of the vibration frequencies for pure N₂ and for the infinite dilution of N₂ in He. Because it turned out that in both systems the vibration-rotation coupling has an important influence on the density dependence of the line width, the numerical approach by Chesnoy and Weis seems not to be very helpful for a quantitative study.

In this paper, more detailed information is given about the time correlation functions, including the influence of the separate contributions on the total correlation function. Apart from realistic model systems, based on potential parameters for N₂, He and their mutual interactions, fictitious models have been introduced as well, in order to reveal separately the influence of mass and size of the diluent molecules. From the results of these simulations it can be concluded that the difference in the time correlation functions for pure nitrogen and the dilute mixture of nitrogen in helium is due primarily to the mass and to the mutual interaction between the diluent molecules, and less to the inter-

actions of the nitrogen molecule with the solvent molecules.

2. Method

A full description of the calculation procedure is given in [15] and [17]. For convenience the method is given briefly below.

2.1. The dynamics

Nitrogen has been modelled by a two-site potential model with a fixed interatomic distance of 1.094 Å. The potential between the atoms (sites) of distinct nitrogen molecules has been defined with an exponential short range energy and a long range dispersive potential, proportional to the inverse sixth power of the distance; a quartic spline deals with intermediate distances. The parameters used are those given by Eters *et al.* [18], but in contrast to that potential, no quadrupole interaction was taken into account. For the interaction between nitrogen atoms and helium molecules and for the mutual interaction in helium use has been made of Buckingham (exponential-6) potentials:

$$\varphi(r) = \frac{\varepsilon}{\alpha - 6} \left\{ 6 \exp \left[\alpha \left(1 - \frac{r}{r_m} \right) \right] - \alpha \left(\frac{r_m}{r} \right)^6 \right\}. \quad (1)$$

For the interaction between a nitrogen atom and a helium atom values for the molecular parameters have been chosen such that a numerical potential for the N₂-He potential, obtained by *ab initio* calculations by Rijks *et al.* [19] is fairly well approximated. For the mutual helium interactions, the values given by Kortbeek and Schouten [20] have been applied. The numerical values will be given in section 3. All simulations consider a system of 256 particles in the *NVE* ensemble.

2.2. Calculation of the vibration frequency

The change in the vibration frequency due to the surrounding molecules was calculated from the momentary axial force and the derivative of that force to the bondlength. These effects will be indicated with, respectively, the 'external first order' (e1) and the 'external second order' (e2). The third cause for the change in the frequency is the vibration-rotation coupling (vr). In these calculations, use has been made of the values for the harmonic and cubic potential parameters of the intramolecular forces in nitrogen, given by Herzberg [21] and Lavorel *et al.* [22]. Moreover, a fourth effect, due to the change in the dispersion energy at excitation (d) is taken into account. In [15] the procedure is given for how this effect is quantified by comparison of simulation results with experimental data for the line shift. Thus, the resulting vibration frequency ω_{vib} of a molecule

as function of time can be written as

$$\begin{aligned} \omega_{\text{vib}} &= \omega_0 + \omega(t) \\ \omega(t) &= \omega_{\text{e1}}(t) + \omega_{\text{e2}}(t) + \omega_{\text{vr}}(t) + \omega_{\text{d}}(t), \end{aligned} \quad (2)$$

with ω_0 the frequency of an isolated, non-rotating molecule.

Next, the amplitude of modulation Δ , the autocorrelation function Ω and the correlation time τ_c have been calculated with the relations:

$$\Delta = \left\{ \langle \omega(t)^2 \rangle - \langle \omega(t) \rangle^2 \right\}^{1/2}, \quad (3)$$

$$\Omega(t) = \frac{\langle \omega(0)\omega(t) \rangle - \langle \omega(0) \rangle \langle \omega(t) \rangle}{\Delta^2}, \quad (4)$$

$$\tau_c = \int_0^\infty \Omega(t) dt. \quad (5)$$

The brackets in equations (3) and (4) denote the averaging over all particles throughout the entire simulation run. Finally, the linewidth, defined as the full width at half maximum (FWHM) can be obtained with

$$\text{FWHM} = 2\Delta^2\tau_c. \quad (6)$$

3. Results

3.1. Pure nitrogen

New simulations have been performed for nitrogen at 296 K and at pressures of 0.45, 1.1 and 2.0 GPa. The results for the autocorrelation function during the first 0.3 ps are displayed in figure 1. For this and the following figures the reproducibility of the correlation

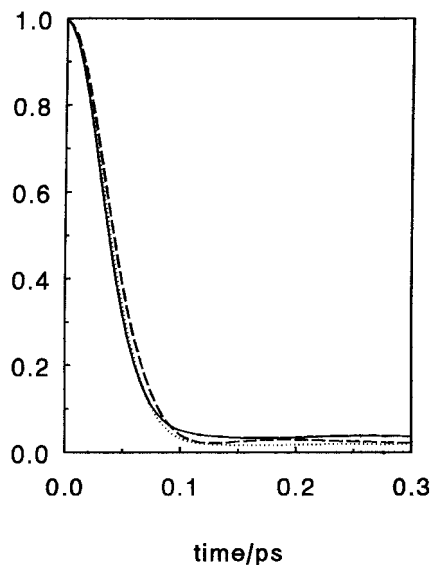


Figure 1. Autocorrelation function of the vibration frequency of nitrogen at 296 K: dashed line, 0.45 GPa; dotted line, 1.1 GPa; and solid line, 2.0 GPa.

functions was always better than the thickness of the lines for values of the functions above 0.2, and less than 0.01 for values smaller than 0.2, thus, in the long term region. At all these pressures $\Omega(t)$ falls off rapidly during the first 0.1 ps; the decay increases slightly with pressure. At 0.45 GPa a small but reproducible maximum is seen at about 0.2 ps, after which the function diminishes gradually. At 1.1 GPa the hump has disappeared. At the highest pressure, a long term tail is seen which is the main cause for an increase in the linewidth under increasing pressure above ≈ 0.6 GPa, as found experimentally. Since one would expect a decrease in the correlation time at higher densities due to the increase in the rate of scattering interactions, it is interesting to find out which mechanism is responsible for this effect. Therefore, the autocorrelation function has been determined in separate terms for each of the four effects mentioned above:

$$\Omega_{\alpha,\beta}(t) = \{ \langle \omega_\alpha(0)\omega_\beta(t) \rangle - \langle \omega_\alpha(0) \rangle \langle \omega_\beta(0) \rangle \} / \Delta^2 \quad (7)$$

$$\Omega(t) = \sum_{\alpha,\beta} \Omega_{\alpha,\beta}, \quad (8)$$

where α and β denote e1, e2, vr or d, and Δ is again the total amplitude of modulation. From these functions the separate contributions to the correlation time and the total correlation time have been obtained by the integrations

$$\tau_{\alpha,\beta} = \int_0^\infty \Omega_{\alpha,\beta}(t) dt, \quad (9)$$

$$\tau_c = \sum_{\alpha,\beta} \tau_{\alpha,\beta}. \quad (10)$$

The total correlation function consists of 4 self-correlations and 6 cross terms. (The off-diagonal terms are in pairs symmetric.) These functions are presented separately in figure 2, and table 1 gives the values for the terms $\tau_{\alpha,\beta}$, together with the values for all correlation functions $\Omega_{\alpha,\beta}$ at $t = 0$. For completeness, the amplitude of modulation (equation (3)) and the linewidth, obtained from equation (6) have been added to the table.

