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Vibrational frequency shifts in dense molecular fluids

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A theory is presented for calculating the bond length and vibrational frequency shifts in dense molecular fluids. We combine equation-of-state calculations based on the effective spherical potentials of Shaw, Johnson, and co-workers with a simple model for the interactions of a molecule with the surrounding fluid. The repulsive interactions are approximated with the hard-sphere model of Schweizer and Chandler. We extend their model by including an improved treatment of the long-range attractive interactions and the centrifugal forces. We apply this model to fluid nitrogen and compare with static and shock wave experimental frequency shifts, as well as computer simulation data, over a wide range of pressures and temperatures. We find that while the results using this simple model are reasonably close to experiment in the region appropriate to shock conditions, agreement with data taken under static high-pressure conditions (at lower temperatures) is not as good. Inadequacies of the model and possible improvements are discussed.

I. INTRODUCTION

Recent advances in both static and shock wave high-pressure research have made it possible to measure molecular vibrational frequency shifts in fluids and solids over a very wide range of pressures and temperatures. These shifts provide a great deal of information about the forces exerted on the molecules by their local environment, and thus, the structure of that environment. The most studied of the simple molecular systems is nitrogen. Static experiments, using spontaneous Raman spectroscopy to measure the frequency of the stretching mode, have been carried out at room temperature to pressures as high as 150 GPa (1.5 Mbar), at low temperatures (15 K) to 27 GPa, and at temperatures as high as 950 K to 5–10 GPa. Recently, Schmidt et al. measured the coherent anti-stokes Raman scattering (CARS) in shocked, fluid nitrogen to temperatures and pressures as high as 4400 K and 34 GPa. The shock data appears to agree well with trends in the static experiments and analysis of intensities suggests that the vibrations are in thermal equilibrium with the other degrees of freedom.

A number of theoretical models have been proposed to calculate these frequency shifts. For low temperature solids, Etters and co-workers have developed a simple perturbation scheme that uses known inter- and intramolecular interaction potentials and involves calculating the effective force constants as lattice sums over these interactions. In liquids, Zakin and Herschbach showed that a simple model developed by Schweizer and Chandler could explain much of their data on the pressure dependence of the frequency shifts of pyridine in solution. Other models have been proposed for calculating frequency shifts in liquids, but only that of Schweizer and Chandler provides a way to directly evaluate the interactions. Recently, Etters et al. proposed a Monte Carlo technique that uses the perturbation scheme of Etters to calculate the shifts in solid and fluid nitrogen at high temperatures and pressures.

Statistical mechanical models have been quite successful in calculating the thermodynamics of simple fluids. Use of a variety of perturbation, variational, or integral equation methods leads to essentially exact thermodynamics for systems interacting with spherically symmetric potentials. Recently, Shaw, Johnson, and co-workers showed through an approximate variational procedure that effective spherical potentials for molecular interactions could be found that yield excellent thermodynamic and equation-of-state data. For dense, fluid N₂, for example, the optimal spherical potential is the median of the full anisotropic potential. However, no information about internal molecular properties is available with their methods.

Here we present a simple model for calculating frequency shifts in molecular fluids over wide ranges of pressure and temperature. The equation of state is calculated with the sphericalization procedure of Shaw and Johnson. Hard-sphere diameters, which are determined as part of that procedure, are then used in the model suggested by Schweizer and Chandler to calculate the repulsive forces. We derive a simple expression for the attractive interactions and the centrifugal term. The model requires no simulations and accounts reasonably well for the experimental data in shocked, fluid nitrogen. Agreement with experimental data taken under static high pressures (with temperatures lower than those of the shock experiments) and with computer simulation results is less good.

II. MOLECULAR INTERACTIONS

The basic idea behind the model is to find a simple expression for the forces acting on a molecule in a fluid. To that end, we partition the interactions into separate parts that are treated in somewhat different ways. Before we can calculate the intermolecular interactions, however, the equation of state and properties of the molecular fluid are needed.

