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An improved intermolecular potential for nitrogen

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Using new *ab initio* calculations for the multipole and short range interactions and the results for the dispersion interactions recently calculated in our institute, we have constructed a new intermolecular potential for nitrogen. Its distance and angular dependence is expressed analytically in a spherical expansion. The long range dispersion interactions have been damped for charge penetration and exchange effects via the parameter-free damping functions of Tang and Toennies, generalized to the case of an anisotropic potential, and we have introduced two scaling constants in the short range repulsion in order to obtain a second virial coefficient that lies within the experimental error in the entire temperature range. The use of the new potential in lattice dynamics calculations yields good results for several properties of solid nitrogen.

I. INTRODUCTION

Although the knowledge of intermolecular potentials is crucial for understanding the properties of molecular matter, it is practically impossible to obtain this knowledge in sufficient detail from the measured properties alone. The reason for this difficulty is that the potential does not only depend on the distance between the molecules, as in the case of (rare gas) atoms, but also on their orientations in a rather intricate way. More specifically, the different long range (multipole, induced-multipole, and London dispersion) interactions, and short range (charge penetration and exchange) effects, which determine the potential surface in the physically important region of the van der Waals minimum, exhibit a qualitatively different orientational dependence. Therefore, it is very useful that detailed quantitative information about these interactions can presently be obtained, at least for small molecules, from *ab initio* quantum chemical calculations.

A few years ago, the complete angularly dependent intermolecular potential for nitrogen has been obtained from such calculations by Berns and van der Avoird.[1] Their potential, which was represented in two analytic forms, (a site–site model and an expansion in spherical harmonics), has subsequently been used in the evaluation of several bulk properties: the second virial coefficient,[2–4] rotational relaxation rate, Rayleigh linewidth, viscosity, self-diffusion coefficient and thermal conductivity,[5] various liquid state properties via perturbation theory and molecular dynamics simulations[6,7] and the lattice constants, sublimation energy, phase transition pressures, and temperatures[3,8–10] and phonon dispersion relations[8–11] of solid nitrogen. Several of these properties are satisfactorily given by the Berns–van der Avoird (BvdA) potential.[5,8–11] In particular, the phonon frequencies in the various phases of solid nitrogen, which are generally believed to depend very sensitively on the distance and angular dependence of the potential, are very accurately described, provided that one employs a lattice dynamics scheme which correctly deals with the strongly anharmonic large amplitude motions of the molecules.[8–10] From other properties it appeared, however, that the *ab initio* potential could still be improved significantly (with respect to the experimental errors in these properties) by introducing semiempirical scaling[4] and damping[3] functions with parameters fitted to the measured data.

Also from the computational point of view, we think that the BvdA potential is now amenable to improvement. The long range interaction coefficients of Mulder *et al.*[12] which were incorporated in the BvdA potential, have been recalculated by Visser *et al.*[13] using a better theoretical procedure (the time-dependent coupled Hartree–Fock method, whereas Mulder *et al.* have used the uncoupled Hartree–Fock method with virtual orbitals obtained from the V_{HF} potential). Visser's result for the isotropic coefficient C_6 in the expansion $-\Sigma_n C_n R^{-n}$ for the dispersion energy agrees much better with the accurate semiempirical value for this coefficient[14] than Mulder's result; also the higher coefficients C_8 and C_{10} and especially their anistropy, i.e., their angular dependence, are rather different. With present day computer facilities, one can also improve the *ab initio* calculations of Berns and van der Avoird[1] which have produced the short range terms in their potential. One can use a better basis set for the N_2 monomer wave functions and calculate many more points on the potential surface in order to construct a better analytic representation. (The best analytic fit in Ref. 1 still had a mean deviation of 7% from the *ab initio* values for the exchange repulsion, which led to significant errors in the van der Waals well depth for specific orientations.) Such improved calculations are described in Sec. II of the present paper. We have constructed a new N_2–N_2 potential by combining the short range results with the long range interactions of Visser *et al.*,[13] while using the damping functions of Tang and Toennies,[15] generalized to the molecular case, in order to correct the dispersion interactions for charge penetration and exchange effects. In Sec. III this potential is gauged by a calculation of the second virial coefficient and several solid state properties. In Sec. IV we summarize our findings.