Before going into a discussion about the results, it may be useful to call to mind that the origin of the frequency change due to vibration–rotation coupling is fundamentally different from the other three effects. While the latter are due to molecular interaction, the vr coupling is due to the velocity of rotation. It is an axiom in statistical physics that these entities are momentary independent. Thus, all cross correlations with vr terms must be zero at $t = 0$, as is seen indeed (apart from the statistical errors) in the MD results. Consequently, cross terms that include the vibration–rotation coupling do not contribute to the amplitude

of modulation, defined with relation (3). Another corollary deals with the definition of the correlation time, especially with the partial contribution for each effect. Levesque *et al.* [7] introduced another partial correlation function $\Omega'_{\alpha,\beta}(t)$ and correlation time $\tau'_{\alpha,\beta}$:

$$\Omega'_{\alpha,\beta}(t) = \frac{\langle \omega_\alpha(0)\omega_\beta(t) \rangle - \langle \omega_\alpha(0) \rangle \langle \omega_\beta(0) \rangle}{\Delta_{\alpha,\beta}^2}, \quad (11)$$

with

$$\Delta_{\alpha,\beta} = \{ \langle \omega_\alpha(0)\omega_\beta(0) \rangle - \langle \omega_\alpha(0) \rangle \langle \omega_\beta(0) \rangle \}^{1/2} \quad (12)$$

and

$$\tau'_{\alpha,\beta} = \int_0^\infty \Omega'_{\alpha,\beta}(t) dt. \quad (13)$$

Because $\Delta_{\alpha,\beta}$ equals zero in the case when *either* α or β denotes the vibration–rotation coupling, the corresponding $\tau'_{\alpha,\beta}$ becomes undefined and cannot be included in the total correlation time. Therefore their definition is less satisfactory. In our definition (equation (10)) the correlation time τ_c is written as a sum of terms $\tau_{\alpha,\beta}$ for each of the effects.

The results are presented in table 1 and figure 2. The total amplitude of modulation Δ increases by about 50% when the pressure is increased from 0.45 GPa to 2.0 GPa. The value of $\Omega_{\alpha,\beta}$ at $t = 0$ gives the relative contribution of the mechanism under consideration to the total amplitude. The relative contribution of $\Omega_{vr, vr}(0)$ reduces from 20% at 0.45 GPa to 8.5% at 2 GPa, but still is considerable. The relative contribution of $\Omega_{e1, d}(0)$ increases substantially. The contributions of the cross correlations to the amplitude are very important since they sum up to 27% at 0.45 GPa and even to 37% at 2 GPa. It is obvious that, due to the finite statistical uncertainties, the observed values for $\Omega_{vr, \alpha}(0)$ with $\alpha \neq vr$ will not exactly equal zero. Figure 2 shows that the self-correlation due to both the e1 and the vr effects (and cross correlation) is significant at times above 0.1 ps and that this behaviour is responsible for the long term tail. At low pressures the contribution from the vibration–rotation coupling to the tail is dominant but at high pressures the e1 effect prevails. At the lowest pressures the correlation time decreases rapidly as a function of pressure [15] In the pressure range under consideration here, τ_c varies only slowly and increases with about 20% from 1.1 GPa to 2 GPa. Also in this case the cross correlations are very important. It should be noted that all cross terms that include the vr effect are negative. At 0.45 GPa the largest single contribution comes from the self-correlation of the vibration–rotation coupling, but this value has been reduced by a factor of 7 at 2 GPa. The total vr effect, including the cross correlations, on τ_c is negative (8.5% at 0.45 GPa, 33% at 1.1 GPa, and 20% at 2 GPa).