A. Equation of state of fluid N₂

We base our calculations of the equation of state (EOS) for N₂ on the effective spherical potentials of Shaw, Johnson, and co-workers. The Ross perturbation procedure is then
used with these spherical potentials to calculate the thermodynamics and EOS. The equation of state calculated for nitrogen with this method is very accurate (with an error of 2 to 3 percent). The Ross procedure yields an effective diameter for a hard-sphere fluid that approximates the real fluid. We use that density- and temperature-dependent hard-sphere diameter in our description of the intermolecular forces below. There are some uncertainties in the use of this reference hard-sphere diameter in the calculations of the force. First, the hard-sphere diameter obtained with the Ross procedure is not unique, and other perturbation or variational procedures may yield a different hard-sphere reference fluid. Also, it has been shown that the effective spherical potential calculated with the Shaw-Johnson procedure does not give very accurate results for radial distribution functions, which are used below in the calculation of the intermolecular interactions. Finally, the hard-sphere diameters we use are calculated from interaction potentials with both repulsive and attractive parts. Below, we include the contributions from the repulsive and attractive forces separately, and so may include some overcounting of the effects of attractions. However, for the present study we fix the diameter of the hard-sphere reference fluid for each pressure and temperature as described.

B. Intramolecular potential

We represent the intramolecular potential as an expansion about the equilibrium gas-phase bond length \( r_e \),

\[
V_r = \frac{1}{2} f x^2 + \frac{1}{2} g x^2, \tag{1}
\]

where \( x = r - r_e \), \( r \) is the bond length, and \( f \) and \( g \) are the usual quadratic and cubic force constants. Even at the highest pressures and temperatures considered in this paper, the deviation from the gas-phase bond length is small enough that this is a good representation of the potential. The gas-phase vibrational frequency is \( \omega_0 = \sqrt{f/\mu} \).

C. Centrifugal force

The characteristic rotational temperature for gas-phase \( N_2 \) is 2.88 K, so a classical treatment is appropriate. In the dense fluid, of course, the molecules are not freely rotating. However, in the spirit of Gordon’s \( m \) diffusion model, we assume that the molecules rotate freely between collisions and that the direction of the angular momentum is randomized upon collision. We then use the fact that the average rotational contribution to the energy is \( k_B T^2 \) to write an approximate form of the centrifugal force. We write the average rotational energy as

\[
\langle E \rangle = \frac{P^2}{2 \mu r_m^2} = k_B T, \tag{2a}
\]

where \( P \) is the average angular momentum and \( r_m \) is the minimum bond length at a given pressure and temperature. The \( r \) dependence of the centrifugal potential is then approximated by

\[
V_c = \frac{k_B T}{(1 + x/r_e)^2}, \tag{2b}
\]

where we have replaced \( r_m \) by \( r_e \) in the last expression, which is a good approximation since the changes in \( r \) are small. We then write

\[
V_c = -\frac{2 k_B T}{r_e} + \frac{3 k_B T}{r_e^2} x^2. \tag{2b}
\]

D. Repulsive intermolecular interactions

We use the approximate expression for the repulsive forces acting along the bond of a molecule in a molecular fluid introduced by Schweizer and Chandler. Namely, all molecules in the fluid but one are represented by a hard sphere with diameter \( \sigma_s \), in our case determined for each pressure and temperature from the Shaw–Johnson potentials and the Ross procedure. The remaining molecule is given shape by representing it with two interpenetrating, noninteracting, hard spheres of diameter \( \sigma \) centered on the atoms. For the purposes of calculating the repulsive forces, the molecule interacts with the rest of the molecules in the fluid with a hard-sphere interaction. Schweizer and Chandler recognized that the mean force along the molecular bond can be calculated from the two-site cavity distribution function \( \gamma \) for an infinitely dilute solution of two spheres of diameter \( \sigma \) in a fluid of hard spheres with diameter \( \sigma_s \). This distribution function \( \gamma \) is a function of the bond length \( r \), the ratio of the hard-sphere diameters \( \sigma/\sigma_s \), and the reduced density of the fluid \( \rho \sigma_s^3 \). If \( \gamma \) is written in terms of a potential of mean force, it is easy to see that the mean force along the bond (averaged over the positions of the hard spheres representing the rest of the fluid and evaluated here at \( r_e \)) is

\[
F_r = -k_B T \left( \frac{\partial \ln(\gamma)}{\partial r} \right) r_e. \tag{3}
\]

