

Calculation of the vibrational linewidth and line shape of Raman spectra using the relaxation function : II. application to the mixture neon-nitrogen with inhomogeneous broadening due to concentration fluctuations

Citation for published version (APA):

Kooi, M. E., Michels, J. P. J., & Scheuten, J. A. (2000). Calculation of the vibrational linewidth and line shape of Raman spectra using the relaxation function : II. application to the mixture neon-nitrogen with inhomogeneous broadening due to concentration fluctuations. *Journal of Chemical Physics*, 112(3), 1404-1412.
<https://doi.org/10.1063/1.480694>

DOI:

[10.1063/1.480694](https://doi.org/10.1063/1.480694)

Document status and date:

Published: 01/01/2000

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Download date: 04. Oct. 2023

Calculation of the vibrational linewidth and line shape of Raman spectra using the relaxation function. II. Application to the mixture neon–nitrogen with inhomogeneous broadening due to concentration fluctuations

M. Eline Kooij, Jan P. J. Michels,^{a)} and Jan A. Schouten

Van der Waals–Zeeman Institute, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

(Received 7 April 1999; accepted 13 October 1999)

The Raman spectra of nitrogen in the mixture neon–nitrogen have been measured for neon mole fractions, x_M , of 0.10, 0.65, and 0.95 at 296 K and 408 K up to the solidification pressure. It was found that the frequency increases as a function of x_M . The linewidth is strongly composition dependent, with a very large value for $x_M=0.65$. Further, it is shown that the width decreases as a function of temperature. Molecular dynamics simulations have been performed in order to calculate the linewidth and shape, using the relaxation function. The simulations are in good agreement with experiment. It is shown that the increase in linewidth in the intermediate concentration range is due to an increase of the correlation time, rather than an increase of the amplitude of modulation. In this range inhomogeneous broadening due to concentration fluctuations occur: the vibrational line shape starts to deviate from a Lorentzian curve, and gets a Gaussian component. The simulations also provide insight into the relatively large decrease of the width as a function of temperature in the intermediate concentration range. When the temperature is increased from 296 to 408 K, the amplitude of modulation increases, but the correlation time decreases more. © 2000 American Institute of Physics. [S0021-9606(00)51602-X]

INTRODUCTION

Although the vibration frequency of a molecule originates mainly from the *intramolecular* forces, in a dense system the contribution of the *intermolecular* forces is important too. The influence of these forces is also evident in the linewidth and the shape of the spectrum, which reflects the variations in the local environment of the molecule in space and time. The experimental linewidth is, in general, different from the amplitude of modulation due to the dynamics of the system. Thus, both the fluctuations in space and time are relevant. In a pure system density fluctuations far from the critical point have a small wavelength and a high frequency, resulting in motional narrowing of the spectral line. In mixtures, concentration fluctuations may also play a role. Recently, Muller, vanden Bout, and Berg¹ have shown that in mixtures far from the critical point, the lifetime of concentration fluctuations is rather long, namely 4–7 ps. This can lead to inhomogeneous broadening of the spectral line. Gallego, Somoza, and Blanco² have determined the concentration fluctuations in mixtures of hard spheres. For hard spheres of equal size the maximum in fluctuations occurs for equimolar systems while for systems with different diameters the maximum shifts to lower concentrations of the smaller component. On the other hand, Moser, Asenbaum, and Döge³ have measured the vibrational linewidth of the C–H vibration of CH₂I₂ diluted with liquid CCl₄ as a function of composition. They found a maximum in width for 60% CCl₄, the component with the smaller diameter. The

reason for this discrepancy is not clear. The linewidth at the maximum is almost twice that of pure CH₂I₂.

In a later paper⁴ these authors extended the model proposed by Knapp and Fisher⁵ for calculating the line shape. They considered two-particle exchange processes in the nearest-neighbor shell of the reference molecule and finite interaction times between the molecules. The calculated band shapes in pure liquids deviate from Lorentzian profiles, in contrast with the results of Knapp and Fisher, but in agreement with experimental data obtained for CH₂I₂.

In earlier papers^{6,7} it was shown that the linewidth of Lorentzian profiles can be obtained from computer simulations using the Kubo⁸ expression for the fast modulation regime. In paper I both the line shape and linewidth of non-Lorentzian profiles (the intermediate Kubo regime) have been determined by computer simulations using the relaxation function. This method is particularly suitable for mixtures where inhomogeneous line broadening is important. Computer simulations of the relaxation function of liquid N₂ and CH₃I have been performed recently by Gayathri and Bagchi⁹ in order to investigate the subquadratic quantum number dependence of vibrational overtone dephasing. They found that the nonquadratic dependence can be expected when the decay of the frequency autocorrelation function is largely Gaussian and the time scale of this decay is comparable to that of the autocorrelation function of the normal coordinate. In our work we are primarily interested in the calculation of the Raman linewidth and line shape, which requires Fourier analyses of the relaxation function. Gayathri and Bagchi (GB) did not take into account the dispersion correction but in many cases this gives a considerable con-

^{a)}Electronic mail: jmichels@wins.uva.nl

tribution to the linewidth (and thus to the dephasing time).⁶ It might be expected that in mixtures the contribution is even more important. Vibration–rotation (VR) coupling is also important, in particular at higher temperatures. GB neglected the cross correlation between the VR term and the other contributions. However, these cross terms have a larger value and are of opposite sign compared to that of the autocorrelation.^{10,11} This also explains the discrepancy between the results of Oxtoby and co-workers¹⁰ and of GB with respect to the VR term. In order to predict quantitatively the vibrational line shape one needs to know the potential surface very accurately.¹⁰ Therefore, we have used a more realistic potential than the Lennard-Jones model, namely the van der Waals part of the Eters potential.¹² To speed up the calculations we have omitted the quadrupole interaction. Moreover, it provides an opportunity to study the underlying mechanisms in more detail since the various contributions to the frequency autocorrelation function are obtained separately. Possibly, the discrepancy with respect to the maximum in concentration fluctuations between the hard sphere results and those of Moser, Asenbaum, and Döge³ can be explained.