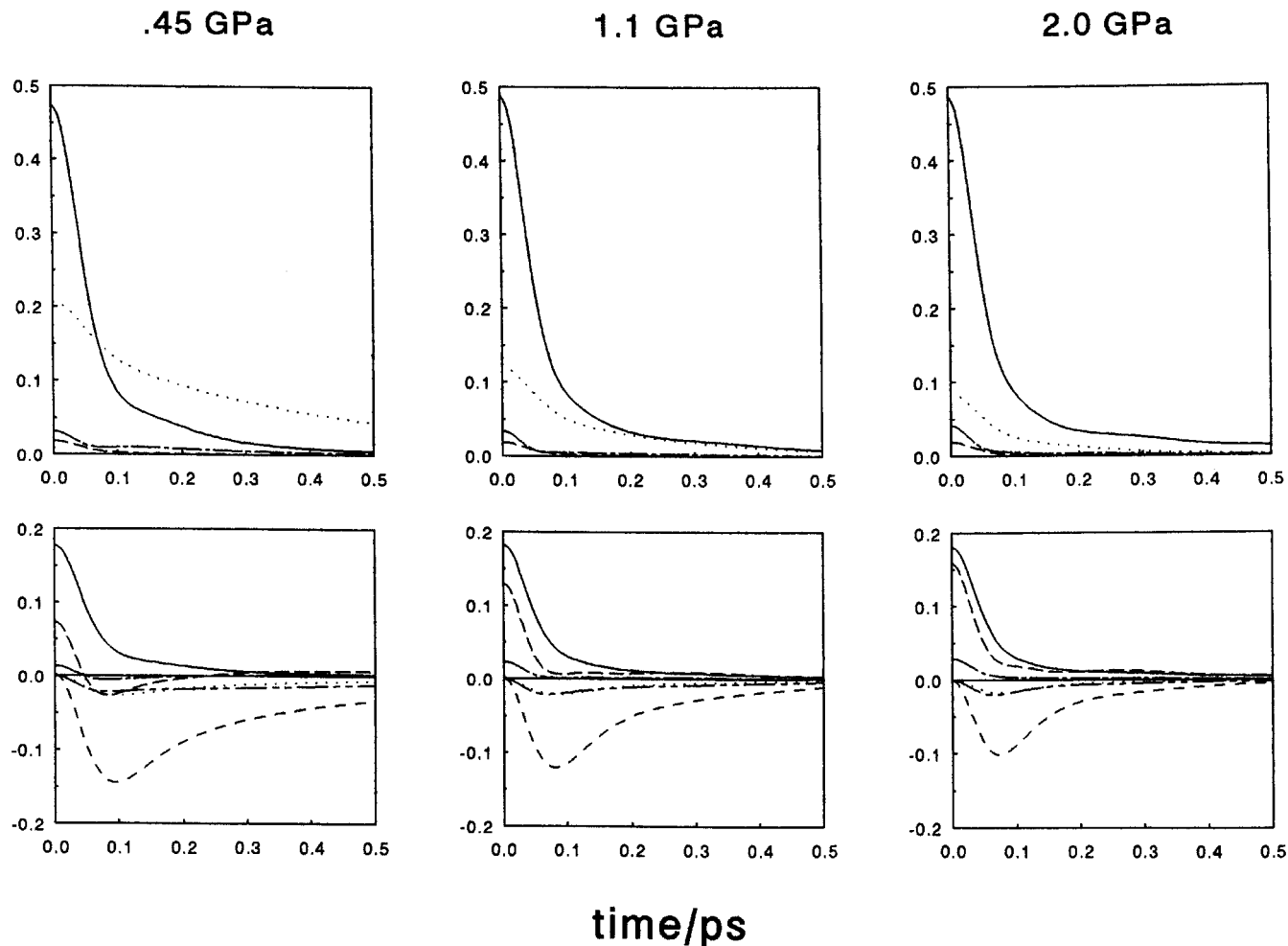


Figure 2. Contributions to the correlation function of the vibration frequency of nitrogen at several pressures. Upper figures: solid line, the autocorrelations due to the first-order (e_1) effect; dashed line, the second-order (e_2); dotted line, vibration-rotation coupling (vr); and dash-dotted line, dispersion correction (d). Lower figures, due to the cross-correlations with nonzero values at $t = 0$: solid line, e_1 - e_2 ; dashed line, e_1 - d ; dash-dotted line, e_2 - d ; and with zero values at $t = 0$: dashed line, e_2 - vr ; dotted line, e_2 - vr ; and dash-dot-dot line, vr - d .

Remarkably, the cross correlations of the dispersion with e_1 and e_2 increase considerably under pressure while the self-correlations of e_1 , e_2 and d vary only slightly. The total effect of the dispersion on τ_c is negative at 0.45 GPa but positive at 2 GPa. A clear conclusion is that the influence of the vibration-rotation coupling in detail on the correlation time and the amplitude of modulation is large across the whole pressure range. Due to cancellations between self-correlation and cross terms, and between amplitude and correlation time, the net effect on the linewidth is modest at the highest pressures, but still present.

3.2. Nitrogen in helium

It is known from experimental results that at room temperature and high pressures the linewidth of the

Raman line of nitrogen diluted in helium [23, 24] is considerably less than that of pure nitrogen [23, 25]. This phenomenon has been observed also with computer simulations [15, 17]. It is seen from these simulations that this difference in linewidth is predominantly caused by the much shorter total correlation time of nitrogen in the dilute solution. In order to study this effect in more detail, some new simulations have been performed of one N_2 particle in helium, with special attention to the separate time correlation functions as has been done in the previous section for pure nitrogen. As has been noted in [17], the change in dispersion energy due to excitation is negligible in this case. Consequently, correlations including this effect have been omitted. In figure 3 the initial part of the total correlation functions for $p = 1.1, 2.0, 5.3$ and 8.7 GPa, all at

Table 1. Results for the correlation times and functions, amplitude of modulation and linewidth for nitrogen at 296 K and three pressures, obtained by molecular dynamics simulations. The values indicated with 'total' denote the integral τ_c of the total correlation function $\Omega(t)$ and the value of this correlation function at $t = 0$. Small differences between these 'total' values and the sum of the separate contributions are due to arithmetical and round off errors.

α, β	$p = 0.45 \text{ GPa}$		$p = 1.1 \text{ GPa}$		$p = 2.0 \text{ GPa}$	
	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$
e1-e1	0.0391	0.4711	0.0403	0.4887	0.0423	0.4862
e2-e2	0.0014	0.0184	0.0014	0.0189	0.0015	0.0189
vr-vr	0.0657	0.2061	0.0195	0.1198	0.0093	0.0845
d-d	0.0051	0.0317	0.0030	0.0341	0.0037	0.0417
e1-e2	0.0146	0.1788	0.0147	0.1830	0.0153	0.1814
e1-vr + vr-e1	- 0.0482	0.0025	- 0.0257	0.0013	- 0.0156	- 0.0004
e1-d + d-e1	0.0027	0.0742	0.0090	0.1303	0.0127	0.1590
e2-vr + vr-e2	- 0.0090	0.0004	- 0.0046	0.0003	- 0.0027	0.0000
e2-d + d-e2	0.0005	0.0135	0.0017	0.0235	0.0023	0.0287
vr-d + d-vr	- 0.0134	0.0000	- 0.0065	0.0002	- 0.0038	0.0000
Total	0.0585	1.0000	0.0528	1.0000	0.0649	1.0000
	$\Delta = 4.029 \text{ cm}^{-1}$ FWHM = 0.358 cm^{-1}		$\Delta = 5.245 \text{ cm}^{-1}$ FWHM = 0.547 cm^{-1}		$\Delta = 6.184 \text{ cm}^{-1}$ FWHM = 0.935 cm^{-1}	

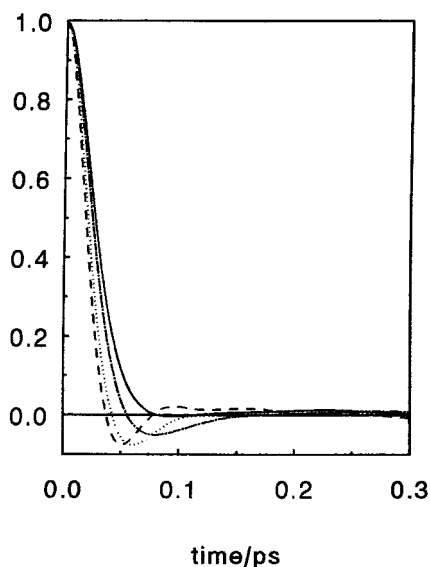


Figure 3. Autocorrelation function of the vibration frequency of a single nitrogen molecule in helium at 296 K and at various pressures: solid line, 1.1 GPa; dash-dotted line, 2 GPa, dotted line, 5.3 GPa and dashed line, 8.7 GPa.

