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Molecular-dynamics study of the dynamical structure factor of liquid N_2

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The equilibrium and dynamical structure factors of a nitrogenlike system near its triple point are computed by a molecular-dynamics simulation using an "atom-atom" potential. Both structure factors are shown to be almost identical to the structure factors of a system of spherical molecules when the intramolecular contributions have been subtracted and the rotational degrees of freedom taken into account in a trivial way. Thus only very little information on the anisotropic part of the intermolecular interaction can be gained from these two quantities. For the dynamical structure factor, a strong and unexpected disagreement between our computation and the experiment of Carneiro and McTague at small wave numbers probably indicates that the experimental results should be corrected for double-scattering contributions.

I. INTRODUCTION

The dynamics of monatomic liquids are by now fairly well understood, and increasing effort is being spent on systems presenting rotational degrees of freedom. One of the simplest of these systems is the homonuclear diatomic molecule, e.g., N_2. Liquid nitrogen has been studied very recently by a large variety of experimental techniques such as nuclear spin echo for the self-diffusion constant,[1] nuclear magnetic spin relaxation,[2] elastic[3,4] and inelastic[5,6] neutron scattering, light scattering,[7,8] far-infrared absorption,[9] and Raman scattering.[10] For most of these experiments, molecular-dynamics simulations have also been done.[9,11-14] On the theoretical side, integral equations[15-17] and perturbation theories[18-24] have been used to describe the thermodynamic and structural properties of liquid N_2.

Most commonly, the interaction between two molecules is described by a sum of spherical potentials centered at the atom positions ("atom-atom potential"). The atom-atom interaction is generally of a hard-sphere or Lennard-Jones $(n, 6)$ type. As an alternative one can use a quadrupole-quadrupole potential in conjunction (or not) with an "effective" Lennard-Jones (LJ) potential between the molecular centers. A third way is to combine the two methods just described.

Once preference has been given to one or the other potential forms we can adjust the parameters by fitting experimental properties, generally solid-state properties such as equilibrium lattice constants, sublimation heats, the normal mode frequencies (translational and/or librational), etc. But the values of these parameters may be erroneous because the relation between the potential and the experiments is established by approximate theories such as classical harmonic calculations, quantum-mechanical treatments, or, to take account of the large anharmonic contribution self-consistent phonon techniques. Thorough documentation on this aspect can be found in Refs. 25 and 26. The main conclusion is that, in fact, none of these potentials is entirely satisfactory.

In particular, the dynamical structure factor calculated "exactly" by molecular dynamics[27] for the atom-atom potential gives normal mode frequencies in only moderate agreement with the inelastic neutron-scattering results of Kjems and Dolling.[26] Also, the pure atom-atom potential considerably underestimates the α-β transition temperature.[27,28] The long-range anisotropic part of a quadrupole-quadrupole interaction seems more appropriate to reproduce this transition, as shown by a recent Monte Carlo calculation of a classical quadrupole solid.[29] More generally it appears that a model including the electrostatic interaction between the molecules, in addition to the atom-atom potential, gives the best over-all agreement with experiment (in the solid), at least if an "effective" bond length 20% lower than the true one is used.[26]

In the liquid phase, where the short-range repulsive part of the potential is dominant, the atom-atom potential gives a very satisfactory description of the thermodynamics and structural properties of N_2.[11,13] Cheung and Powles,[13] using an atom-atom potential

$$v(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \tag{1}$$

with a distance $2d$ between the interaction centers equal to the true bond length of the molecule, determine best parameters ϵ and σ by fitting the pressure and internal energy of their molecular-dynamics (MD) calculations to experimental measurements over a large region of the liquid state.

The best parameters they find are

$$\epsilon/k = 37.32\,^\circ\mathrm{K}, \quad \sigma = 3.31\ \text{Å}. \tag{2}$$

Moreover, the effect of adding a quadrupole-quadrupole term results in just slightly changing the potential parameters.[13]

In this paper we report MD calculations of the dynamic structure factor $S(k,\omega)$ using the atom-atom potential (1) for a state which in reduced units is $T^* = kT/\epsilon = 1.61$ and $\rho^* = \rho\sigma^3 = 0.6964$ where ρ is the molecular density. Using the potential parameters of Ref. 11,