The advantages of nitrogen as a model system have been elucidated previously.¹³ As the second component we have chosen neon for the following reasons. The molecule is spherical, nonpolar, and has a simple interaction with nitrogen. Thus, the simulations are similar to those for pure nitrogen and the results are not complicated by extra rotational degrees of freedom or polar effects. The vibration frequency of nitrogen diluted with neon shows a large shift compared to that of pure nitrogen, which is a necessary condition to obtain an appreciable inhomogeneous line broadening. Since inhomogeneous line broadening also occurs due to critical density and/or concentration fluctuations,¹³ and since the critical region extends far from the critical line, the system should be far from critical conditions as well. The critical line of neon–nitrogen moves from the critical point of nitrogen (122 K) toward lower temperatures and disappears under the crystallization surface of nitrogen at 70 K and 0.02 GPa.¹⁴ Thus, at room temperature and high pressure, this system is far from any critical state.

To make a comparison with experiment, we have performed measurements on three mixtures, one of the mixtures having a neon mole fraction of 0.65. If the diameters of the molecules are far from equal, the mole fraction is not a good measure of the composition for the description of the effects under consideration. In the case of $\text{CH}_2\text{I}_2\text{--CCl}_4$ the *microscopic* composition turns out to be a good alternative.^{3,4} A similar parameter is the volume fraction, often used to describe critical phenomena. In the case of neon–nitrogen the volume fractions are equal for 65% neon. Therefore, the maximum in linewidth is to be expected at this composition.

EXPERIMENTAL METHOD AND RESULTS

The experimental procedure can be found in Ref. 15. Three mixtures were prepared with neon mole fractions, x_M , of 0.10, 0.65, and 0.95. The Raman spectra of nitrogen in the fluid neon–nitrogen mixtures have been measured at constant temperature as a function of pressure up to the solidi-

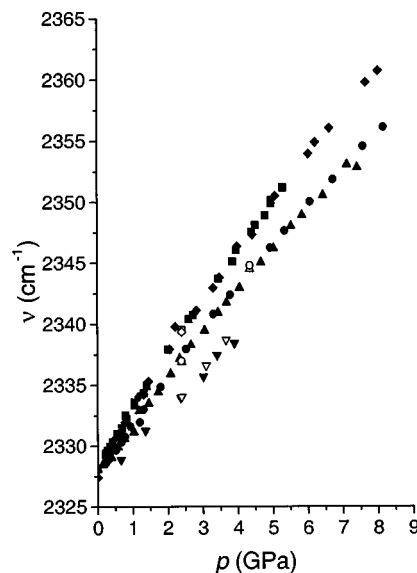


FIG. 1. Results of the Raman frequency of N_2 in Ne--N_2 vs the pressure at constant temperature. $T=296$ K: inverted triangles, $x=0.10$; triangles, $x=0.65$; squares, $x=0.95$. $T=408$ K: circles, $x=0.65$; diamonds, $x=0.95$. Closed symbols, experiments; open symbols, simulations.

fication point. The mixtures with $x_M=0.95$ and 0.65 were investigated at 296 and 408 K, and the mixture with $x_M=0.10$ at 296 K.

The experimental spectra have to be deconvoluted with the experimentally determined instrumental resolution function. The resolution function has a Voigt profile with a full width at half-maximum (FWHM) of 0.74 cm^{-1} . It turns out that most of the spectra can be fitted better by the convolution of the instrumental function with a Lorentzian curve than with a Gaussian curve, using the least-squares criterion. Therefore, we convoluted several Lorentzians with the resolution function and compared the result with the experimental spectrum. The Lorentzian which provides the best agreement with experiment is used to determine the FWHM.

The peak position of the vibrational spectra, ν , as a function of pressure have been plotted in Fig. 1. The Raman frequencies increase monotonically as a function of pressure. At higher pressure, the slope is slightly decreasing. It is shown that the frequency is strongly composition dependent, and increases as a function of x_M . Within experimental accuracy the vibrational spectra at 296 and 408 K have the same frequency for the mixtures with $x_M=0.95$ and 0.65.

In Fig. 2 the Raman frequency as a function of the mole fraction, x_M (closed symbols), and the volume fraction, x_V (open symbols), at 296 K has been plotted. In the next section it will be described how the mole fractions are converted to volume fractions. It is shown that the frequency is linear dependent on the volume fraction within experimental accuracy.

The FWHM of the deconvoluted spectra have been plotted in Fig. 3. It can be seen that the FWHM is strongly composition dependent, and that the largest value for the width occurs for $x_M=0.65$ for all pressures and temperatures. The linewidth increases strongly as a function of pressure. It is interesting to note that the width of $x_M=0.10$ as a

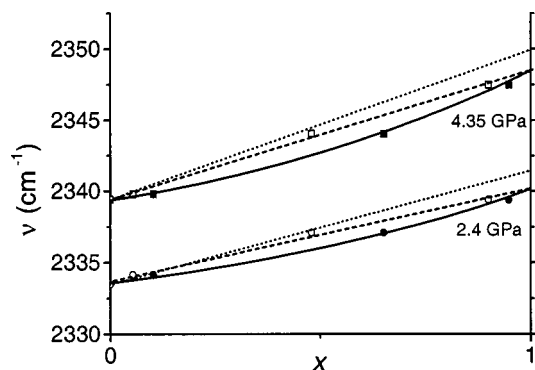


FIG. 2. Experimental results of the Raman frequency of N_2 in Ne- N_2 at 296 K vs the mole fraction (solid symbols) and the volume fraction (open symbols). Solid lines and dashed lines are guides to the eyes. Points for pure N_2 are from Ref. 16. Note, that the frequency of pure fluid N_2 at 4.35 GPa has been obtained by extrapolation, since pure N_2 is in the solid phase at 4.35 GPa and 296 K. The dotted line is the Raman frequency of N_2 in He- N_2 as a function of volume fraction (Ref. 16).

function of pressure shows a steeper increase than that of $x_M=0.95$, and above 2.7 GPa the width of $x_M=0.10$ is larger than that of $x_M=0.95$. Note that the mixture with $x_M=0.10$ solidifies at 4.4 GPa. Finally, it is shown that the width at 296 K is larger than that at 408 K. For the sake of clarity, the linewidth of pure nitrogen is not plotted in Fig. 3, but this width is slightly smaller than that of $x_M=0.10$.