296 K, have been plotted simultaneously. In comparison with pure nitrogen, these functions fall off more rapidly during the first moments: the higher the pressure, the faster this decrease. Above $\approx 1 \text{ GPa}$ the correlation functions become negative, a phenomenon that is not seen in the system of pure nitrogen. Even a superficial comparison between figures 1 and 3 will make clear that the integral of these functions, and hence the correlation times, are much less in the case of diluted nitrogen.

Numerical results for the distinct correlation times $\tau_{\alpha,\beta}$ and $\Omega_{\alpha,\beta}(0)$, together with the amplitude Δ and the corresponding width of the resulting line, are given in table 2. Figure 4 displays the separate correlations for the first 0.3 ps. A marked feature is seen in the behaviour of the self-correlation of the first-order effect: for all pressures considered the function becomes negative before levelling out to zero. At 5.3 GPa and 8.7 GPa the function changes in sign again. The correlation reveals a long time persistence at 8.7 GPa. The oscillations seen above $\approx 0.1 \text{ ps}$ are small but still significant. The time interval between $t = 0$ and the transition to negative values as well as the oscillations become shorter at higher pressures. As in the case for pure N_2 the self-correlation for the vibration-rotation coupling decreases rapidly with increasing pressure. In the figures of the cross correlations, negative parts are seen not only for the terms which include the vr coupling but also in the 'e1-e2' term. Again the functions fade out more rapidly at higher pressures.

3.3. Fictitious diluent models

It is obvious that the differences that occur in the vibration of a nitrogen molecule, when surrounding nitrogen molecules are substituted by helium molecules, are due to the large differences in the molecular properties. Most pronounced is the difference in mass, but also the difference in size, i.e., the range and strength of the intermolecular forces is considerable. Moreover, the absence of rotational freedom in helium must be considered. Computer simulations offer an unique tool for the investigation of the influences of these factors

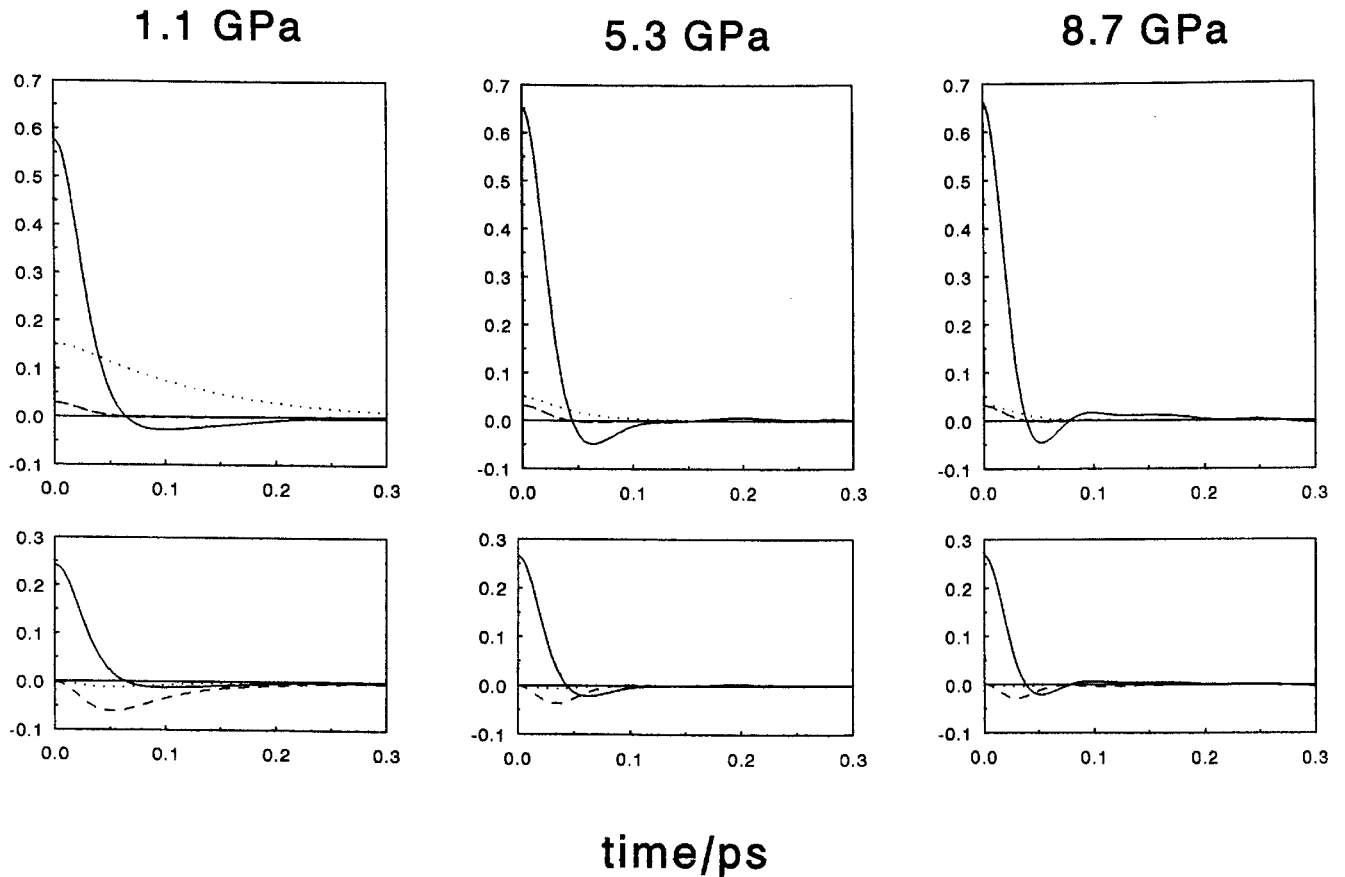


Figure 4. Contributions to the correlation function of the vibration frequency of a single nitrogen molecule in helium at various pressures. Top figures, the autocorrelations due to: solid line, the first-order effect (e1); dashed line, the second-order effect (e2); and dotted line, the vibration-rotation coupling (vr); lower figures, due to the cross correlations: solid line, e1-e2; dashed line, e1-vr; and dotted line, e2-vr.

Table 2. Results for one nitrogen molecule in helium at 296 K, obtained by molecular dynamics simulations.