$$\sigma = 3.341\ \text{Å},\quad \epsilon/k = 44\ ^\circ\text{K}$$

(these parameters will be used for N_2 throughout this paper), this corresponds to $T = 71\ ^\circ\text{K}$ and $\rho = 0.868\ \text{g/cm}^3$. Alternatively, the parameters (2) would give $T = 60\ ^\circ\text{K}$ and $\rho = 0.892\ \text{g/cm}^3$, and the thermodynamic state would correspond to a slightly supercooled liquid. The compressibility factor $p/\rho kT$ equals 0.7. As in Ref. 11, the half-distance between interaction centers was taken to be $d^* = d/\sigma = 0.1646$, and the interaction was set equal to zero after $r = 3.2\sigma$. The motion of 500 molecules, with periodic boundary conditions, was followed using the algorithm described in Ref. 11 over a period of 6400 time steps of $\Delta t = 5 \times 10^{-15}$ sec [$\Delta t = 0.01674\tau_0$, where the time unit $\tau_0 = (m\sigma^2/96\epsilon)^{1/2} = 1.9848 \times 10^{-13}$ sec, where m is the molecular mass]. The relevant time-dependent quantities were then averaged over 6–10 runs with different initial conditions. For static properties, 20 times fewer statistics were asked for.

Section II is devoted to the static structure factor, and Sec. III to the dynamic structure factor.

II. STATIC STRUCTURE FACTOR

In this section we present the static structure factors (atomic and center-of-mass) for the thermodynamic state under consideration. Atomic structure factors have been given previously,[11,13] and the agreement with experiment has been shown to be very satisfactory. However, no comparison has apparently been done with the center-of-mass factor, which, one might hope, could give some information on orientational correlations. We will show that this is in fact not the case.

The atomic static structure factor for a diatomic homonuclear molecule can be defined by

$$S(k) = \frac{1}{4N} \sum_{i,j}^{N} \langle \rho_i(k) \rho_j^*(k) \rangle , \tag{3}$$

where

$$\rho_i(k) = \sum_{\alpha=1}^{2} e^{i\vec{k}\cdot\vec{r}_{i\alpha}} . \tag{4}$$

Here $\vec{r}_{i\alpha}$ denotes the position of atomic nucleus α in the ith molecule (with respect to a laboratory fixed reference frame). The summations on i and j in (3) extend over the N molecules of the system, and $\langle\ \rangle$ means averaging over an appropriate equilibrium ensemble.

If $\vec{R}_i$ is the center-of-mass coordinate of molecule i,

$$\vec{r}_{i\alpha} = \vec{R}_i + \vec{l}_{i\alpha} . \tag{5}$$

For a rigid diatomic molecule, $\vec{l}_{i\alpha} = \pm d\vec{u}_i$ ($\vec{u}_i$ is the unit vector along the symmetry axis of molecule i), and consequently

$$\rho_i(k) = 2 e^{i\vec{k}\cdot\vec{R}_i} \cos(d\vec{k}\cdot\vec{u}_i) . \tag{6}$$

It is convenient to separate the $i=j$ and $i \neq j$ in terms in (3):

$$\begin{aligned} S(k) &= \tfrac{1}{4}\langle |\rho_1(k)|^2 \rangle + \tfrac{1}{4}(N-1)\langle \rho_1(k)\rho_2^*(k)\rangle \\ &\equiv S_{\text{intra}}(k) + S_{\text{inter}}(k) . \end{aligned} \tag{7}$$

The intramolecular contribution is

$$S_{\text{intra}}(k) = \tfrac{1}{4} \sum_{\alpha,\gamma=1}^{2} \langle e^{i\vec{k}\cdot(\vec{l}_{1\alpha} - \vec{l}_{1\gamma})} \rangle = \tfrac{1}{2}[1 + j_0(2kd)] , \tag{8}$$

where $j_n(x)$ is the spherical Bessel function of order n and $j_0(x) = (\sin x)/x$, whereas

$$S_{\text{inter}}(k) = (N-1)\langle e^{i\vec{k}\cdot(\vec{R}_1 - \vec{R}_2)} \cos(d\vec{k}\cdot\vec{u}_1) \cos(d\vec{k}\cdot\vec{u}_2) \rangle . \tag{9}$$

The intermolecular contribution can be expressed either in terms of an atom-atom radial distribution function $g_a(r)$ or in terms of the molecular pair correlation function $g(R_{12}, \Omega_1, \Omega_2)$. In the former case $g_a(r)$ is proportional to the probability of finding two atomic centers located on different molecules at a distance r, and

$$S_{\text{inter}}(k) = \rho \int [g_a(r) - 1] e^{-i\vec{k}\cdot\vec{r}} d\vec{r} \tag{10}$$