MOLECULAR DYNAMICS SIMULATIONS AND RESULTS

The procedure which has been used for the calculations is described in paper I. The dynamical simulations of fluid mixtures of neon and nitrogen have been performed on a model system with a total number of 256 particles. In order to cover the whole composition range, also two simulations on pure nitrogen have been made; the latter with 384 particles. For the mutual nitrogen interaction, the same model potential has been adopted as described in part I. For the

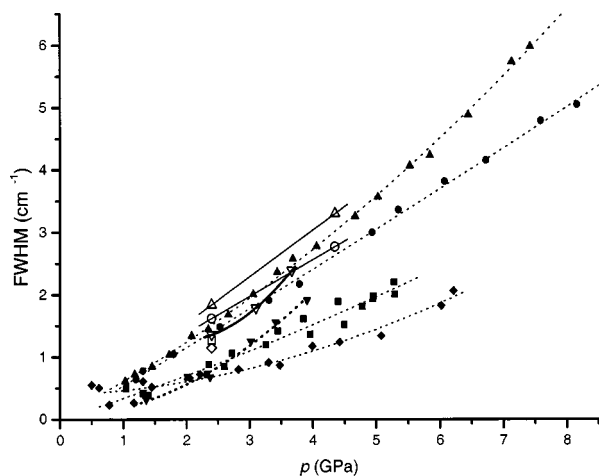


FIG. 3. FWHM of the vibrational spectrum of N_2 in Ne- N_2 vs the pressure at constant temperature. $T=296$ K: inverted triangles, $x=0.10$; triangles, $x=0.65$; squares, $x=0.95$. $T=408$ K: circles, $x=0.65$; diamonds, $x=0.95$. Closed symbols, experiments; open symbols, simulations. Dotted lines, fits through experimental data; solid lines, fits through simulation data.

mutual interaction of neon, and the interaction between neon and the atom sites of nitrogen, exponential-6 potentials have been adopted:

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

in which ϵ represents the well depth of the potential, α the stiffness of the repulsive part at short distances, and r_m the diameter at the minimum of the well. The following parameter values have been applied:

	$r_m(\text{\AA})$	$\epsilon/k_B(\text{K})$	α
Ne-Ne	3.147	38.0	14.50
Ne- N_{atom}	3.440	38.7	14.52
($N_{\text{atom}}-N_{\text{atom}}$)	3.73	39.4	14.55

The last quoted parameters are not applied for the dynamics, but only used for the calculation of the Ne- N_{atom} interaction using the Lorentz-Berthelot rule. During the simulations, four terms (and their cross correlations) that contribute to a change of the frequency with respect to a nonrotating molecule were registered:

- The external force acting along the molecular axis (E1).
- The derivative of the external force along the axis, contributing to the harmonic force of the vibrator (E2).
- The vibration-rotation coupling (VR).
- The dispersion correction, which corrects for the change in polarizability at excitation of the vibrator (DC).

The resonant-transfer term was not taken into account since its contribution is already small for liquid nitrogen,⁹ thus certainly at high temperatures and in mixtures.

The calculations are performed on systems with pressures from 2.4 to 4.35 GPa, and at 296 and 408 K. Note that at 296 K and 2.4 GPa, and at 408 K and 4.35 GPa, nitrogen is near the melting line. In order to determine the volume fraction of neon as a function of the mole fraction eight relative short simulation runs have been done at 296 K and 2.4 GPa as a function of mole fraction. For each run the density has been determined, and is compared to the densities of the pure systems. From these parameters the volume fraction can be calculated. Next, the volume fractions have been plotted as a function of mole fraction, and a polynomial function of the fourth order is fitted through these points.

In order to determine the dispersion correction (DC) for nitrogen in neon, a series of eleven relative short runs have been made for *one* nitrogen particle in a box of 255 neon particles. From these runs the frequency shift without DC was obtained as a function of pressure at 296 K. As mentioned in the previous section, a linear behavior is seen for the Raman shift as a function of the volume fraction in the mixtures. For comparison between the simulations and experimental data, the values of the shift, measured at 296 K with volume fractions of 0.48 and 0.90 have been extrapolated linearly to 100% neon. The results can be given in a functional form:

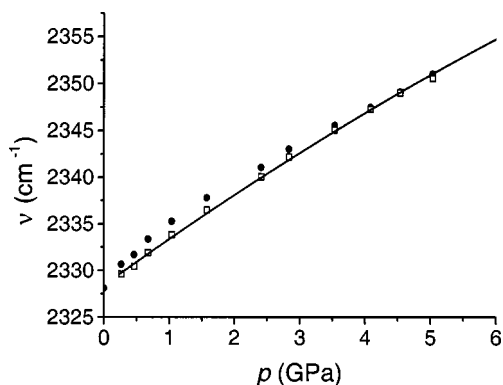


FIG. 4. MD simulations of the Raman frequency of N_2 infinitely diluted in Ne ($x_V=1.0^*$) vs pressure at 296 K. Circles, without DC; squares, with DC; solid line, extrapolation from experimental data to $x_V=1.0$.

$$\nu = 2328.46 + 5.06p - 0.11p^2 \quad (2)$$

with ν in cm^{-1} , and p in GPa, valid for $0.25 \text{ GPa} < p < 5.0 \text{ GPa}$. Both the extrapolation and the molecular dynamics (MD) results are given in Fig. 4.

As has been done in previous studies,^{6,7} the DC is introduced as an addition of a Lennard-Jones 12-6 potential to the site-site interaction between a neon and a nitrogen atom. Appropriate parameter values turned out to be: $\epsilon/k_B = 0.11 \text{ K}$; $\sigma = 3.29 \text{ \AA}$. The results for the shift including this DC are also given in Fig. 4.

The dispersion correction for each of the four site-site interactions between nitrogen molecules has been determined in previous work; a suitable set of parameters has been found to be $\epsilon/k_B = 0.32 \text{ K}$; $\sigma = 2.96 \text{ \AA}$. Thus, the DC

for the neon-nitrogen interaction is considerably less than for the nitrogen-nitrogen interaction, reflecting the relative low polarizability of neon.