α, β	$p = 1.1 \text{ GPa}$		$p = 2.0 \text{ GPa}$		$p = 5.3 \text{ GPa}$		$p = 8.7 \text{ GPa}$	
	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$
e1-e1	0.0138	0.5783	0.0133	0.6169	0.0128	0.6541	0.0132	0.6650
e2-e2	0.0007	0.0285	0.0007	0.0300	0.0006	0.0312	0.0006	0.0315
vr-vr	0.0198	0.1516	0.0083	0.0979	0.0024	0.0484	0.0013	0.0335
e1-e2 + e2-e1	0.0058	0.2428	0.0055	0.2564	0.0051	0.2669	0.0052	0.2685
e1-vr + vr-e1	- 0.0071	- 0.0009	- 0.0032	- 0.0009	- 0.0015	- 0.0005	- 0.0013	0.0012
e2-vr + vr-e2	- 0.0013	- 0.0003	- 0.0005	- 0.0002	- 0.0002	- 0.0001	- 0.0002	0.0003
Total	0.0317	1.0000	0.0240	1.0000	0.0193	1.0000	0.0189	1.0000
	$\Delta = 4.703 \text{ cm}^{-1}$ FWHM = 0.264 cm^{-1}		$\Delta = 5.748 \text{ cm}^{-1}$ FWHM = 0.299 cm^{-1}		$\Delta = 8.222 \text{ cm}^{-1}$ FWHM = 0.491 cm^{-1}		$\Delta = 9.911 \text{ cm}^{-1}$ FWHM = 0.698 cm^{-1}	

separately. We have studied the various mechanisms by varying the molecular quantities of helium to that of nitrogen in four discrete steps.

First, simulations have been performed for one nitrogen particle in an environment of fictitious particles which are identical with helium as far as the molecular

interactions are concerned, but with atomic mass $m = 10$ and $m = 28$; for convenience indicated hereafter with ^{10}He and ^{28}He . The density of the system was fixed to 125 kmol m^{-3} , which resulted in a pressure of 2 GPa at 296 K. The results for the total and partial correlation functions are given in figures 5 and 6, respectively, and

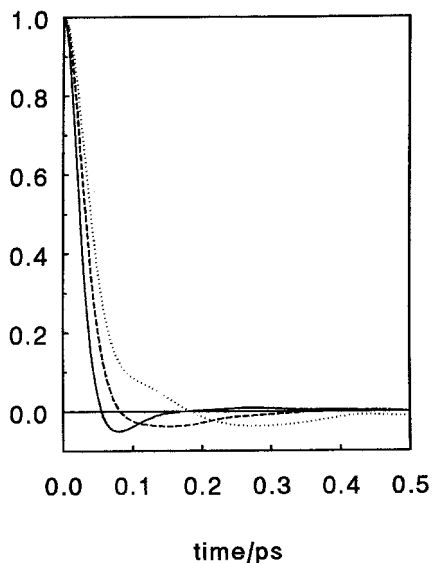


Figure 5. Influence of the atomic mass m of the solvent molecules on the correlation function $\Omega(t)$ of a single nitrogen molecule for $p = 2$ GPa; $T = 296$ K: solid line, $m = 4$; dashed line, $m = 10$; and dotted line, $m = 28$.

in table 3. For comparison the results for ${}^4\text{He}$ are repeated in table 3. Clearly, the values for $\Omega_{\alpha,\beta}(0)$, and consequently for Δ , are independent of the mass, which is understandable since the momentary forces are independent of the mass, but the evolution of the correlations progress more slowly, apparently due to the decrease in the speed of the ${}^m\text{He}$ atoms with increase of m . The remarkable negative part in $\Omega_{e1,e1}(t)$ becomes less pronounced but persists for a longer time with increasing m and clearly is still present in ${}^{28}\text{He}$. All self-correlation times and the cross correlation time $\tau_{e1,e2}$ increase with m , giving rise to an increase in the linewidth, although this increase is reduced to half its value by growing negative contributions of $\Omega_{e1,vr}(t)$ and $\Omega_{e2,vr}(t)$.

Another large difference between helium and nitrogen is the strength of the interaction potential. The mutual interactions between the helium atoms, as well as the site-site interactions with the nitrogen atoms are modelled in the simulations with a Buckingham potential,