[an unimportant $\delta(k)$ term has been omitted]. Alternatively, if $g(R_{12}, \Omega_1, \Omega_2)$ is proportional to the probability of finding two molecules with their centers separated by a distance R_{12} and orientations Ω_1 and Ω_2,

$$\begin{aligned} S_{\text{inter}}(k) = \frac{\rho}{(4\pi)^2} \int & e^{i\vec{k}\cdot(\vec{R}_1 - \vec{R}_2)} \cos(d\vec{k}\cdot\vec{u}_1) \cos(d\vec{k}\cdot\vec{u}_2) \\ & \times g(R_{12}, \Omega_1, \Omega_2)\, d\vec{R}_{12}\, d\Omega_1\, d\Omega_2 . \end{aligned} \tag{11}$$

By expanding the molecular scattering function $\rho_i(k)$ and the pair correlation function g in spherical harmonics, one can show[20,30,31] that

$$S_{\text{inter}}(k) = j_0^2(kd)[S_{\text{cm}}(k) - 1] + S_a(k) , \tag{12}$$

where the center-of-mass structure factor

$$S_{\text{cm}}(k) = 1 + \rho \int [g_{\text{cm}}(R) - 1] e^{-i\vec{k}\cdot\vec{R}} d\vec{R}, \tag{13}$$

and

$$g_{\mathrm{cm}}(R)=\langle g(R,\Omega_1,\Omega_2)\rangle_{\Omega_1,\Omega_2} \tag{14}$$

$$=\frac{1}{(4\pi)^2}\int g(R,\Omega_1,\Omega_2)\,d\Omega_1\,d\Omega_2 \tag{15}$$

denotes averaging over the orientations of the two molecules. The anisotropic part $S_a(k)$ would vanish if no anisotropic part was present in the interaction potential.

The "exact" $S(k)$ and $S_{\mathrm{cm}}(k)$ are shown in Fig. 1 together with $S_a(k)$. The anisotropic contribution is quite small (but larger than the statistical error on the MD calculations, which is believed to be of the order of 3% and probably somewhat larger at the first peak). Because of the presence of $j_n(kd)$ $(n\neq 0)$ factors, $S_a(k)$ should go to zero at small k and high k. From Fig. 1 we see that this is realized for $k\sigma\sim 20$. At this k value, $S_{\mathrm{cm}}(k)$ is practically equal to 1, so that for $k\sigma\gtrsim 20$ only the intramolecular structure is seen.

We also note that the structure factor associated with the center-of-mass motion bears close resemblance to the one of a monatomic liquid. If we assume that a correspondence principle is valid for N_2, our thermodynamic state should correspond approximately to a state near the triple point of a LJ liquid. This can be achieved by choosing LJ parameters equal to $\sigma=3.562$ Å and $\epsilon/k=98\,^\circ\mathrm{K}$. The corresponding LJ state would be $\rho^*=0.8442$ and $T^*=0.722$. A comparison of the corresponding LJ structure factor with $S_{\mathrm{cm}}(k)$ is made in Fig. 1. The small differences can probably be ascribed to the anisotropy of the potential and to the choice of the corresponding LJ state. Note that the value of σ is considerably smaller than the value obtained from gas data ($\sigma=3.70$ Å). Table I gives the numerical values of $S(k)$, $S_{\mathrm{cm}}(k)$, and the atom-atom radial distribution function $g_a(r)$; it is hoped that this might be useful for comparison with perturbation theories.

In conclusion, hardly any information on the anisotropic part of the interaction potential and the orientational motion of N_2 can be gained from the study of the structure factors. This confirms previous analyses by Gubbins *et al.*[20] based on perturbation techniques and by Sandler *et al.*,[31] who use an N_2 model consisting of two overlapping hard spheres treated in the Percus-Yevick approximation.

III. DYNAMICAL STRUCTURE FACTOR

The computer simulation study of Levesque *et al.*[32] on a liquid argonlike system near its triple point has revealed the existence of sound modes propagating for k vectors much larger than those predicted by linear hydrodynamics. A similar behavior, manifested by a secondary peak at finite frequency in the dynamical structure factor $S(k,\omega)$, has also been shown to exist in liquid N_2.[5,14] The computer results for the smallest k vector ($k=0.21$ Å^{-1}) compatible with the periodic boundary conditions of our system have been given previously.[14] Here we present results for larger k values and compare them with inelastic neutron-scattering experiments.