The \( \gamma \) function cannot be calculated directly, but an approximate functional form has been given by Grundke and Henderson to interpolate between the known values of \( \gamma \) and its first derivative at \( r = 0 \) and \( r = \sigma \). Pratt et al. provide a tabulation of the parameters for this function for a range of \( \sigma/\sigma_s \) and \( \rho \sigma_s^3 \) values. A convenient functional fit to these parameters is given by Zakin and Herschbach that obviates a two-dimensional interpolation. Note that since \( \sigma_s \) is fixed here by the Ross procedure with the Shaw–Johnson potential, the only free parameter is \( \sigma/\sigma_s \), which cannot vary too much for the model to be physically reasonable.

Unfortunately, the mean curvature of the repulsive contribution to the potential cannot be simply written in terms of derivatives of the \( \gamma \) function; there are fluctuations terms which we cannot evaluate. Thus we use an approximate form of the curvature obtained by Oxtoby, Schwartz et al., and Zakin and Herschbach. The curvature is proportional to

\[
G_r = \frac{F_r}{2 L}, \tag{4}
\]

where \( L \) is a range parameter and is given by \( L = 0.0571 r_0 \) and \( r_0 = 1/2(\sigma + \sigma_s) \). The factor 0.0571 = 1/17.5 comes from an empirical relation of Schwartz et al. The total repulsive potential (expanded about \( r_e \)) is then

\[
V_r = F_r x + \frac{1}{2} G_r x^2. \tag{5}
\]
E. Attractive intermolecular interactions

Zakin and Herschbach\textsuperscript{8} used the empirical formula suggested by Schweizer and Chandler\textsuperscript{9} to calculate the contribution of the attractive forces to the frequency shifts, namely ∆ω = −C₄/ρ\textsubscript{a}, where C₄ was fixed by comparing to some experimental data. They noted that use of this relation gave results that did not seem to match with the trends seen in their data. In our early studies of this model, we also found this form to be inadequate. Here we present a different formulation that seems to give a better description of the attractive forces.

We write the long-range interaction between two diatomic molecules a and b as a sum of atomic site–site potentials,

\[ V_a = -C \left( \frac{1}{r_{13}^2} + \frac{1}{r_{14}^2} + \frac{1}{r_{23}^2} + \frac{1}{r_{24}^2} \right), \]

where sites 1 and 2 are located at the atoms of molecule a and sites 3 and 4 are at the atomic sites on b. We fix the bond length of molecule b at r\textsubscript{e} and calculate the force along the bond of a by taking the derivative of V\textsubscript{a} with respect to the bond length of a. We then expand that force to third order in powers of r\textsubscript{e}/R and r\textsubscript{b}/R, the bond lengths divided by the distance between the centers of mass of the molecules. We assume that in a fluid there is no angular dependence to the pair distribution function and thus can calculate the average force on molecule a by integrating over angles in the force expression to find (expanded about r\textsubscript{e})

\[ F_a = -\rho_a C \left[ 5\gamma_a r_a^2 \right], \]

where the parameters \( \gamma_a \) are determined by

\[ \gamma_a = \int_{r_e} g_{hs}(r) \frac{r \rho_a r^2}{\rho_a r^3} \, dr. \]

We assume the radial dependence of the fluid structure factor is given by that of the hard-sphere reference fluid g\textsubscript{hs}(r\rho\textsubscript{a}r\textsuperscript{2}). The cutoff r\textsubscript{e} is determined from the average of the contact between σ and the molecule, as described by two spheres of diameter σ separated by r\textsubscript{e}. The \( \gamma_a \) are determined by a numerical integration over the Percus–Yevick solution for g\textsubscript{hs}.\textsuperscript{21} The net attractive potential (expanded about r\textsubscript{e}) is then

\[ V_a = F_a r_a + 3G_a r_a^2, \]

where

\[ G_a = -\rho_a C \left[ 5\gamma_a + 3\gamma_a r_a^2 \right]. \]

The parameter C, giving the strength of the attraction, is taken from the nitrogen site–site potential of Etters \textit{et al.}\textsuperscript{7} and is 1.79 × 10\textsuperscript{3} K Å\textsuperscript{6}.