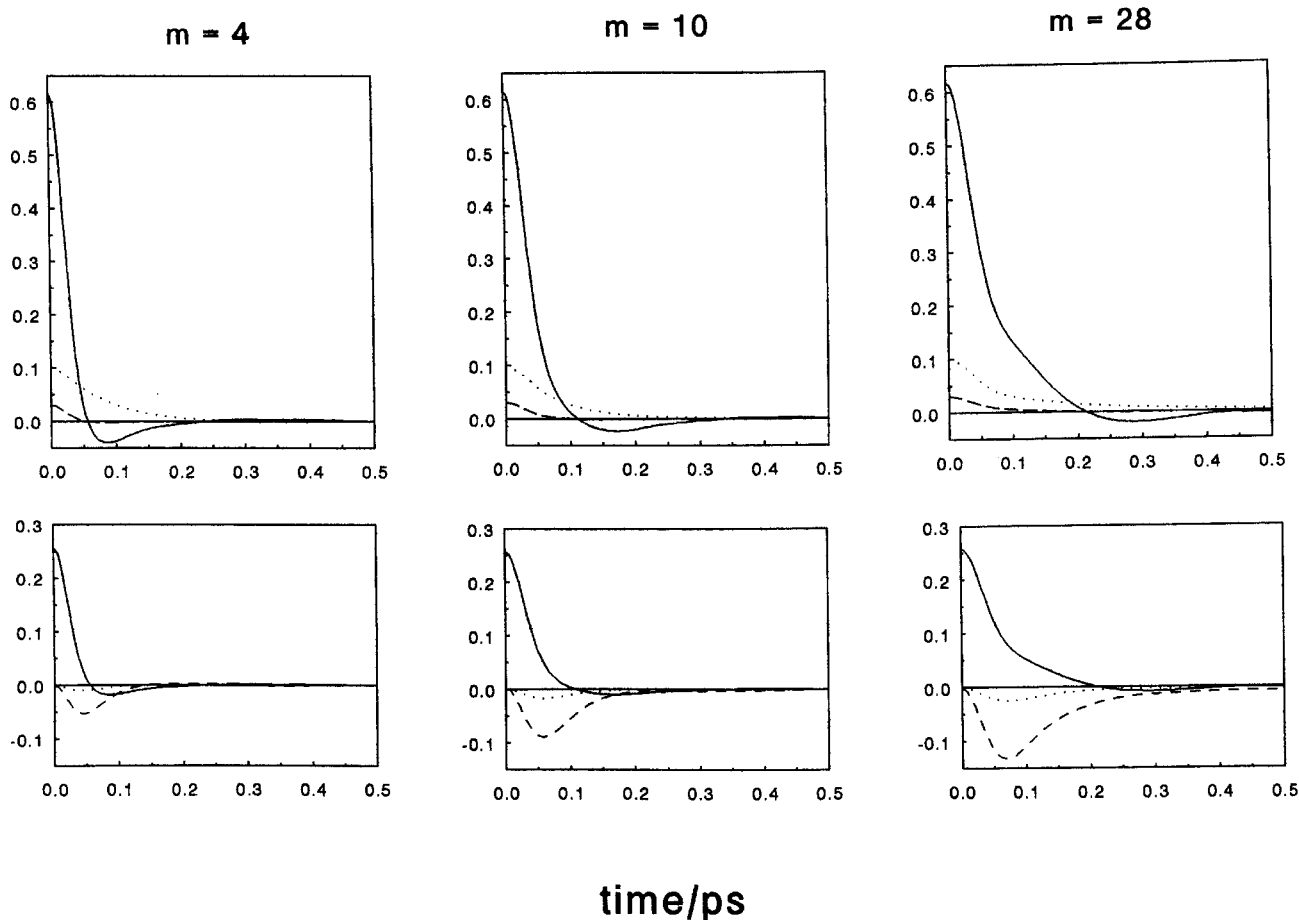


Figure 6. Influence of the mass of the solvent molecules on the correlation functions of the vibration frequency of a single nitrogen molecule for $p = 2$ GPa. Symbols as for figure 4.

Table 3. Influence of the atomic mass m of the surrounding molecules on a single nitrogen molecule. The parameters for the intermolecular interactions are in conformity with those for helium.

α, β	$m = 4$		$m = 10$		$m = 28$	
	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$
e1-e1	0.0133	0.6169	0.0220	0.6145	0.0386	0.6165
e2-e2	0.0007	0.0300	0.0011	0.0302	0.0018	0.0302
vr-vr	0.0083	0.0979	0.0082	0.0975	0.0112	0.0985
e1-e2 + e2-e1	0.0055	0.2564	0.0091	0.2565	0.0159	0.2572
e1-vr + vr-e1	- 0.0032	- 0.0009	- 0.0087	0.0011	- 0.0212	- 0.0019
e2-vr + vr-e2	- 0.0005	- 0.0002	- 0.0016	0.0002	- 0.0042	- 0.0005
Total	0.0240	1.0000	0.0300	1.0000	0.0421	1.0000
	$\Delta = 5.748 \text{ cm}^{-1}$ FWHM = 0.299 cm^{-1}		$\Delta = 5.751 \text{ cm}^{-1}$ FWHM = 0.374 cm^{-1}		$\Delta = 5.748 \text{ cm}^{-1}$ FWHM = 0.525 cm^{-1}	

defined in equation (1). For the He-He interaction, parameter values given by Kortbeek and Schouten [20] have been applied:

$$\begin{aligned} \varepsilon_{\text{He}}/k_{\text{B}} &= 9.76 \text{ K}, \\ r_{m,\text{He}} &= 3.0826 \text{ \AA}, \\ \alpha_{\text{He}} &= 12.55. \end{aligned} \quad (14)$$

For interactions between an He atom and each site (atom) of a N_2 molecule these values have been chosen as [17]

$$\begin{aligned} \varepsilon_{\text{He-N}}/k_{\text{B}} &= 16 \text{ K}, \\ r_{m,\text{He-N}} &= 3.5 \text{ \AA}, \\ \alpha_{\text{He-N}} &= 14.5. \end{aligned} \quad (15)$$

Some subsequent simulations have been performed with other values for ε/k_{B} and r_m than noted in definitions (14) and (15). In all these simulations the temperature was 296 K, while the pressure was adjusted to 2 GPa by choosing the appropriate density.

For the investigation of the influence of the potential strength between the helium atoms, simulations have been performed with three different values for ε_{He} , but all with the same interaction between N_2 and 'He' (definition (15)). In contrast with previous simulations, given in [17] the cutoff length had been increased to 7 \AA . The following values for $\varepsilon_{\text{He}}/k_{\text{B}}$ have been chosen: 9.76 K (i.e., the 'realistic' value); 40 K; and 90 K, this being about the value for nitrogen, together with $\varepsilon_{\text{He-N}}/k_{\text{B}} = 16 \text{ K}$. Next, one run has been made with $\varepsilon_{\text{He}}/k_{\text{B}} = 90 \text{ K}$ but with $\varepsilon_{\text{He-N}}/k_{\text{B}} = 40 \text{ K}$. The results are given in table 4 and figures 7-9. A comparison with the results given in [17] shows that, at $\varepsilon_{\text{He}}/k_{\text{B}} = 9.76 \text{ K}$, the increase in cutoff length mentioned above indeed does not lead to significant changes in the behaviour of the total correlation function and the amplitude of modulation;

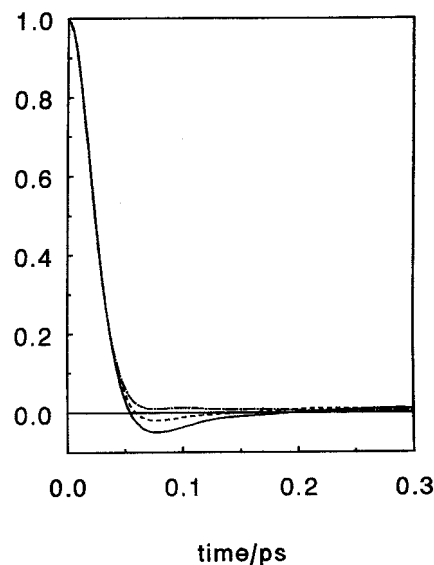


Figure 7. Influence of the potential parameter ε/k_{B} of the mutual interactions between the solvent molecules on the frequency autocorrelation functions solid line, $\varepsilon/k_{\text{B}} = 9.76 \text{ K}$ (helium); dashed line, $\varepsilon/k_{\text{B}} = 40 \text{ K}$; and dash-dotted line, $\varepsilon/k_{\text{B}} = 90 \text{ K}$.

only the density increased from 125 kmol m^{-3} to $127.5 \text{ kmol m}^{-3}$. The total correlation time increases with increasing ε_{He} , mainly due to the contribution of the first-order effect. The reason for this is qualitatively displayed in figure 7: the negative part in the correlation function, characteristic for nitrogen in helium, diminishes and finally disappears with increasing ε_{He} . The effect on the total correlation time is much less than by the change in mass. The increase in $\varepsilon_{\text{He-N}}$ has only a minor influence on the correlation time, but results in a larger amplitude of modulation and thus to a larger linewidth.