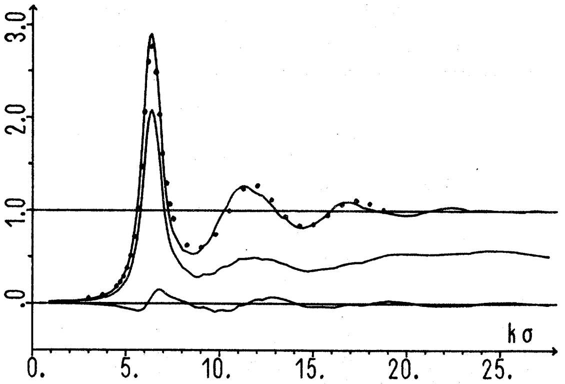

FIG. 1. Structure factor of liquid N_2 at $T^*=1.61$ and $\rho^*=0.6964$. From top to bottom, center-of-mass structure factor $S_{\mathrm{c.m.}}(k)$, atomic structure factor $S(k)$, and the anisotropic contribution $S_a(k)$ defined by (12). The dots represent an equivalent LJ structure factor.

The dynamical structure factor is defined as the Fourier transform

$$S(k,\omega)=\frac{1}{\pi}\int_0^\infty F(k,t)\cos\omega t\,dt \tag{16}$$

of an intermediate scattering function

$$F(k,t)=\frac{1}{4N}\sum_{i,j}^{N}\langle\rho_i(k,t)\rho_j^*(k,0)\rangle, \tag{17}$$

where

$$\rho_i(k,t)=2e^{i\vec{k}\cdot\vec{R}_i(t)}\cos[d\vec{k}\cdot\vec{u}_i(t)] \tag{18}$$

is the time-dependent analog of (6).

The static structure factor $S(k)$ defined in (3) is the zeroth moment of $S(k,\omega)$, i.e.,

$$S(k)=\int_{-\infty}^{+\infty}S(k,\omega)\,d\omega. \tag{19}$$

Again the angular part in (16) can be expanded on a basis set of spherical harmonics and $F(k,t)$ separated into an isotropic and an anisotropic term

$$F(k,t)=j_0^2(kd)F_{\mathrm{cm}}(k,t)+F_{\mathrm{aniso}}(k,t), \tag{20}$$

where

$$F_{\mathrm{cm}}(k,t)=\frac{1}{N}\sum_{i,j}^{N}\langle e^{i\vec{k}\cdot\vec{R}_i(t)}e^{-i\vec{k}\cdot\vec{R}_j(0)}\rangle. \tag{21}$$

TABLE I. Center-of-mass structure factor $S_{\mathrm{c.m.}}(k)$, atomic structure factor $S(k)$, and atom-atom radial distribution function $g_a(r)$ for liquid N_2 at $T^*=1.61$ and $\rho^*=0.6964$.

$k\sigma$	$S_{\mathrm{c.m.}}(k)$	$S(k)$	r/σ	$g_a(r)$
0.8303	0.0216	0.0216	0.8400	0.0000
1.0876	0.0196	0.0193	0.8800	0.0530
1.3449	0.0237	0.0231	0.9200	0.1120
1.6022	0.0249	0.0239	0.9600	0.5380
1.8595	0.0270	0.0251	1.0000	1.1750
2.1168	0.0267	0.0244	1.0400	1.6540
2.3740	0.0284	0.0255	1.0800	1.8530
2.6313	0.0350	0.0301	1.1200	1.8660
2.8886	0.0386	0.0320	1.1600	1.8000
3.1459	0.0479	0.0380	1.2000	1.7280
3.4032	0.0589	0.0453	1.2400	1.6680
3.6605	0.0769	0.0575	1.2800	1.6070
3.9177	0.0955	0.0682	1.3200	1.4960
4.1750	0.1186	0.0838	1.3600	1.3360
4.4323	0.1618	0.1139	1.4000	1.1620
4.6896	0.2306	0.1583	1.4400	1.0030
4.9469	0.3385	0.2306	1.4800	0.8740
5.2042	0.4959	0.3354	1.5200	0.7750
5.4615	0.8000	0.5492	1.5600	0.7020
5.7187	1.2985	0.8928	1.6000	0.6520
5.9760	2.1178	1.4795	1.6400	0.6220
6.2333	2.8280	2.0132	1.6800	0.6170
6.4906	2.7903	2.0082	1.7200	0.6320
6.7479	2.2154	1.6193	1.7600	0.6680
7.0052	1.4085	1.0449	1.8000	0.7270
7.2624	0.9807	0.7182	1.8400	0.7950
7.5197	0.7646	0.5523	1.8800	0.8690
7.7770	0.6661	0.4664	1.9200	0.9450
8.0343	0.5763	0.3873	1.9600	1.0170
8.1922	0.5628	0.3674	2.0000	1.0830
8.5079	0.5342	0.3136	2.0400	1.1390
8.8237	0.5470	0.2844	2.0800	1.1820
9.1395	0.6202	0.3160	2.1200	1.2100
9.4552	0.6805	0.3131	2.1600	1.2200
9.7710	0.8225	0.3298	2.2000	1.2180
10.0867	0.9478	0.3842	2.2400	1.2030
10.4025	1.0522	0.3993	2.2800	1.1760
10.7183	1.1791	0.4316	2.3200	1.1420
11.0340	1.2381	0.4814	2.3600	1.1040
11.3498	1.2659	0.4831	2.4000	1.0630
11.6655	1.2297	0.4906	2.4400	1.0180
11.9813	1.1887	0.4943	2.4800	0.9740
12.2970	1.1638	0.4761	2.5200	0.9370
12.6128	1.0973	0.4798	2.5600	0.9020
12.9286	1.0301	0.4699	2.6000	0.8780
13.2443	0.9454	0.4436	2.6400	0.8630
13.5601	0.9173	0.4255	2.6800	0.8550
13.8758	0.8579	0.3967	2.7200	0.8600
14.7154	0.8299	0.3502	2.7600	0.8720
15.4371	0.9117	0.3716	2.8000	0.8930
16.1588	1.0499	0.3865	2.8400	0.9200
16.8806	1.0949	0.4319	2.8800	0.9500
17.6023	1.0412	0.4427	2.9200	0.9810
18.3240	1.0041	0.4898	2.9600	1.0110
19.0458	0.9799	0.5301	3.0000	1.0380
19.7675	0.9539	0.5361	3.0400	1.0610
20.4892	0.9609	0.5356	3.0800	1.0760
21.2110	0.9981	0.5291	3.1200	1.0840
21.9327	1.0292	0.5358	3.1600	1.0890
22.6544	1.0375	0.5439		
23.3762	1.0020	0.5486		
24.0979	1.0092	0.5710		
24.8196	0.9990	0.5712		
25.5414	0.9958	0.5675		
26.2631	0.9909	0.5488		
26.9848	1.0075	0.5293		
27.7066	0.9871	0.5068		