The results of the simulations have been presented in Table I. In order to maintain the statistical accuracy, the number of time steps in a simulation run, N , is increased at decreasing nitrogen concentrations. In the first columns the static parameters are plotted. At these temperatures and pressures the mixtures are in the homogeneous fluid phase. In the next columns the parameters which can be derived directly from the MD simulations have been presented. The amplitude of modulation, Δ , is plotted in Fig. 5(a). It increases slightly as a function of x_M . The difference in Δ for pure nitrogen, and for infinite dilution, is only 6%. The value of Δ increases by about 23% when the pressure is increased from 2.4 to 4.35 GPa, and it increases by about 20% when the temperature is increased from 296 to 408 K. The correlation time, τ_c , is plotted in Fig. 5(b). It is strongly composition dependent, and has a maximum value for concentrations in the range 50–75 mol % neon. At 2.4 GPa and 296 K its value decreases by more than a factor of 3 from 75 mol % neon to infinite dilution. The correlation time increases by 24%–42% when the pressure is increased from 2.4 to 4.35 GPa, and it decreases by 39%–54% when the temperature is increased from 296 to 408 K.

According to the Kubo theory⁸ the FWHM of the spectral line is given by $2\Delta^2\tau_c$ in the fast modulation regime, which is defined by the condition that $\Delta\tau_c \ll 1$. Therefore, the values of $2\Delta^2\tau_c$ and the Kubo parameter are also given in Table I. It is shown that the Kubo parameter, defined by $\Delta\tau_c$, is composition dependent, and has a maximum value at 50–75 mol %. The value of $\Delta\tau_c$ decreases as a function of

TABLE I. Results of analysis of MD simulations.

Mol % Ne	p (GPa)	T (K)	$\langle \nu \rangle$ (cm^{-1})	$\Delta/2\pi c$ (cm^{-1})	τ_c (ps)	$\Delta\tau_c$	$2\Delta^2\tau_c$ (cm^{-1})	ν_{peak} (cm^{-1})	FWHM (cm^{-1})	χ^2 (Gauss)/ χ^2 (Lorentz)	t_n (ps)	t_m (ps)	N (time steps)
0	2.4	296	2333.60	6.660	0.0736	0.090	1.23	2333.57	1.20	1000	1	15	5×10^4
12.55	2.4	296	2334.05	6.690	0.0852	0.107	1.44	2334.02	1.36	30	7.5	22.5	6×10^4
25.10	2.4	296	2334.59	6.754	0.0915	0.117	1.57	2334.56	1.57	9	7.5	22.5	8×10^4
37.65	2.4	296	2335.21	6.801	0.1069	0.137	1.86	2335.19	1.70	4	7.5	22.5	10×10^4
50.20	2.4	296	2335.89	6.812	0.1299	0.167	2.27	2335.86	1.86	2	15	30	12×10^4
65.88	2.4	296	2336.90	6.908	0.1337	0.174	2.41	2336.91	1.84	4	18	21	20×10^4
75.29	2.4	296	2337.62	6.969	0.1457	0.191	2.67	2337.64	1.84	2	15	37.5	20×10^4
87.84	2.4	296	2338.81	7.048	0.1168	0.155	2.19	2338.82	1.61	4	15	35	40×10^4
94.12	2.4	296	2339.48	7.074	0.0726	0.097	1.37	2339.50	1.27	10	7.5	37.5	40×10^4
97.25	2.4	296	2339.85	7.087	0.0534	0.075	1.01	2339.88	1.01	40	15	30	80×10^4
100 ^a	2.4	296	2340.10	7.117	0.0445	0.060	0.85
12.55	3.10	296	2336.62	7.314	0.0904	0.125	1.82	2336.60	1.79	50	7.5	15	6×10^4
12.55	3.67	296	2338.75	7.822	0.1029	0.152	2.37	2338.69	2.39	10	7.5	15	8×10^4
65.88	4.35	296	2344.51	8.509	0.1657	0.266	4.52	2344.51	3.31	2	12	18	20×10^4
0	2.4	408	2333.93	8.030	0.0481	0.073	1.17	2333.91	1.18	700	5	25	5×10^4
12.55	2.4	408	2334.28	8.083	0.0511	0.078	1.26	2334.25	1.32	70	3	37.5	7×10^4
25.10	2.4	408	2334.79	8.129	0.0530	0.083	>1.32	2334.76	1.45	20	3	37.5	8×10^4
37.65	2.4	408	2335.40	8.230	0.0650	0.100	1.66	2335.37	1.51	20	3	37.5	10×10^4
50.20	2.4	408	2335.99	8.193	0.0776	0.120	1.97	2335.99	1.54	10	7.5	45	12×10^4
65.88	2.4	408	2336.98	8.286	0.0656	0.102	1.70	2336.96	1.62	10	18	30	20×10^4
75.29	2.4	408	2337.66	8.342	0.0674	0.106	1.77	2337.66	1.51	9	3	37.5	40×10^4
94.12	2.4	408	2339.35	8.465	0.0414	0.066	1.12	2339.35	1.15	50	7.5	37.5	40×10^4
0	4.35	408	2341.34	9.910	0.0656	0.123	2.43	2341.30	2.43	200	2	10	5×10^4
65.88	4.35	408	2344.81	10.21	0.0931	0.179	3.66	2344.78	2.77	6	12	18	20×10^4

^aNitrogen infinitely diluted in neon.

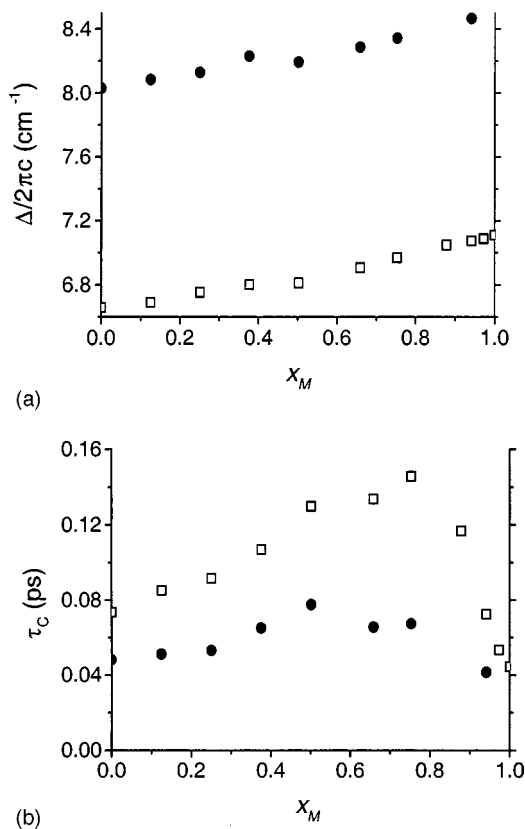


FIG. 5. (a) The amplitude of modulation, Δ , as a function of the neon mole fraction at 2.4 GPa. Squares, $T=296$ K; circles, $T=408$ K. (b) Correlation time, τ_c , vs x_M at 2.4 GPa. Squares, $T=296$ K; circles, $T=408$ K.

temperature, and increases as a function of pressure in the temperature and pressure range investigated in this work.