III. FREQUENCY AND BOND-LENGTH SHIFTS

A. Shifts in bond length

For each pressure and temperature, the equilibrium bond-length shift, \( x_m = r_m - r_e \), where r\textsubscript{m} is the new bond length, is determined by finding the zero of the force. Using the expressions for the force described above (dropping terms of order \( x_m^2 \) ) we have

\[ x_m \approx -\frac{\left( F_a - \frac{2k_B T}{r_e} + F_a \right)}{\left( \frac{f + 6k_B T}{r_e^2} + G_a + G_b \right)}. \]

The intramolecular quadratic force constant \( f \) is much greater than the force constants due to the centrifugal, repulsive, and attractive interactions. Thus, the sign of the bond-length shift is given by the numerator in Eq. (9). The repulsive contribution \( F_r \), is positive, thus yielding a negative shift, i.e., compressing the bond. The centrifugal and attractive terms are negative [see Eq. (6) for \( F_a \)], thus leading to a lengthening of the bond.

B. Frequency shifts

The new frequency is given by \( \omega = \sqrt{k/T/\mu} \), where \( k_T \), the second derivative of the total potential, is given by

\[ k_T \approx f + 6k_B T \left( \frac{x_m + \frac{2k_B T}{r_e} + G_a + G_b}{r_e^2} \right). \]

Since the intramolecular force constant \( f \) is much greater than \( \Delta f \), we can write

\[ \Delta \omega = \frac{\omega - \omega_0}{\omega_0} \approx \frac{\Delta f}{f}. \]

From Eqs. (10) and (11) we have

\[ \Delta \omega \approx 3 \gamma \frac{\omega_0}{f} x_m + \frac{\omega_0}{2f} \frac{G_a + G_b}{r_e^2}. \]

From Eq. (12) we see that the total frequency shifts can be divided into a term involving the change in the intramolecular force constant (caused by a change in bond length) and terms involving the direct contributions from the repulsive, attractive, and centrifugal terms.

Below we shall compare our results to experimental Raman data over a wide range of pressures and temperatures. The Raman frequency is given by

\[ \omega_R = \omega - \omega_e x_e, \]

where \( \omega_e x_e \) is a measure of the anharmonicity of the potential. Since we cannot include changes in \( \omega_e x_e \) in our model (we cannot calculate the higher order force constants for the repulsive contribution), we take the gas-phase value\textsuperscript{10} for our calculations. This is reasonable since \( \omega_e x_e \) has been found both experimentally\textsuperscript{5} and theoretically\textsuperscript{13} to remain essentially constant with pressure and temperature.

IV. RESULTS

The only parameter not fixed in this model is the ratio of hard-sphere diameters, σ/σ\textsubscript{j}, used in calculating the repulsive contribution. For normal liquid nitrogen Schweizer and Chandler\textsuperscript{4} used for \( \sigma_j \), the diameter of the hard sphere describing the molecular fluid, the known effective hard-sphere diameter for N\textsubscript{2}. For σ, the diameter of the hard spheres making up the one molecule with shape in the system, they took the value where the Leonard-Jones site–site
TABLE I. Experimental vibrational frequency shifts.\(^a\)

<table>
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<tr>
<th>(P) (GPa)</th>
<th>(T) (K)</th>
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\(^a\)The pressure \(P\) is measured in GPa (100 GPa = 1 Mbar), the temperature \(T\) in Kelvin, and the Raman frequencies \(\omega_{\text{R}}\) in \(\text{cm}^{-1}\). \(\omega_{\text{calc}}\) are the calculated frequencies.