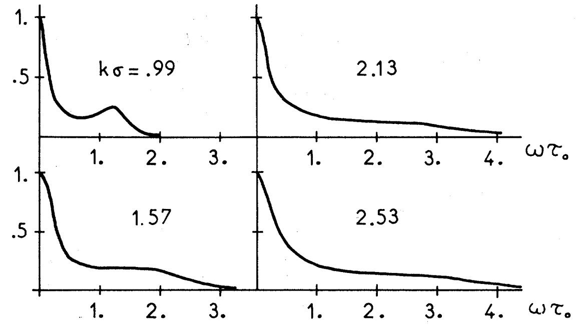

FIG. 2. Dynamical structure factor $S(k,\omega)$ (normalized to unity) for the k vectors $k\sigma=0.992$, 1.565, 2.126, and 2.530.

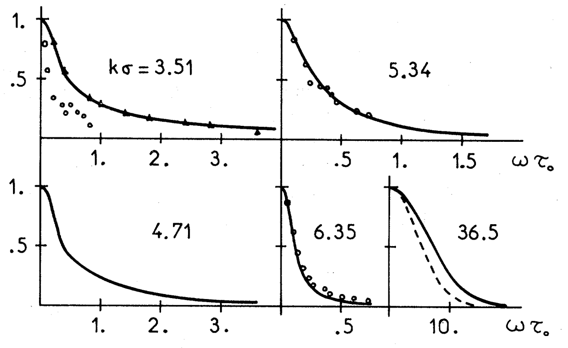

FIG. 3. Dynamical structure factor $S(k,\omega)$ (normalized to unity) for the k vectors $k\sigma=3.508$, 4.707, 5.344, 6.354, and 36.5. The circles represent the inelastic neutron scattering results of Carneiro and McTague (Ref. 5). The triangles represent the dynamical structure factor of an equivalent LJ fluid. For $k\sigma=36.5$, the dotted line represents the dynamical structure factor $S_{\mathrm{c.m.}}(k,\omega)$ for the center-of-mass motion.

In Figs. 2 and 3 we show $S(k, \omega)$ (normalized to unity) for $k\sigma = 0.99-6.35$ and for one higher k value, $k\sigma = 36.5$. $S(k, \omega)$ for $k\sigma = 1.565$ is the average of the three $S(k, \omega)$ functions corresponding to $k\sigma = 1.403$, 1.569, and 1.719; $S(k, \omega)$ for $k\sigma = 2.13$ is the average of the $S(k, \omega)$ for $k\sigma = 1.985$, 2.105, and 2.219. The value $k\sigma = 6.35$ corresponds to the main peak in the static structure factor. In Table II we list the values for $S(k, \omega = 0)$.