II. CALCULATION OF THE POTENTIAL

The intermolecular potential between two (rigid) linear molecules can be expanded as follows:

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$$V(\mathbf{R}, \hat{r}_{\rm A}, \hat{r}_{\rm B}) = (4\pi)^{3/2} \sum_{L_{\rm A}, L_{\rm B}, L} v^{L_{\rm A}, L_{\rm B}, L}(R) A_{L_{\rm A}, L_{\rm B}, L}(\hat{R}, \hat{r}_{\rm A}, \hat{r}_{\rm B}) \tag{1}$$

with the complete orthogonal set of angular functions given by

$$A_{L_{\rm A}, L_{\rm B}, L}(\hat{R}, \hat{r}_{\rm A}, \hat{r}_B) = \sum_{M_{\rm A}, M_{\rm B}, M} \begin{pmatrix} L_{\rm A} & L_{\rm B} & L \\ M_{\rm A} & M_{\rm B} & M \end{pmatrix} \times Y_{L_{\rm A} M_{\rm A}}(\hat{r}_a) Y_{L_{\rm B}, M_{\rm B}}(\hat{r}_{\rm B}) Y_{LM}(\hat{R}). \tag{2}$$

The vector $\mathbf{R} = (R, \hat{R}) = (R, \Theta, \Phi)$ points from the center of mass of molecule A to that of molecule B, the unit vectors $\hat{r}_{\rm A} = (\theta_{\rm A}, \phi_{\rm A})$ and $\hat{r}_{\rm B} = (\theta_{\rm B}, \phi_{\rm B})$ describe the orientations of the respective molecular axes. All these vectors are expressed relative to an arbitrary (space fixed) coordinate system. The functions $Y_{lm}(\hat{r})$ are spherical harmonics and the symbol in large brackets is a 3-*j* coefficient. Since the angular basis is constructed such that it is invariant with respect to rotations of the space fixed coordinate frame, one may use, when calculating the potential, a special frame with $\hat{R} = (0, 0)$ and $\hat{r}_{\rm B} = (\theta_{\rm B}, 0)$ and vary only the "internal" angles $(\theta_{\rm A}, \theta_{\rm B}, \phi_{\rm A})$ of the AB dimer. The expansion coefficients can then be written as

$$v^{L_{\rm A}, L_{\rm B}, L}(R) = \pi^{1/2} \int_{\theta_{\rm A}=0}^{\pi} d(\cos\theta_{\rm A}) \int_{\theta_{\rm B}=0}^{\pi} d(\cos\theta_{\rm B}) \int_{\phi_{\rm A}=0}^{2\pi} d\phi_{\rm A} \times A_{L_{\rm A}, L_{\rm B}, L}(\theta_{\rm A}, \theta_{\rm B}, \phi_{\rm A}) V(R, \theta_{\rm A}, \theta_{\rm B}, \phi_{\rm A}). \tag{3}$$

As proposed already in Ref. 1, the actual calculation of these coefficients can be performed by calculating, for a given value of R, the potential $V(R, \theta_{\rm A}, \theta_{\rm B}, \phi_{\rm A})$ in a grid of points $(\theta_{\rm A}, \theta_{\rm B}, \phi_{\rm A})$ such that the integrations in Eq. (3) can be carried out by numerical quadrature. The symmetry of the N_2–N_2 dimer, which leads to the relation $v^{L_{\rm A}, L_{\rm B}, L}(R) = v^{L_{\rm B}, L_{\rm A}, L}(R)$ with coefficients that are nonzero only for even $L_{\rm A}$, $L_{\rm B}$, and L, allows a considerable reduction of the number of $(\theta_{\rm A}, \theta_{\rm B}, \phi_{\rm A})$ quadrature points for which the potential has to be calculated. If this procedure is repeated for several values of R, the expansion coefficients $v^{L_{\rm A}, L_{\rm B}, L}(R)$ can be fitted by analytical functions.