Since the value of $\Delta\tau_c$ is larger in the mixture than in pure nitrogen, it is questionable whether the mixtures are in the fast modulation regime.

The results of the calculated spectra obtained by Fourier transformation of the relaxation function are plotted in the next columns. As described in paper I, the relaxation function has been fitted by an exponential function in the range $t_n < t < t_m$, and this function has been used for extrapolation for $t > t_m$. The parameters t_n and t_m have been given in Table I as well. It has been verified that the exponential decay sets in for $t < t_n$ and that the results are not sensitive to the choice of these parameters. The peak positions of the calculated spectra show good correspondence with $\langle \nu \rangle$. The deviation is less than 0.04. The FWHM of the calculated spectra are plotted in Figs. 6(a) and 6(b) (closed symbols) as a function of mole and volume fraction, respectively. The solid and dashed curves are given as a guide to the eyes. The width at 408 K is smaller than that at 296 K. The maximum in the width occurs for $x_M \approx 0.65$, and $x_V \approx 0.5$.

The values of the FWHM of the calculated spectra have been compared with those obtained using the assumption that the systems are in the fast modulation regime (open symbols) ($\Delta\tau_c \ll 1$), where the FWHM is equal to $2\Delta^2\tau_c$.⁸ For $x_M=0.97$, and pure nitrogen, the values obtained for the FWHM using these two methods are the same within the accuracy of the calculations. For the other compositions the

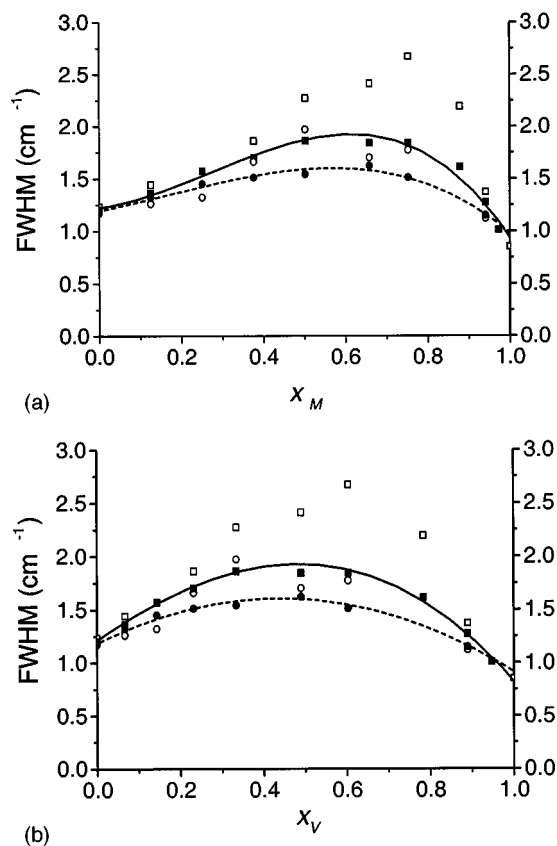


FIG. 6. (a) Calculated FWHM as a function of neon mole fraction at 2.4 GPa; open symbols, according to $2\Delta^2\tau_c$; closed symbols, full analysis by calculation of the Fourier transform of relaxation function; squares, $T=296$ K; circles, $T=408$ K. (b) Similar to (a), but as a function of volume fraction.

linewidths of the calculated spectra are considerably smaller than the values obtained using the assumption that the system is in the fast modulation regime. Due to the uncertainty in τ_c , the scatter in the values $2\Delta^2\tau_c$ is much more than in the width of the calculated spectra.

In Fig. 1 it can be seen that the simulation results of the vibrational peak positions are in good agreement with the experimental data. In Fig. 3 the widths of the calculated spectra with $x_M=0.13$, 0.66, and 0.94 have been compared with the experimental results. There is a good qualitative and reasonable quantitative correspondence between the experimental data and the simulation results. In conformity with experiment the width at 296 K is larger than at 408 K. The calculated slopes of the spectral width versus the pressure are also similar to experimental findings. In addition, again in accordance with experiments, the spectral linewidth of $x_M=0.66$ is much larger than that of $x_M=0.13$ and 0.94. The calculated linewidths are slightly overestimated compared to experiment, but this is also the case for pure nitrogen. Since the values of $2\Delta^2\tau_c$ are larger than the FWHM of the calculated spectra, especially in the intermediate concentration range, it is obvious that the widths of the calculated spectra are in better agreement with experiment than the values $2\Delta^2\tau_c$.

Three typical relaxation functions for mixtures with $x_M=0.97$, 0.66, and pure nitrogen at 296 K have been plotted