Up to $k\sigma = 6.35$ no difference in shape could be detected between $F(k,t)$ and $F_{\mathrm{cm}}(k,t)$ (within statistical errors). On the contrary, at $k\sigma = 36.5$ the decrease of $F_{\mathrm{cm}}(k,t)$ is noticeably slower in time and anisotropic terms seem no longer negligible (cf. Fig. 3).

The results for the intermediate scattering functions $F(k,t)$ are given in Tables III–V. The corre-

TABLE II. Values $S(k, \omega = 0)$ of the dynamical structure factor (in units of τ_0). In brackets are the experimental values of Ref. 5.

$k\sigma$	$S(k, \omega = 0)$
0.702	0.052
0.992	0.026
1.565	0.016
2.126	0.017
2.530	0.016
3.508	0.023 (0.30)
4.707	0.104
5.344	0.436 (0.63)
6.354	6.61 (4.25)
36.46	0.032

TABLE III. Intermediate scattering functions $F(k,t)$ for $k\sigma = 0.99$, 1.57, 2.13, and 2.53. The time t (column 1) is in intervals of $2 \times 10^{-14}\,\Delta t$ sec.

$k\sigma$	0.99	1.57	2.13	2.53
Δt	4	2	2	2
0	0.0443	0.0466	0.0502	0.0573
1	0.0432	0.0459	0.0488	0.0555
2	0.0400	0.0437	0.0451	0.0504
3	0.0352	0.0404	0.0397	0.0433
4	0.0295	0.0363	0.0334	0.0353
5	0.0236	0.0316	0.0270	0.0279
6	0.0180	0.0269	0.0213	0.0219
7	0.0132	0.0224	0.0168	0.0177
8	0.0095	0.0184	0.0136	0.0154
9	0.0071	0.0149	0.0117	0.0145
10	0.0060	0.0122	0.0110	0.0147
11	0.0060	0.0103	0.0110	0.0153
12	0.0069	0.0091	0.0121	0.0159
13	0.0083	0.0086	0.0125	0.0162
14	0.0100	0.0086	0.0128	0.0161
15	0.0118	0.0089	0.0127	0.0155
16	0.0132	0.0095	0.0131	0.0147
17	0.0143	0.0103	0.0132	0.0136
18	0.0148	0.0111	0.0125	0.0125
19	0.0148	0.0117	0.0117	0.0116
20	0.0143	0.0123	0.0109	0.0107
21	0.0133	0.0126	0.0100	0.0101
22	0.0121	0.0128	0.0093	0.0096
23	0.0107	0.0128	0.0086	0.0092
24	0.0092	0.0126	0.0081	0.0089
25	0.0079	0.0122	0.0077	0.0087
26	0.0067	0.0118	0.0074	0.0084
27	0.0057	0.0112	0.0072	0.0082
28	0.0050	0.0107	0.0070	0.0079
29	0.0046	0.0101	0.0069	0.0076
30	0.0045	0.0095	0.0068	0.0072
31	0.0045	0.0090	0.0067	0.0069
32	0.0046	0.0086	0.0066	0.0065
33	0.0049	0.0081	0.0065	0.0062
34	0.0051	0.0078	0.0063	0.0059
35	0.0054	0.0075	0.0062	0.0056
36	0.0056	0.0073	0.0060	0.0053
37	0.0056	0.0071	0.0059	0.0051
38	0.0056	0.0069	0.0057	0.0049
39	0.0053	0.0068	0.0055	0.0048
40	0.0050	0.0067	0.0054	0.0047
41	0.0045	0.0065	0.0053	0.0046
42	0.0040	0.0064	0.0051	0.0045
43	0.0035	0.0063	0.0050	0.0043
44	0.0030	0.0062	0.0049	0.0042
45	0.0026	0.0061	0.0048	0.0041
46	0.0023	0.0059	0.0047	0.0039
47	0.0022	0.0058	0.0046	0.0038
48	0.0022	0.0056	0.0045	0.0036
49	0.0023	0.0053	0.0044	0.0034
50	0.0025	0.0051	0.0043	0.0033
51	0.0027	0.0048	0.0042	0.0031
52	0.0029	0.0046	0.0041	0.0030
53	0.0030	0.0043	0.0040	0.0028
54	0.0031	0.0040	0.0040	0.0027
55	0.0031	0.0038	0.0039	0.0025
56	0.0030	0.0036	0.0039	0.0024
57	0.0029	0.0035	0.0039	0.0024
58	0.0026	0.0033	0.0038	0.0024
59	0.0023	0.0032	0.0038	0.0023