\(^b\)From Ref. 5. Given are the 0–1 Raman transitions. The first three data points are from singly shocked states and have an error in pressure of about \(\pm 1\) GPa and in temperature of about \(\pm 300\) K. The last three data points are from doubly shocked states and have an error in pressure of about \(\pm 2\) GPa and in temperature of about \(\pm 300\) K. The line positions were determined to within about \(\pm 2\) cm\(^{-1}\).

\(^c\)From Ref. 4. The errors in pressure are roughly \(\pm 0.5\) GPa, the errors in temperature \(\pm 5\) K, and the errors in frequency about \(\pm 1\) cm\(^{-1}\).

The potential for the \(\text{N}_2–\text{N}_2\) interaction goes to zero. This approximation yields \(\sigma/\sigma_c = 0.9\). It is not obvious that this value is the optimal one for describing the repulsive interactions, but it does seem to give a rough measure of the shape of the molecule. Unless noted, we take \(\sigma/\sigma_c = 0.9\) for all calculations reported here. Below we shall examine how variations in \(\sigma/\sigma_c\) can account for frequency shifts over a wide range of conditions.

In Table I we compare to experimental data in fluid nitrogen from two sources, static Raman data that was taken by Schiferl and Zinn\(^a\) in a resistively heated diamond-anvil cell, and the frequencies of the 0–1 transitions found in shocked \(\text{N}_2\) by Schmidt et al.\(^b\) The pressures and temperatures of the shocked state were calculated with the same effective spherical potential for \(\text{N}_2\) used here. The shock data explore a much broader pressure–temperature range than the static data, with temperatures sufficient to populate the higher vibrational levels. Indeed, at the highest temperature (4400 K), transitions from level 4–5 were observed. Analysis of peak intensities and comparison with calculated shock temperatures indicates that the molecular vibrations are likely in thermal equilibrium with the other degrees of freedom. Thus, we can compare the shock data with the results from the equilibrium model presented here. Comparison of the splittings between the lines indicates that the \(\psi_x\) term discussed above is roughly constant.

In Fig. 1 we plot the shock data from Table I and a series of calculated curves corresponding to the nominal temperatures of the shocked states. To compare with the data that clusters around 2200 K, we plot curves corresponding to \(T = 2000, 2250,\) and \(2500\) K (the solid lines in Fig. 1). From the experimental data\(^4,5\) and other theoretical results,\(^13\) one expects a softening of the vibrational frequency with increasing temperature due to an increase in volume and the increased centrifugal force. In Fig. 1 we see such a softening at low pressures (e.g., 7.5 GPa), but as the pressure increases there is a crossover and we obtain an anomalous temperature dependence. At constant temperature, the agreement with data seems to worsen as the pressure is increased (see, for example, the data corresponding to about 2200 K). How-
ever, in Table I we see that the differences between the calculated and experimental values are, in general, small, with an error of no more than 5 cm$^{-1}$.

In Table I and Fig. 2 we see that there is considerable disagreement between the calculated frequency shifts and those determined experimentally at static high pressures. The agreement with experiment worsens as the density of the system increases (higher pressure and lower temperature). There seems to be a correlation between the error in the calculations and how close to the freezing line the data points are. In particular, at about 12 GPa and 650 K, which is almost on the freezing line, the frequency is underestimated by about 12 cm$^{-1}$ out of a total shift of 26 cm$^{-1}$. As the temperature is increased and the state point moves away from the freezing line, the agreement with experiment improves. Below we shall discuss possible reasons for the increase in error as the freezing line is approached.

The variation in bond length $r_m$ with pressure is shown for a number of temperatures (ranging from 500 to 4500 K) in Fig. 3. Note that $r_m$ is the position of the minimum of the potential. The average bond length of the molecules would be longer due to the vibrational motions. The increase in bond length with temperature at constant pressure is due both to the increased centrifugal forces and to the increase in volume. The calculated changes are quite small, with a maximum change on this plot of only +0.0027 Å.