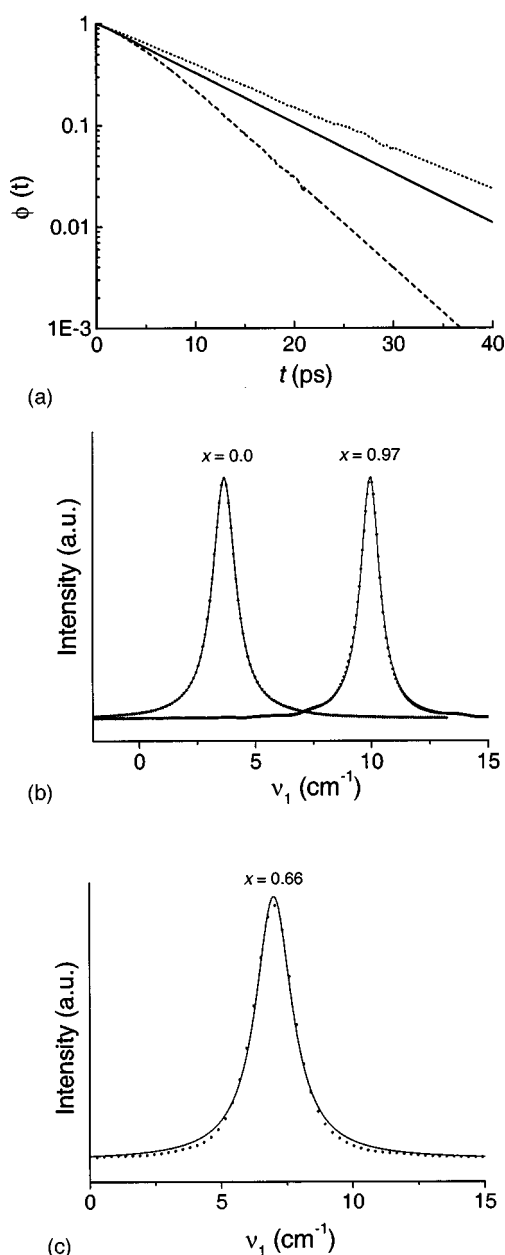


FIG. 7. (a) Relaxation functions. Solid line, $x_M=0.0$; dashed line, $x_M=0.66$; dotted line, $x_M=0.97$. (b) Calculated spectra (dots), obtained by Fourier transformation of the relaxation functions for $x_M=0.0$ and $x_M=0.97$ given in (a). Solid lines are Lorentzian fits of the spectra. (c) Similar to (b) but for $x_M=0.66$.

on a logarithmic scale in Fig. 7(a). The slowest decay of the relaxation function occurs for $x_M=0.97$, and the fastest decay for $x_M=0.66$. For small t the relaxation functions of the system with $x_M=0.66$ clearly decays nonexponentially. The exponential decay of the relaxation sets in for $t < 0.2$ ps, at 7 ps, and at 2 ps for pure nitrogen, $x_M=0.66$, and $x_M=0.972$, respectively. Three typical calculated spectra are given in Figs. 7(b) and 7(c). The points represent the calculated spectra, the solid line represents a Lorentzian fit. The line shape of the calculated spectrum of pure nitrogen can be fitted very well with a Lorentzian curve. The calculated line shape for $x_M=0.66$ deviates from the Lorentzian fit, in agreement with expectations, since the relaxation function of this mixture decays nonexponentially for small values of t . The spectrum for $x_M=0.97$ can be fitted well with a Lorentzian curve, although the spectrum is slightly asymmetric.

In Table I the ratio of the values of χ^2 for a Gaussian and Lorentzian fit have been given. For all systems investigated in this work this ratio is larger than unity, indicating that the calculated spectra can be fitted better with a Lorentzian than a Gaussian curve. Since the ratio decreases a few orders of magnitude in the composition range 50–75 mol % neon, it is concluded that in this range the shape of the calculated spectrum deviates most from a Lorentzian line shape, and that the line shape gets a Gaussian component. The calculated spectra of all the systems investigated in this work can be fitted very well with Voigt functions. In Table II the frequency correlation times of the various mechanisms for pure N_2 and for $x_M=0.66$ are compared. In most cases the changes are not essential, except for τ_c of the dispersion correction. In this case τ_c has increased by a factor 20. Also given are the relative values for the amplitude of modulation. These values do not differ much.

As described in paper I, for $t > t_m$ the relaxation function has been extrapolated using an exponential fit. In the fast modulation regime ($\Delta\tau_c \ll 1$) the linewidth can be calculated from these exponents, according to

$$\text{FWHM} = (T_2 \pi c)^{-1}, \quad (3)$$

where T_2^{-1} is the exponent of the exponential fit of the relaxation function, and c the speed of light. For pure nitrogen, the values of the FWHM calculated according to Eq. (3) give consistent results with the FWHM of the calculated spectra.

TABLE II. The simulated frequency correlation times of the various mechanisms and the relative contributions to the amplitude of modulation for pure N_2 and for $x_M=0.66$.

ij	100% N_2		66% Ne	
	τ_c (ps)	$\Delta_{i,j}/\Delta_{\text{total}}$	τ_c (ps)	$\Delta_{i,j}/\Delta_{\text{total}}$
E1–E1	0.0441	0.4823	0.0356	0.5029
E2–E2	0.0015	0.0187	0.0017	0.0234
VR–VR	0.0077	0.0744	0.0062	0.0684
DC–DC	0.0039	0.0460	0.0781	0.0381
E1–E2+E2–E1	0.0160	0.1795	0.0142	0.2026
E1–VR+VR–E1	–0.0141	0	–0.0123	0
E1–DC+DC–E1	0.0141	0.1679	0.0154	0.1371
E2–VR+VR–E2	–0.0024	0	–0.0023	0
E2–DC+DC–E2	0.0025	0.0302	0.0097	0.0274
VR–DC+DC–VR	–0.0034	0	–0.0022	0

For the neon–nitrogen mixtures this is no longer valid. The deviation gets large for the systems with a large value of the Kubo parameter. For example, for the 38% mixture at 296 K and 2.4 GPa, the FWHM of the calculated spectrum is equal to 1.70 cm^{-1} , but the value of $(T_2\pi c)^{-1}$ is equal to 3.08 cm^{-1} .

DISCUSSION AND CONCLUSION

It is shown that the Raman frequency of nitrogen increases as a function of x_M . Four contributions to the frequency shift can be distinguished in the MD simulations, namely the external force acting along the molecular axis, the derivative of the external force along the axis, the vibration–rotation (VR) coupling, and the dispersion correction (DC). The first contributions are positive, the VR coupling is always negative, and the DC is negative for the systems discussed in this work. The contribution of the VR coupling does not depend on the composition. The simulations show that the first two contributions are hardly sensitive to the composition. Therefore, the change in Raman frequency is mainly caused by the change in the DC. The contribution of the dispersive term of nitrogen in neon is considerably smaller than that of nitrogen in pure nitrogen, but larger than that of nitrogen in helium.¹⁶ The DC corrects for the difference in the intermolecular potential of an excited and a nonexcited molecule.⁶ For example, it is known that the polarizability increases at excitation. This explains the fact that this contribution is the largest for pure nitrogen, and the lowest for nitrogen in helium, since the polarizability of nitrogen is larger, and the polarizability of helium is smaller than that of neon. Analogous to the system helium–nitrogen, in neon–nitrogen the Raman frequency is linear dependent on the volume fraction, but not on the mole fraction. This indicates that, for this system, the volume fraction is indeed a more suitable order parameter than the mole fraction.