TABLE III *(Continued)*

$k\sigma$	0.99	1.57	2.13	2.53
Δt	4	2	2	2
60	0.0021	0.0031	0.0037	0.0023
61	0.0018	0.0031	0.0036	0.0023
62	0.0015	0.0030	0.0036	0.0022
63	0.0014	0.0030	0.0035	0.0022
64	0.0013	0.0030	0.0034	0.0021
65	0.0012	0.0030	0.0033	0.0021
66	0.0013	0.0029	0.0032	0.0021
67	0.0013	0.0029	0.0031	0.0021
68	0.0014	0.0029	0.0030	0.0022
69	0.0016	0.0028	0.0029	0.0022
70	0.0017	0.0027	0.0029	0.0022
71	0.0019	0.0026	0.0028	0.0022
72	0.0019	0.0024	0.0028	0.0021
73	0.0020	0.0022	0.0027	0.0021
74	0.0020	0.0021	0.0027	0.0020
75		0.0019	0.0026	0.0020
76		0.0017	0.0026	0.0019
77		0.0015	0.0025	0.0018
78		0.0014	0.0025	0.0018
79		0.0013	0.0025	0.0017
80		0.0011	0.0025	0.0016
81		0.0011	0.0025	0.0015
82		0.0010	0.0025	0.0014
83			0.0025	0.0013
84			0.0025	0.0012
85			0.0025	0.0011
86			0.0024	0.0010
87			0.0024	0.0008
88			0.0024	0.0007
89			0.0023	0.0006
90			0.0023	0.0005
91			0.0023	0.0004
92			0.0022	0.0004
93			0.0022	0.0004
94			0.0022	0.0004
95			0.0021	0.0004
96			0.0021	0.0004
97			0.0020	0.0004
98			0.0020	0.0004
99			0.0021	0.0004
100			0.0022	0.0003
101			0.0022	0.0003
102			0.0020	
103			0.0019	
104			0.0018	
105			0.0017	
106			0.0016	
107			0.0015	
108			0.0014	
109			0.0013	
110			0.0013	
111			0.0013	
112			0.0013	
113			0.0013	
114			0.0013	
115			0.0013	
116			0.0012	
117			0.0012	
118			0.0011	
119			0.0011	
120			0.0011	
121			0.0010	
122			0.0010	
123			0.0010	
124			0.0010	
125			0.0010	
126			0.0011	
127			0.0011	
128			0.0011	
129			0.0011	
130			0.0011	
131			0.0012	
132			0.0012	
133			0.0012	
134			0.0012	
135			0.0013	
136			0.0013	
137			0.0013	
138			0.0012	
139			0.0012	
140			0.0012	
141			0.0011	
142			0.0010	
143			0.0010	
144			0.0009	
145			0.0007	
146			0.0006	
147			0.0005	
148			0.0005	
149			0.0004	

sponding dynamical structure factors $S(k, \omega)$ are then obtained by (16).

As for the static case, we can compare the dynamical structure factors of the center-of-mass motion of N_2 and of an LJ liquid. This is done in Fig. 3 for $k\sigma = 3.51$, using the LJ parameters determined in Sec. II. The agreement is almost perfect except for large ω ($\omega\tau_0 > 3.5$) where the LJ $S(k, \omega)$ seems to decrease more rapidly (which indicates different small-time behaviors). No precise comparison could be made for other k values (because the k values do not correspond), but it is apparent that for lower k values also both structure factors look very similar. For N_2 the secon-

TABLE IV. Intermediate scattering functions $F(k,t)$ for $k\sigma = 3.51$, 4.71, 5.34, and 6.35. The time t (column 1) is in intervals of $2\times 10^{-14}\Delta t$ sec.