We plot in Fig. 4 the change in vibrational frequency ($\Delta \omega_R$) as a function of the change in bond length ($\Delta r_m = x_m$) for the temperatures used in Fig. 3. The relationship between the two is nearly linear, with a slope that is essentially independent of temperature. At a first look at Eq. (12) it may seem that the slope should equal $3g(\omega_0^2/2f)$. However, since $G_r$ is directly proportional to $F_r$ [Eq. (4)], and since $x_m$ is proportional to $F_r$, there is an almost equal dependence of $\Delta \omega_R$ on $x_m$ due to the repulsive contribution, with a slope equal to roughly $\omega_0^2/2L$ where $L$ is the range parameter in Eq. (4). The contribution to the slope from the repulsive forces remains reasonably constant (within 20%) over the temperature range plotted in Fig. 3. The slight dependence of the slope on the attractive contribution tends to offset that of the repulsive contribution.

The contributions of each of the terms in Eq. (12) to the frequency shift is shown in Fig. 5 as a function of pressure for $T = 2500$ K. We plot the change in frequency due to change in bond length ($\Delta \omega_r = 3g(\omega_0x_m/2f)$), as well as the direct contributions from the repulsive ($\Delta \omega_r$), attractive ($\Delta \omega_a$), and centrifugal ($\Delta \omega_c$) forces. The contribution from the change in bond length depends, of course, on the repulsive, attractive, and centrifugal forces as well. The pressure de-

FIG. 3. Variation in bond length $r_m$ with pressure $P$ for temperatures of 500, 1000, 1500, 2000, 3500, and 4500 K. The curves are in ascending order of temperature, i.e., the curve at the bottom of the figure is at $T = 500$ K and that at the top at $T = 4500$ K. The line at $r_m = 1.09768$ Å is the gas-phase value.

FIG. 4. The calculated change in Raman frequency $\Delta \omega_R$ plotted vs the change in bond length $\Delta r_m = x_m$ for temperatures in Fig. 3 (500, 1000, 1500, 2000, 3500, and 4500 K). The curves are in ascending order of temperature, i.e., the curve at the top of the plot corresponds to 4500 K and that at the bottom to 500 K.

FIG. 5. Calculated contributions to the frequency shift $\Delta \omega_R$ as a function of pressure $P$ for $T = 2500$ K. The solid curve is the contribution to the shift from the change in bond length, the dashed curve (---) is the contribution from the repulsive forces, the chain-dashed (----) curve from the centrifugal force, and the long-dashed curve (-----) from the attractive forces.
V. DISCUSSION

While the agreement with experiment is not perfect and, in particular, gives the incorrect temperature dependence at higher pressures, it is perhaps remarkable that the model works as well as it does. There are a number of uncertainties in the quality of the approximations used, from our description of the structure of the fluid to the model for the forces. We shall try to cover those we feel are most important and present possible improvements.

The descriptions of the intermolecular forces (both repulsive and attractive) are given in terms of the pair distribution functions of the molecular fluid, and so depend on how well we represent those functions. There are a number of uncertainties in the procedure we used. First of all, while the Shaw–Johnson effective $N_s$ spherical potential gives good thermodynamics, MacGowan et al. 18 found that the center-of-mass to center-of-mass pair distribution function $g_{cm}(r)$ calculated from a molecular dynamics simulation with the spherical potential does not agree well with that calculated from a molecular dynamics calculation with the full anisotropic potential. For the pressure–temperature point they examined ($P \approx 30$ GPa and $T = 2972$ K), use of the effective spherical potential led to an overestimation of the nearest neighbor peak in $g_{cm}$ by about 30% and a somewhat different shape. In the present model we approximate the fluid structure even more by using not the true $g_{cm}$ for the spherical potentials, but rather the distribution functions for the hard-sphere system that approximates the molecular system. The use of a spherical potential to determine structure should become a worse approximation as the freezing pressure increases, which seems not to be a very accurate method to calculate fluid structures. 14

In addition to errors in structure, the model used to calculate the force constants is only approximate. It is not clear that using a hard-sphere, totally impulsive, model for the repulsive forces is a reasonable representation of the forces due to an exponentially varying interaction, or that the model representing one anisotropic molecule in a fluid of spherical ones is at all accurate. Also, in addition to the neglect of angle-dependent forces in the calculation of the attractive forces and the use of a hard-sphere $g(r)$, there are errors due to truncation of the expansion. Since part of the contribution of the attractive interactions is included in the effective spherical potential, 16(a) there may be an overcounting of the effects of attraction, and thus the repulsive forces may be underestimated. Finally, the expression used to calculate the centrifugal forces neglects the effects of collisions and librational-type motions.