There are several advantages in using this expansion. It yields an analytic expression for the potential which shows explicitly its dependence on the molecular orientations, with respect to a general coordinate frame. In contrast with site-site models, this expression is in principle an exact representation of the potential surface. In practice, one can represent the potential to any accuracy by truncating the summation (1) at values of $L_{\rm A}$, $L_{\rm B}$ and L which are sufficiently large. Of course, the number of quadrature points required to carry out the integrations in Eq. (3) accurately, is related to these values. Finally, we note that the expansion (1) for the potential is convenient in scattering calculations and calculations of the second virial coefficient, in calculations of the bound states of N_2–N_2 dimers[16,17] and in lattice dynamics calculations which include large amplitude motions of the molecules.[8–10]

The different interactions that contribute to the N_2–N_2 potential can be distinguished by the distance dependence of the corresponding terms in the expansion coefficients $v^{L_{\rm A}, L_{\rm B}, L}(R)$. By definition, the long range terms vary as R^{-n}, while the short range effects decay exponentially with increasing R. The important long range interactions are the electrostatic multipole–multipole interactions, which for linear molecules in a Σ state are given by[18]

$$v_{\rm elec}^{L_{\rm A}, L_{\rm B}, L}(R) = \delta_{L_{\rm A}+L_{\rm B}, L}\, C^{L_{\rm A}, L_{\rm B}} R^{-L_{\rm A}-L_{\rm B}-1} \tag{4}$$

with

$$C^{L_{\rm A}, L_{\rm B}} = (-1)^{L_{\rm A}} \left[\frac{(2L_{\rm A} + 2L_{\rm B})!}{(2L_{\rm A} + 1)!(2L_{\rm B} + 1)!} \right]^{1/2} Q_{L_{\rm A}} Q_{L_{\rm B}}, \tag{5}$$

in terms of the molecular multipole moments $Q_{L_{\rm A}}$ and $Q_{L_{\rm B}}$ (starting with the quadrupoles $L_{\rm A} = 2$, $L_{\rm B} = 2$), and the London dispersion interactions

$$v_{\rm disp}^{L_{\rm A}, L_{\rm B}, L}(R) = - \sum_{n=6,8,\ldots} C_n^{L_{\rm A}, L_{\rm B}, L} R^{-n}. \tag{6}$$

The dispersion coefficients $C_n^{L_{\rm A}, L_{\rm B}, L}$ have been calculated by Visser *et al.*[13] by means of the time-dependent coupled Hartree–Fock method. Via an angular momentum recoupling scheme proposed earlier[19,20] the dispersion interactions

TABLE I. Long range interaction coefficients.

	Electrostatic[a] Eq. (4)	Dispersion Eq. (12)		
$L_{\rm A}, L_{\rm B}, L$	$C^{L_{\rm A}, L_{\rm B}}$ (kJ mol^{-1} nm$^{L_{\rm A}+L_{\rm B}+1}$)	$C_6^{L_{\rm A}, L_{\rm B}, L}$ (kJ mol^{-1} nm^6)	$C_8^{L_{\rm A}, L_{\rm B}, L}$ (kJ mol^{-1} nm^8)	$C_{10}^{L_{\rm A}, L_{\rm B}, L}$ (kJ mol^{-1} nm^{10})
0, 0, 0	···	4.119×10^{-3}	3.795×10^{-4}	3.491×10^{-5}
2, 0, 2	···	2.165×10^{-4}	9.780×10^{-5}	1.380×10^{-5}
2, 2, 0	···	5.454×10^{-6}	1.458×10^{-6}	3.150×10^{-7}
2, 2, 2	···	6.518×10^{-6}	-2.179×10^{-6}	-8.662×10^{-7}
2, 2, 4	1.624×10^{-3}	5.247×10^{-5}	1.133×10^{-5}	5.778×10^{-6}
4, 2, 6	6.771×10^{-5}	···	···	···
4, 4, 8	5.411×10^{-6}	···	···	···
6, 2, 8	8.024×10^{-7}	···	···	···
6, 4, 10	1.046×10^{-7}	···	···	···
6, 6, 12	2.996×10^{-9}	···	···	···

[a] Molecular multipole moments: $Q_2 = -0.944 e\, a_0^2$, $Q_4 = -7.089 e\, a_0^4$, $Q_6 = -18.806 e\, a_0^6$.

could be directly calculated in the form of the spherical expansion (1). The multipole induced–multipole interactions appear to be negligible with respect to the dispersion interactions.[12,13] All the relevant long range coefficients are collected in Table I.