Since direct information is not available, the DC of nitrogen in neon has been determined using the Raman frequency of nitrogen infinitely diluted in neon at 296 K. The DC for pure N_2 at 296 K has been determined previously. However, the calculated peak positions for all other compositions are in good agreement with experiment, also at 408 K.

Experimentally, a large increase of the Raman linewidth is observed for $x_M=0.65$, compared to $x_M=0.10$, 0.95, and pure nitrogen. For example, the spectral width of $x_M=0.65$ is almost twice as large as that of $x_M=0.95$.

The linewidth, obtained by the Fourier transform of the relaxation function, is in good qualitative, and reasonable quantitative agreement with experiment. The pressure, temperature, and concentration dependence are the same as observed experimentally. It is interesting to note that the calculated FWHM shows a sharp increase as a function of pressure for $x_M=0.13$, in conformity with experiment. The calculated linewidth is slightly larger than the experimental width, but since this is also the case for pure nitrogen, the deviation is systematic and does not essentially affect the composition dependence. The maximum in the calculated linewidth occurs at $x_M \approx 0.65$, and $x_V \approx 0.5$. This confirms

that the volume fraction is a more suitable order parameter than the mole fraction for the description of concentration fluctuations.

For pure nitrogen, and nitrogen infinitely diluted in neon, the calculated line is in agreement with the Kubo predictions for the fast modulation regime ($\Delta\tau_c \ll 1$):⁸ a Lorentzian shape, with a FWHM equal to $2\Delta^2\tau_c$. In the intermediate concentration range inhomogeneous broadening has been found: The shape starts to deviate from a Lorentzian shape, and gets a Gaussian component. The linewidth is no longer determined by the relation $2\Delta^2\tau_c$. In addition, the relaxation functions of the mixtures clearly show a nonexponential decay for small t [Fig. 7(a)]. Therefore, when employing Eq. (3), which is only valid for the fast modulation regime, too large values for the linewidth are obtained. As already concluded in paper I, the Kubo parameter is not an unambiguous criterion for the fast modulation regime. For example, in Table I it is shown that the calculated line shape of pure nitrogen at 4.35 GPa and 408 K, with a Kubo parameter of 0.12, still has a Lorentzian line shape with a FWHM equal to $2\Delta^2\tau_c$, while the calculated line shape of 66 mol % neon at 2.4 GPa and 408 K, with a Kubo parameter of 0.10 deviates from a Lorentzian shape and the width is no longer determined by $2\Delta^2\tau_c$.

The dephasing time, calculated from the relaxation function, is 8.7 ps for pure N_2 and 6.74 ps for $x_M=0.66$; the values for τ_c are 0.0736 and 0.1337 ps, respectively. Gayathri and Bagchi⁹ attribute the deviation from the Kubo theory (the subquadratic n dependence of the linewidth of the overtones) to the fact that in CH_3I the time scales of the frequency correlation (τ_c) and of the dephasing (T_2) are not widely separated as in N_2 . Indeed for N_2 the ratio T_2/τ_c is about 23 times larger than for CH_3I . However, for N_2 at 296 K and 2.4 GPa the ratio is only 1.8 times that of the mixture with $x_M=0.66$ at the same pressure and temperature but still there is a considerable deviation from the Kubo theory in the case of the mixture and not in N_2 . Also the other conditions mentioned in Ref. 9 (such as low frequency) are not fulfilled and, in any case, the values are the same in pure nitrogen and in the mixtures. Clearly the problem is rather complicated and there does not exist a simple rule. We suggest that in the case of the mixtures the deviation from Kubo theory is due to the fact that the τ_c of the DC, having a non-Gaussian time dependence, is comparable to the τ_c of the first-order term (E1–E1 in Table II) which has a Gaussian time dependence.

In Ref. 1 it is stated that both density and concentration fluctuations originate in long-ranged attractive forces, and that therefore both types of fluctuations should have the same correlation time. It is also stated that the change in the amplitude of modulation is responsible for the inhomogeneous line broadening. The MD simulations enable us to study the underlying mechanisms of the concentration fluctuations. It is shown that, for Ne– N_2 mixtures, the increase of the linewidth in the intermediate concentration range is caused by an increase of the correlation time, τ_c , rather than an increase of the amplitude of modulation, Δ (Fig. 5). The correlation time of the concentration fluctuations is much longer than that of the density fluctuations, since the total correlation time increases more than a factor of 3 in the mixture. As

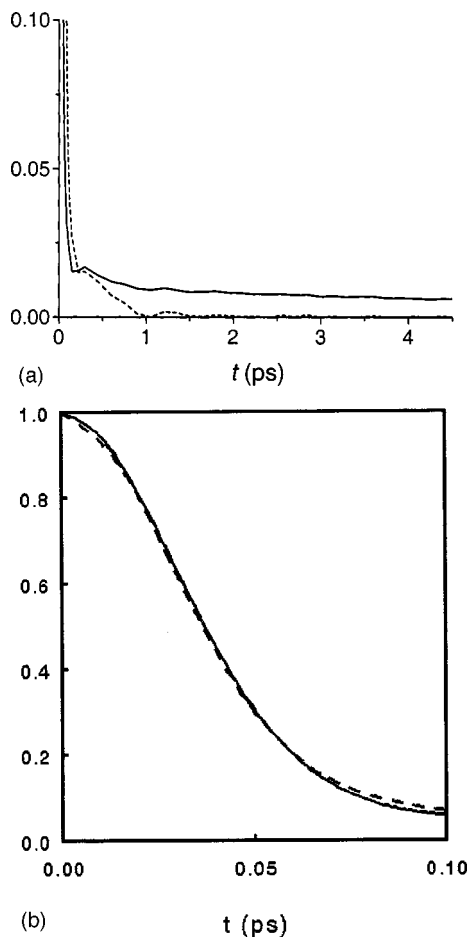


FIG. 8. (a) Contributions to the autocorrelation function of the vibration frequency of N_2 in $Ne-N_2$ at 296 K and 2.4 GPa and for $x_M=0.66$. Solid line, contribution of the self- and cross correlations of the DC. Dashed line, the autocorrelation function without the contribution of the self- and cross-correlations of the DC. (b) Initial part of the frequency autocorrelation functions at 2.4 GPa and 296 K. Solid line: pure nitrogen; dashed line: 66% neon.