Finally, the size effect has been studied by adding an increase Δr to $r_{m,\text{He}}$ and a simultaneous increase of

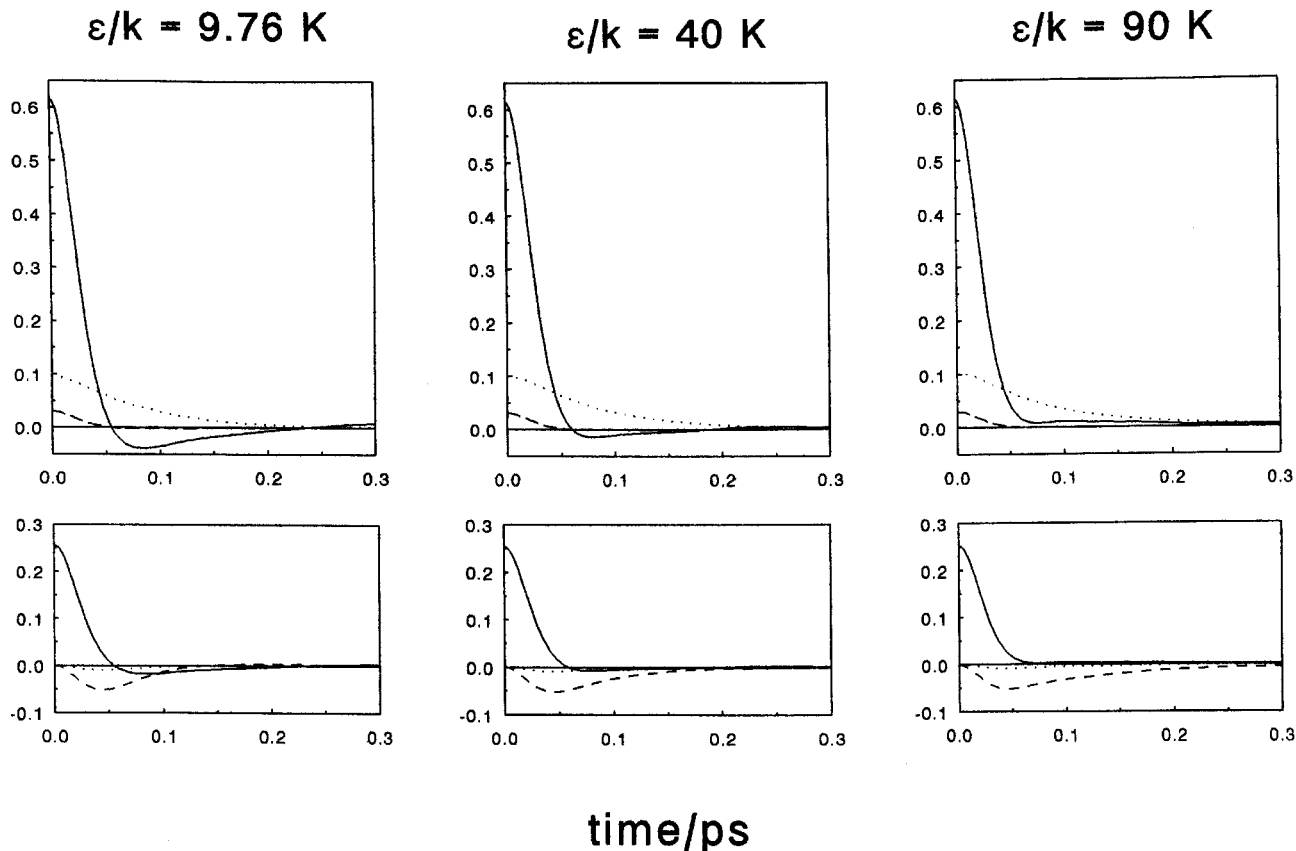


Figure 8. Contributions to the correlation function of the vibration frequency of a single nitrogen molecule in a solvent as a function of the potential strength of the mutual interaction between the solvent molecules. $\varepsilon/k = 9.76$ K is the optimal value for helium. ε/k for the interaction with the sites of the nitrogen molecule is 16 K. Symbols as for figure 4.

Table 4. Influence of the potential strength ε of the surrounding ('solvent') molecules on a single nitrogen molecule at 2 GPa and 296 K. In contrast with all the other simulations dealing with helium, the cutoff distance for the mutual helium interaction had been increased from 3.0826 Å to 7 Å. The values $\varepsilon/k_B = 9.76$ K and 16 K are appropriate values for the mutual interaction between the helium atoms with respect to the interaction between helium atoms and nitrogen atoms ('sites').

α, β	$\varepsilon/k_B = 9.76$ K		$\varepsilon/k_B = 40$ K		Solvent Unlike		$\varepsilon/k_B = 90$ K	
	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$	$\tau_{\alpha,\beta}/\text{ps}$	$\Omega_{\alpha,\beta}(0)$
e1-e1	0.0129	0.6164	0.0155	0.6147	0.0179	0.6154	0.0170	0.6234
e2-e2	0.0006	0.0301	0.0007	0.0301	0.0008	0.0300	0.0008	0.0317
vr-vr	0.0081	0.0962	0.0093	0.0998	0.0100	0.1022	0.0070	0.0798
e1-e2 + e2-e1	0.0052	0.2564	0.0062	0.2549	0.0072	0.2533	0.0070	0.2641
e1-vr + vr-e1	- 0.0030	- 0.0008	- 0.0051	0.0005	- 0.0067	0.0008	- 0.0054	0.0008
e2-vr + vr-e2	- 0.0004	- 0.0002	- 0.0008	0.0000	- 0.0011	0.0000	- 0.0010	0.0003
Total	0.0234	1.0000	0.0258	1.0000	0.0280	1.0000	0.0251	1.0000
	$\Delta = 5.883 \text{ cm}^{-1}$		$\Delta = 5.649 \text{ cm}^{-1}$		$\Delta = 5.658 \text{ cm}^{-1}$		$\Delta = 6.441 \text{ cm}^{-1}$	
	FWHM = 0.305 cm^{-1}		FWHM = 0.310 cm^{-1}		FWHM = 0.338 cm^{-1}		FWHM = 0.393 cm^{-1}	

$\Delta r/2$ to $r_{m,\text{He-N}}$. In order to maintain the pressure at 2 GPa, the density had to be adapted: from 125 kmol m^{-3} with $r_{m,\text{He}} = 3.0826$ Å to 106.6 kmol m^{-3} at $r_{m,\text{He}} = 3.35$ Å and to 90.5 kmol m^{-3} at $r_{m,\text{He}} =$

3.5 Å. The cutoff distance of the mutual interactions of the solvent molecules was always equal to r_m . The results are presented in table 5. It is seen that the total correlation time increases due to the self-correlations of