The most important short range interactions are the effects of charge penetration and exchange on the first order multipole–multipole interactions and on the second order dispersion interactions. Meath, Allnatt *et al.*[21,22] have calculated the charge penetration effects on the first order multipole interactions and they have proposed an empirical scaling relation which yields the exchange interactions. The first order charge penetration and exchange effects are both contained in the following expression:

$$V^{(1)} = \frac{\langle \hat{A}\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}} | H | \hat{A}\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}} \rangle}{\langle \hat{A}\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}} | \hat{A}\psi_0^{\mathrm{A}}\psi_0^{\mathrm{B}} \rangle} - \langle \psi_0^{\mathrm{A}} | H^{\mathrm{A}} | \psi_0^{\mathrm{A}} \rangle - \langle \psi_0^{\mathrm{B}} | H^{\mathrm{B}} | \psi_0^{\mathrm{B}} \rangle, \qquad (7)$$

where H, H^{A}, and H^{B} are the Hamiltonians of the dimer and of monomers A and B, respectively, ψ_0^{A} and ψ_0^{B} are the monomer ground state wave functions and $\hat{A}$ is the intermolecular antisymmetrizer. We have calculated this quantity, with monomer bond lengths[23] fixed at $r_{\mathrm{A}} = r_{\mathrm{B}} = 2.0744\ a_0$, using Hartree–Fock wave functions ψ_0^{A} and ψ_0^{B} obtained in a (11*s*, 6*p*, 2*d*) Gaussian-type orbital basis, contracted to [6*s*, 4*p*, 2*d*]. This basis is smaller than the basis used in the calculations[13] of the dispersion coefficients. We believe, however, that it is sufficiently large, since it only needs to describe the ground states ψ_0^{A} and ψ_0^{B} accurately, whereas the dispersion coefficients involve the complete (effective) monomer spectrum. The sensitivity of the exchange repulsion with respect to basis set extension has been tested in a similar study on the O_2–O_2 potential.[24] The calculations were made in a 10×10 points Gauss–Legendre grid for θ_{A} and θ_{B} and a 10 points Gauss–Chebyshev grid for ϕ_{A}, in order to obtain the spherical expansion coefficients by numerical integration, see Eq. (3), with the appropriate weights.[25] Using the full symmetry we needed only 75 angular points, however, which was sufficient to obtain the coefficients through $L_{\mathrm{A}} = L_{\mathrm{B}} = 8$ and $L = 14$. If all these coefficients were included, the spherical expansion would have converged to 0.01% root mean square deviation (rmsd) from the *ab initio* results. By truncating the expansion as in Table II we keep the rmsd less than 0.5%. Each point took 25 to 30 min of CPU time on the NAS 9040 university computer at Nijmegen, using the ATMOL program package.[26]

We have carried out this procedure for $R = 5.5$, 6.5, and $7.5\ a_0$. The total first order interaction given by Eq. (7) comprises the long range multipole–multipole interactions. Since these interactions are known already from Eqs. (4) and (5) and they vary with the distance as R^{-5}, R^{-7}, etc., we found it convenient to subtract them from the total first order interaction. The remaining part is due to the overlap between the molecular charge clouds, which leads to electrostatic interactions deviating from the multipole expansion and to exchange effects, both depending exponentially on R. Thus, we can easily represent this part, for all values of L_{A}, L_{B}, and L by the following form:

$$v_{\text{overlap}}^{L_{\mathrm{A}}, L_{\mathrm{B}}, L}(R) = F^{L_{\mathrm{A}}, L_{\mathrm{B}} L} \exp(-\alpha^{L_{\mathrm{A}}, L_{\mathrm{B}}, L} R - \beta^{L_{\mathrm{A}}, L_{\mathrm{B}}, L} R^2). \qquad (8)$$

TABLE II. Short range interaction parameters[a] occurring in Eqs. (8), (13), and (14).