$k\sigma$	3.51	4.71	5.34	6.35
Δt	4	4	8	8
0	0.0950	0.3120	0.8120	4.3300
1	0.0824	0.2900	0.7200	4.1900
2	0.0567	0.2410	0.5790	3.9400
3	0.0368	0.1930	0.4670	3.6800
4	0.0285	0.1570	0.3800	3.4400
5	0.0263	0.1310	0.3160	3.2200
6	0.0241	0.1120	0.2660	3.0300
7	0.0205	0.0952	0.2270	2.8700
8	0.0170	0.0819	0.1960	2.7200
9	0.0147	0.0716	0.1700	2.5900
10	0.0136	0.0639	0.1450	2.4600
11	0.0129	0.0584	0.1250	2.3400
12	0.0124	0.0544	0.1090	2.2200
13	0.0120	0.0514	0.0969	2.1000
14	0.0114	0.0489	0.0876	2.0000
15	0.0105	0.0464	0.0791	1.9100
16	0.0095	0.0438	0.0734	1.8300
17	0.0086	0.0413	0.0718	1.7500
18	0.0080	0.0389	0.0723	1.6700
19	0.0074	0.0367	0.0706	1.5900
20	0.0069	0.0345	0.0664	1.5100
21	0.0063	0.0322	0.0636	1.4400
22	0.0059	0.0301	0.0628	1.3700
23	0.0053	0.0285	0.0645	1.3000
24	0.0047	0.0272	0.0668	1.2500
25	0.0043	0.0258	0.0659	1.2000
26	0.0040	0.0238	0.0627	1.1600
27	0.0039	0.0216	0.0609	1.1100
28	0.0038	0.0195	0.0614	1.0700
29	0.0038	0.0178	0.0635	1.0200
30	0.0035	0.0165	0.0654	0.9760
31	0.0030	0.0156	0.0657	0.9300
32	0.0024	0.0150	0.0663	0.8900
33	0.0021	0.0146	0.0636	0.8580
34	0.0021	0.0143	0.0578	0.8320
35	0.0020	0.0138	0.0518	0.8100
36	0.0019	0.0131	0.0432	0.7880
37		0.0119	0.0310	0.7660
38		0.0102	0.0187	0.7460
39		0.0084	0.0080	0.7250
40		0.0068		0.7060
41		0.0055		0.6870
42		0.0046		0.6680
43		0.0040		0.6500
44		0.0036		0.6330
45				0.6190
46				0.6050
47				0.5910
48				0.5740
49				0.5570
50				0.5430
51				0.5300
52				0.5170
53				0.5050
54				0.4920
55				0.4780
56				0.4590
57				0.4390
58				0.4180
59				0.3960
60				0.3760
61				0.3540
62				0.3220
63				0.2760
64				0.2220
65				0.1660
66				0.1130
67				0.0699
68				0.0392

ary peak, which seems to be slightly more pronounced than in the LJ system, disappears at $k\sigma \sim 1.2$, somewhat later than for the LJ system $k\sigma = 1$).

Finally, in Fig. 3 we compare our MD results with inelastic neutron-scattering measurements[5] for $k\sigma = 3.5$, 5.34, and 6.35. Good agreement is obtained between the normalized structure factors for the two highest k vectors, although the absolute values differ by about 30% (cf. Table II). However, for $k\sigma = 3.51$ the disagreement is complete both for the shape and absolute value of $S(k,\omega)$. In this k region, incoherent scattering S_{inc} contributes significantly to the scattering cross section. In the analysis of their experimental results Carneiro and McTague[5] use a simple diffusion expression for S_{inc}. The reliability of the coherent-scattering results may depend on the adequacy of this model S_{inc}. More seriously, the lack of correction of the experimental results for multiple scattering may entail large errors on $S(k,\omega)$.

IV. CONCLUSION

The main result of this work is that it is very difficult to obtain information on the effect of the

TABLE V. Intermediate scattering functions $F(k,t)$ (column 2) and $F_{\text{c.m.}}(k,t)$ (column 3) for $k\sigma = 36.5$. The time t (column 1) is in intervals of $2\times10^{-14}\Delta t$ sec.

$k\sigma$	36.5	36.5
Δt	1	1
0	0.9550	0.7420
1	0.8760	0.7060
2	0.6780	0.6080
3	0.4470	0.4770
4	0.2530	0.3440
5	0.1240	0.2290
6	0.0527	0.1420
7	0.0195	0.0821
8	0.0068	0.0427
9	0.0032	0.0180
10	0.0027	0.0029
11	0.0028	
12	0.0027	
13	0.0023	
14	0.0020	
15	0.0018	
16	0.0014	
17	0.0008	
18	0.0002	

nonspherical symmetry of the molecules like N_2 from neutron-diffraction experiments because the precision must be greater than 3% for $k < 3$ Å^{-1}. All of the experimental results can be reproduced by using a model system of spherical molecules. This means that $S(k)$ and $S(k, \omega)$ are very insensitive to the anisotropy of the interaction for diatomic molecules, and this also explains the succcess of the perturbation theories in reproducing $g_{\text{cm}}(r)$ and $g_a(r)$. However, the equation of state, namely, the pressure, is much more sensitive to the details of the interaction and seems to be the relevant quantity to be studied to check perturbation theories and molecular potential forms.

For $S(k, \omega)$, the disagreement for $k\sigma < 3$ between our computation and experiment is very large. This result is unexpected because the agreement at higher $k\sigma$ values is quite good and the molecular-dynamics results are easily reproduced by a model system of spherical molecules. Correction of the experimental results for double scattering would probably reduce this disagreement.

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