mentioned before, the external axial forces on the molecule and the derivative of this force are hardly sensitive to the composition. Therefore, the increase in linewidth for the intermediate compositions is caused by the increase of the correlation time of the self- and cross correlations of the DC. In Fig. 8(a) the contributions to the frequency autocorrelation function for a MD simulation with $x_M=0.66$ at 296 K and 2.4 GPa have been plotted. It is shown that the correlation functions without the contribution of the dispersion correction decay fast. In contrast, the self- and cross-correlation functions of the dispersion correction show a long tail. Both density and concentration fluctuations are dictated by diffusion mechanisms, however, the character of these mechanisms is clearly different. For concentration fluctuations an exchange of particles should occur, while for density fluctuations small translational motions are sufficient.

In Fig. 8(b) the initial decay of the frequency autocorrelation functions of nitrogen and of the mixture with 65% neon are compared. It is shown that the composition has only a small influence on the initial decay of the correlation function. The main difference is the very long tail in the mixture, due to the dispersion correction [Fig. 8(a)], which is not

present in pure nitrogen.¹¹ It should be noted that it is difficult to decide whether the initial part is Gaussian or not. The total correlation function is the sum of at least ten contributions (including cross terms). The shape of these individual contributions is very different, e.g., the cross correlations with the vibration-rotation are always negative.¹¹ This is already the case in the fast modulation regime.

The fact that the concentration dependence of the dispersive energy is the main contribution to line broadening due to concentration fluctuations might explain the apparent discrepancy between the simulations of Gallego, Sumoza, and Blanco² and the experimentally observed line broadening in Ref. 3 and in this work. The simulations on hard sphere systems show a slight shift of the maximum in concentration fluctuations to smaller concentrations of the smaller molecule. Only for large differences in molecular diameters does a considerable shift occur. For example, for hard sphere systems with a diameter ratio equal to that of neon-nitrogen, namely 0.74, the shift to lower concentrations would be hardly detectable. Thus, if there is any effect due to the repulsive forces, this effect will be quite small. It was already suggested by Schweizer and Chandler¹⁷ that attractive forces play an important role in inhomogeneous line broadening. Therefore, the hard sphere system is not an appropriate model for real systems, where the dispersion correction results in a shift of the maximum in linewidth to larger concentrations of the smaller molecule.

For neon-nitrogen mixtures, with $x_M=0.65$ and 0.95, it is shown experimentally that the width decreases as a function of temperature. Previous theories predict an increase or at least a constant value of the FWHM as a function of T , except when the critical point is approached.^{18,19} The present simulations provide us with more detailed information about the different contributions to the width. The linewidth will increase when the amplitude of modulation, Δ , or the correlation time, τ_c , increases. In Fig. 5 it is shown that Δ increases, and τ_c decreases as a function of temperature in the whole concentration range. In the intermediate concentration range τ_c is much larger. Therefore, the decrease of τ_c as a function of temperature has a larger effect on the linewidth at intermediate concentrations than for pure nitrogen and the diluted system. This results in a relatively large decrease of the width as a function of temperature in the intermediate concentration range (Fig. 6).

¹L. J. Muller, D. vanden Bout, and M. Berg, *J. Chem. Phys.* **99**, 810 (1993).

²L. J. Gallego, J. A. Somoza, and M. C. Blanco, *Z. Naturforsch. A* **43**, 847 (1988).

³G. Moser, A. Asenbaum, and G. Döge, *J. Chem. Phys.* **99**, 9389 (1993).

⁴G. Moser, A. Asenbaum, J. Barton, and G. Döge, *J. Chem. Phys.* **102**, 1173 (1995).

⁵E. W. Knapp and S. F. Fischer, *J. Chem. Phys.* **76**, 4730 (1982).

⁶J. P. J. Michels, M. I. M. Scheerboom, and J. A. Schouten, *J. Chem. Phys.* **103**, 8338 (1995).

⁷J. P. J. Michels, M. I. M. Scheerboom, and J. A. Schouten, *J. Chem. Phys.* **105**, 9748 (1996).

⁸R. Kubo, in *Fluctuation, Relaxation, and Resonance in Magnetic Systems*, edited by Ter Haar (Oliver and Boyd, Edinburgh, 1962), pp 23-68.

⁹N. Gayathri and B. Bagchi, *J. Chem. Phys.* **110**, 539 (1999).

¹⁰D. W. Oxtoby, D. Levesque, and J.-J. Weis, *J. Chem. Phys.* **68**, 5528 (1978); D. Levesque, J.-J. Weis, and David W. Oxtoby, *ibid.* **72**, 2744 (1980).

- ¹¹J. P. J. Michels and J. A. Schouten, *Mol. Phys.* **91**, 253 (1997).
- ¹²D. Eiters, V. Chandrasekharan, E. Uzan, and K. Kobashi, *Phys. Rev. B* **33**, 8615 (1986).
- ¹³M. I. M. Scheerboom and J. A. Schouten, *Phys. Rev. E* **51**, R2747 (1995).
- ¹⁴W. B. Streett, *Cryogenics* **8**, 88 (1968).
- ¹⁵M. E. Kooi and J. A. Schouten, *Phys. Rev. B* **57**, 10407 (1998).
- ¹⁶M. I. M. Scheerboom, J. P. J. Michels, and J. A. Schouten, *J. Chem. Phys.* **104**, 9388 (1996).
- ¹⁷K. S. Schweizer and D. Chandler, *J. Chem. Phys.* **76**, 2296 (1982).
- ¹⁸M. J. Clouter, *Annu. Rev. Phys. Chem.* **39**, 69 (1988).
- ¹⁹J. Chesnoy and G. M. Gale, *Adv. Chem. Phys.* **70**, 297 (1988).