Although we cannot measure the effects of any single approximation, we can assess the accuracy of the force constants calculated with the present model by comparing them to the Monte Carlo results of Eitters et al. 13 Those results are given in Tables II and III (along with the same quantities calculated with the present model) and are thermodynamic averages of the various contributions to the total force constants. They were determined by averaging over the bond lengths (the molecules were allowed to vibrate) as well as the other thermodynamic variables (positions, orientations and volumes). The frequencies calculated in the Monte Carlo studies tended to run a bit higher than the experiment, with an error of about $+8$ cm$^{-1}$ at the higher static pressures of Table I.

In Table II we see that the repulsive quadratic force constants calculated here are considerably smaller (up to almost 50%) than those calculated in the Monte Carlo calculations. This underestimation of $F_r$ relative to the Monte Carlo results is compensated in the model by the overestimation of $G_r$ using the simple relation in Eq. (4). The result using Eq. (4) gives a ratio of $G_r/F_r$ of about 3, while the Monte Carlo results consistently show $G_r/F_r$ is about 1.3. This discrepancy indicates that the approximate form in Eq. (4) should be reexamined. To get agreement with the Monte Carlo results, the range parameter should be $L = 0.132r_0$, where $0.132 = 1/7.58$. In Table III we see that our approxi-

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<td>9898</td>
<td>16546</td>
<td>13160</td>
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</table>

1 The pressures $P$ are in GPa, the linear force constants $F$ are in K/A, and the quadratic force constants $G$ are in K/A$^2$. The temperature is 1000 K for these calculations.

2 Calculated with the present model.

3 Average values from the Monte Carlo calculations of Ref. 13.

---

TABLE II. Comparison of calculated repulsive force constants.*

<table>
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<tr>
<th>$P$</th>
<th>$F_r$</th>
<th>$F_r$</th>
<th>$G_r$</th>
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<td>2362</td>
<td>2025</td>
<td>2632</td>
<td>2443</td>
</tr>
</tbody>
</table>

* The pressures $P$ are in GPa, the linear force constants $F$ are in K/A, and the quadratic force constants $G$ are in K/A$^2$. The temperature is 1000 K for these calculations.

* Calculated with the present model.

* Average values from the Monte Carlo calculations of Ref. 13.

---

TABLE III. Comparison of calculated attractive force constants.*

<table>
<thead>
<tr>
<th>$P$</th>
<th>$F_a$</th>
<th>$F_a$</th>
<th>$G_a$</th>
<th>$G_a$</th>
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</tbody>
</table>

* The pressures $P$ are in GPa, the linear force constants $F$ are in K/A, and the quadratic force constants $G$ are in K/A$^2$. The temperature is 1000 K for these calculations.

* Calculated with the present model.

* Average values from the Monte Carlo calculations of Ref. 13.
mation of the attractive forces gives results in much closer agreement with the simulation data. Both $F_a$ and $G_a$ are somewhat larger in the present model than in the Monte Carlo data, but the $F_a$ are within 20% and the $G_a$ within about 10% of each other over the entire range of pressures. The pressure dependence is reasonably accurate.

There are a number of ways to consider improving the present model. One approach would be to keep the use of the Schweizer–Chandler model for the impulsive interactions. This approach has the advantage of being able to be used in a calculation of the vibrational dephasing times. \(^9\) We have examined how $\sigma/\sigma_0$ must vary (keeping all else in the model constant) to fit the experimental data and found that choosing $\sigma/\sigma_0$ to vary linearly with $\rho$, the filling fraction of the hard-sphere fluid, led to almost precise agreement with experiment and yielded the correct temperature dependence at all pressures studied. The variation of this ratio, $\sigma/\sigma_0 = 0.351 \rho + 0.644$, indicates that to fit the data the ratio must increase considerably as the filling fraction increases. There is no reasonable physical explanation for this variation. Above we noted that the model with $\sigma/\sigma_0 = 0.9$ underestimated the repulsive contributions and got the attractive contributions reasonably well. Letting $\sigma/\sigma_0$ vary with $\rho$, however, does not increase greatly the repulsive contributions, but rather decreases the attractive component. While the use of that variation of $\sigma/\sigma_0$ is not physically justified, the model then does have predictive capabilities, which may be useful in planning future (and costly) shock wave experiments.