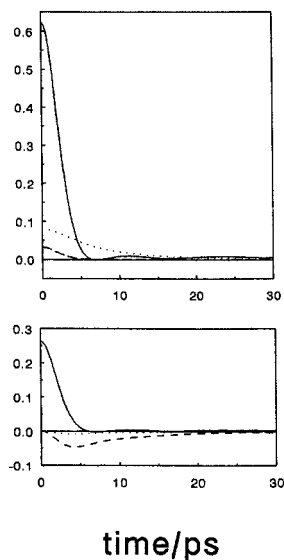


Figure 9. The same correlation functions as for figure 8 with $\varepsilon/k_B = 90$ K for the mutual interactions of the solvent molecules, but with $\varepsilon/k_B = 40$ K for the potential strength with the sites of the nitrogen molecule.

the first order (e1) effect and of the vibration–rotation coupling, although the cross terms that include the vr coupling show an opposite result. Because the amplitude Δ decreases with increasing r_m , 'He', the net effect on the linewidth is not significant. The general behaviour of the correlations functions does not change significantly either: in particular the negative part in the self-correlation of the e1 effect is barely affected.

It can be concluded now from the simulations that the large differences in mass and in the dispersion forces of helium in comparison with nitrogen lead to shorter correlation times and smaller linewidths at high pressures. The short correlation times are due partly to the occurrence of negative values of the correlation function in the N₂–He system. The results suggest that this negative

part is due primarily to mutual interactions between the helium atoms and not to interactions with nitrogen. Because this negative part is due to the oscillating behaviour of the first-order effect, i.e., the intermolecular 'compressing' forces exerted on the nitrogen molecule, we investigated a comparable force acting on the helium atoms. Simulations have been performed on a system of 256 He particles with an intermolecular potential defined in expressions (1) and (12), at $T = 296$ K and $p = 2$ GPa. During the run the forces acting on each particle have been calculated. The projections of these forces on an axis with a fixed orientation (one of the Cartesian coordinates of the elementary box, as usually applied in the MD simulations) have been monitored. The forces along that axis are regarded as being positive if they point towards the centre of the atom considered, and negative if they point away from the centre. The resultant of all these forces acting on an atom has been regarded as a 'compressing' force, qualitatively related to the compressive forces acting on nitrogen molecules in the He–N₂ system. The fixed orientation was chosen because the direction of the forces in helium changes much faster than the average change in orientation of a nitrogen molecule. The normalized autocorrelation of the 'compressive' force in helium, defined in the same way as the autocorrelation function of the frequency (equation (4)), is plotted in figure 10 (solid line). The simulations have been repeated with larger values for ε/k_B , namely 40 K and 90 K, and the results also given in figure 10. Once again, oscillating behaviour is seen, which diminishes with increasing potential strength. These results indicate that the negative part in $\Omega_{e1, e1}(t)$ and thus in the total $\Omega(t)$ for a single nitrogen particle in helium above ≈ 1 GPa is due to the absence of strong attractive forces between the diluent molecules. Influences of the rotational degree of freedom of nitrogen or from the interaction between nitrogen and helium are, if present, not important.

Table 5. Influence of the diameter r_m of the surrounding molecules on a single nitrogen molecule at 2 GPa and 296 K.

α, β	$r_m = 3.0826$ Å		$r_m = 3.35$ Å		$r_m = 3.65$ Å	
	$\tau_{\alpha, \beta}$ /ps	$\Omega_{\alpha, \beta}(0)$	$\tau_{\alpha, \beta}$ /ps	$\Omega_{\alpha, \beta}(0)$	$\tau_{\alpha, \beta}$ /ps	$\Omega_{\alpha, \beta}(0)$
e1–e1	0.0133	0.6169	0.0138	0.6167	0.0149	0.6195
e2–e2	0.0007	0.0300	0.0007	0.0285	0.0006	0.0269
vr–vr	0.0083	0.0979	0.0094	0.1029	0.0104	0.1080
e1–e2 + e2–e1	0.0055	0.2564	0.0055	0.2502	0.0058	0.2446
e1–vr + vr–e1	- 0.0032	- 0.0009	- 0.0040	0.0013	- 0.0049	0.0009
e2–vr + vr–e2	- 0.0005	- 0.0002	- 0.0006	0.0003	- 0.0007	0.0002
Total	0.0240	1.0000	0.0248	1.0000	0.0261	1.0000
	$\Delta = 5.748 \text{ cm}^{-1}$ FWHM = 0.299 cm^{-1}		$\Delta = 5.619 \text{ cm}^{-1}$ FWHM = 0.295 cm^{-1}		$\Delta = 5.470 \text{ cm}^{-1}$ FWHM = 0.295 cm^{-1}	

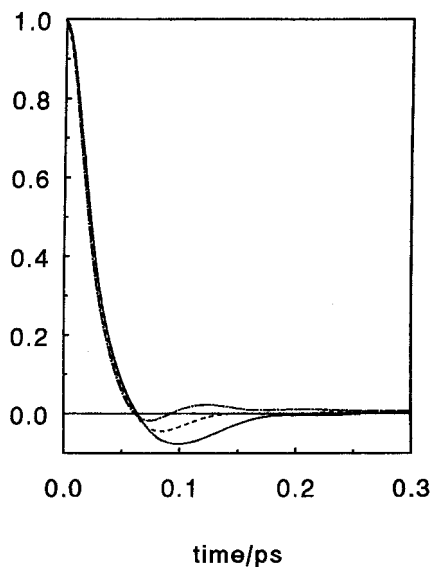


Figure 10. The autocorrelation function of the 'compressive force' (see text) in helium at 296 K and 2 GPa (solid line). The dashed and dash-dotted lines are the results for the same system, but with potential parameter values $\epsilon/k = 40$ K and 90 K, respectively.

4. Conclusion

We have performed molecular dynamics simulations of systems in the fluid phase at ambient temperature of nitrogen and of a single nitrogen molecule in helium as a function of the pressure. From these simulations the vibration frequency of nitrogen was determined and the width and shift of the Raman line could be derived. In conformity with experimental evidence, the linewidth in the surrounding helium was found to be considerably less than in pure nitrogen at the same pressure. A detailed analysis of the time correlations of all the contributions to the vibration frequency, revealed that this phenomenon is due primarily to the intrinsic properties of helium, e.g., the mass and the mutual interaction, but barely at all to the interaction between the helium and nitrogen molecules. It is interesting to see that the time correlation function of the frequency of nitrogen, and thus the derived properties, in helium reflect dynamic behaviour in the (pure) helium system, namely the occurrence of oscillating forces acting on the helium

atoms. In this respect, the single nitrogen molecule acts as a probe in the helium environment.

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