$L_{\mathrm{A}}, L_{\mathrm{B}}, L$	$F^{L_{\mathrm{A}}, L_{\mathrm{B}}, L}$ (kJ mol^{-1})	$\alpha^{L_{\mathrm{A}}, L_{\mathrm{B}}, L}$ (nm^{-1})	$\beta^{L_{\mathrm{A}}, L_{\mathrm{B}}, L}$ (nm^{-2})
0, 0, 0	$4.263\,86 \times 10^5$	26.4733	12.9778
2, 0, 2	$1.975\,71 \times 10^5$	25.7967	13.8556
2, 2, 0	$2.807\,20 \times 10^3$	15.1933	25.4000
2, 2, 2	$-1.038\,25 \times 10^4$	19.2333	21.1333
2, 2, 4	$1.840\,21 \times 10^5$	28.1500	11.8556
4, 0, 4	$4.242\,74 \times 10^4$	27.2733	11.3444
4, 2, 2	$2.473\,13 \times 10^1$	2.7533	38.9556
4, 2, 4	$-1.101\,24 \times 10^3$	17.6700	22.3000
4, 2, 6	$1.001\,49 \times 10^5$	32.5267	6.7000
4, 4, 0	$2.808\,12 \times 10^{-6}$	-60.3767	116.0667
4, 4, 2	$-1.708\,78 \times 10^{-7}$	-78.0400	140.6444
4, 4, 4	$1.547\,77 \times 10^{-1}$	-11.4900	56.1667
4, 4, 6	$-1.614\,99 \times 10^2$	16.2467	24.3444
4, 4, 8	$1.559\,78 \times 10^5$	40.1500	-1.3333
6, 0, 6	$1.979\,22 \times 10^4$	36.2700	-0.2556
6, 2, 4	$7.709\,23 \times 10^{-1}$	1.2700	38.8222
6, 2, 6	$-4.832\,77 \times 10^2$	26.9800	10.0000
6, 2, 8	$1.138\,52 \times 10^5$	44.0067	-7.0333
6, 4, 10	$4.784\,23 \times 10^5$	54.5467	-17.5778
6, 6, 12	$3.972\,50 \times 10^6$	71.7233	-35.7889

[a] The *ab initio* values in this table have to be scaled by Eq. (17) with $X = 1.50$ and $Z = 1.0509$. For $R > 14a_0$ the terms with negative β should be set to zero.

With the parameters $F^{L_{\mathrm{A}}, L_{\mathrm{B}} L}$, $\alpha^{L_{\mathrm{A}}, L_{\mathrm{B}}, L}$, and $\beta^{L_{\mathrm{A}}, L_{\mathrm{B}}, L}$ given in Table II, this completes the analytic representation of the first order interaction potential. The error in this representation is less than 0.5%, for arbitrary molecular orientations, within the distance range $5.5\ a_0 \leqslant R \leqslant 7.5\ a_0$ and somewhat greater for smaller and larger values of R (cf. similar studies on the O_2–O_2 dimer).[24] Fitting the results for the three distances by simple exponential functions with two parameters instead of three would have led to a substantially greater loss of accuracy.

The effects of charge penetration and exchange on the second order dispersion and induction interactions are considerably smaller than the first order overlap effects, and it is much harder to obtain them from *ab initio* calculations. In the present study we follow the common practice of including these effects by introduction of a damping function. Among the various types of damping functions available (see Refs. 15 and 27, and references therein), we have chosen the form proposed by Tang and Toennies,[15] mainly because these authors have chosen the damping proportional to the first order overlap effects (penetration plus exchange) and have not introduced any additional fitting parameters. For the isotropic interactions between atoms, where the first order overlap repulsion can be fitted to the form $A \exp(-aR)$, Tang and Toennies damp the individual terms in the dispersion series $-\sum_n C_n R^{-n}$ as follows:

$$V_{\text{disp}}(R) = -\sum_n f_n(R) C_n R^{-n} \qquad (9)$$

by means of damping functions:

$$f_n(R) = 1 - \left[\sum_{k=0}^{n} \frac{(aR)^k}{k!}\right] \exp(-aR) \tag{10}$$

which behave as

$$\begin{aligned} &f_n(R) \to 1 && \text{if } R \to \infty, \\ &f_n(R) \to 0 + O(R^{n+1}) && \text{if } R \to 0. \end{aligned} \tag{11}$$

The latter condition can be easily verified by noting that the expression between square brackets in Eq. (10) is the truncated Taylor expansion of $\exp(aR)$.