Because of the rather extreme nature of the approximations, we feel that the use of the Schweizer–Chandler approximation in predicting accurate frequency shifts is probably not a fruitful one. We have considered one other approach, namely to expand the repulsive part of an exponential six site-site $N_2-N_2$ interaction potential much the same way as we did the attractive part. The equations for the force constants when determined this way are

$$F_\sigma = \frac{A a_{12}}{2880} \left[ 6 \delta_\sigma \alpha^4 \rho_\sigma^2 + 64 \delta_\sigma \alpha^2 \rho_\sigma^2 + 96 \delta_\sigma \right],$$

(14a)

and

$$G_\sigma = \frac{A a_{12}}{2880} \left[ 3 \delta_\sigma \alpha^4 \rho_\sigma^2 + 112 \delta_\sigma \alpha^2 \rho_\sigma^2 + 96 \delta_\sigma \right].$$

(14b)

The repulsive terms in the site-site potential are given by $A e^{-\alpha r}$, where the $r_i$ are the intermolecular site-site distances. The $\delta_\sigma$ functions are determined by

$$\delta_\sigma = \int e^{-\alpha(r-n)} g(r) dr.$$

We applied this model with varying approximations to $g(r)$. Depending on the approximation, we obtained agreement with experiment as good as with the Schweizer–Chandler model. Improvements would require a more accurate determination of $g(r)$ than is possible with the Shaw–Johnson procedure. MacGowan et al.\(^18\) found that a RAM average potential,\(^25\) obtained by solving

$$0 = \int d\Omega_1 \int d\Omega_2 [e^{-V(r)h_\sigma T} - e^{-V_{RAM}(r)h_\sigma T}],$$

yields much more accurate center-of-mass $g_{cm}(r)$ than does the median potential of Shaw and Johnson. In this equation $\Omega_i$ represents the angular variables. However, the RAM potential does not give accurate thermodynamics. We have not yet examined the use of the RAM potential for the present model.

In none of this work have we considered the effects of molecular dissociation or significant changes in molecular electronic structure. We feel that this is a good approximation for the regimes studied because no unusual shifts in the stretching frequency have been seen experimentally. However, an increase in compressibility along the principle Hugoniot (single-shocked states) above 30 GPa has been attributed to molecular dissociation.\(^26\),\(^27\) If the molecules are in fact dissociating in that regime, then the present model is not likely to work very well in describing such a soup of free atoms and reacting molecules.

VI. CONCLUSIONS

We have presented a very simple model that seems to account reasonably well for the vibrational frequency shifts in shocked, fluid $N_2$. While there are disagreements between the results of the present model and the experimental data, especially for state points near the freezing transitions, we feel that the model is sufficiently accurate to guide future shock-wave experiments. The results with the present model are of comparable quality as those of a recent Monte Carlo study\(^13\) and require much less effort and computing time. Improvements in the model are expected to primarily require improvements in the description of the fluid structure.

ACKNOWLEDGMENTS

We would like to thank Professor Dudley Herschbach for bringing the Schweizer–Chandler model to our attention and for providing a preprint of his paper. We would also like to thank Dr. M. S. Shaw for many helpful discussions and for providing the program to calculate the EOS and hard-sphere diameters for fluid $N_2$. The derivations of Eqs. (6), (8), (14), and (15) were carried out in part with the MACSYMA symbolic manipulator. This work was performed under the auspices of the U. S. Department of Energy and was supported in part by the Division of Materials Sciences of the U. S. D. O. E. Division of Basic Energy Sciences.