We must generalize this idea in two ways. First, we are dealing with the anisotropic interactions between molecules which depend not only on the distance R but also on the molecular orientations. We have chosen to damp each (L_A, L_B, L) term in the dispersion interaction, Eq. (6), depending on the parameters $\alpha^{L_A, L_B, L}$ and $\beta^{L_A, L_B, L}$ that determine the range of the corresponding term in the first order overlap repulsion, see Eq. (8). Thus, the effect of damping on Eq. (6) is given by

$$v_{\rm disp}^{L_A, L_B, L}(R) = -\sum_{n=6,8,\ldots} f_n^{L_A, L_B, L}(R) C_n^{L_A, L_B, L} R^{-n}. \tag{12}$$

Secondly, the form of our damping functions must be slightly more complicated than Eq. (10), because our form of the first order overlap repulsion, Eq. (8), contains a quadratic exponent. We write

$$f_n^{L_A, L_B, L}(R) = 1 - \left[\sum_{k=0}^{n} a_k^{L_A, L_B, L} R^k\right] \times \exp(-\alpha^{L_A, L_B, L} R - \beta^{L_A, L_B, L} R^2) \tag{13}$$

with

$$a_k = \sum_{i=k/2}^{k} \frac{\alpha^{2i-k} \beta^{k-i}}{(2i-k)!(k-i)!}. \tag{14}$$

The latter expression, where we have omitted the labels L_A, L_B, L for typographical reasons, has been chosen such that our damping functions satisfy the same relations (11) as those of Tang and Toennies.

Summarizing, we can now write the full N_2–N_2 potential as the expansion (1) with the coefficients

$$v^{L_A, L_B, L}(R) = v_{\rm elec}^{L_A, L_B, L}(R) + v_{\rm overlap}^{L_A, L_B, L}(R) + v_{\rm disp}^{L_A, L_B, L}(R), \tag{15}$$

where the individual contributions are given by Eqs. (4) and (5), (8), and (12)–(14), respectively, with the numerical values of the parameters in Tables I and II. We reiterate that the effects of charge penetration and exchange on the first, electrostatic, term are contained in the second, overlap, term, while such effects on the dispersion interactions are included in the third term directly, via the damping functions in Eqs. (12)–(14).

III. BULK PROPERTIES

A. Second virial coefficient

Using the potential presented in the previous section we have calculated the second virial coefficient $B(T)$ over the wide temperature range $75\ \mathrm{K} \leqslant T \leqslant 700\ \mathrm{K}$ in which it has been measured.[28] Since our potential has the form of a spherical expansion (1), we can directly use the formulas for two linear molecules presented by Pack,[29] including the first quantum corrections due to the relative translational (R) and rotational (A) motions, including the coriolis term in the latter:

$$B(T) = B_{\rm clas}(T) + B_R^{(1)}(T) + B_A^{(1)}(T). \tag{16}$$

The derivatives required in the quantum corrections have been calculated analytically. The integrations over the four-dimensional configuration space have been made by using the same type of quadrature as described in Sec. II for the angles θ_A, θ_B, and ϕ_A with $12 \times 12 \times 12$ points and a 90 points trapezoidal rule for the distance R in the range from 4.4 to $45a_0$. In the inner region, $R < 4.4a_0$, the function $\exp(-V/kT)$ being effectively zero yields a constant contribution to the classical term and zero to the quantum corrections; in the outer region, $R > 45a_0$, all contributions were assumed to be negligible. We have checked that the result for $B(T)$ is sufficiently stable against changes in the integration parameters and in the region boundaries.

In agreement with previous calculations,[2–4] which have used the BvdA potential[1] and some modifications of it, we find that the contributions from the anisotropic terms in the potential are very important. The quantum corrections are only significant at lower temperatures, where they have about the same size as the experimental uncertainty. The Coriolis term is always small. Our new potential as it emerges directly from the *ab initio* calculations described in Sec. II yields a virial coefficient $B(T)$ that is considerably too high over the entire temperature range. Apparently the van der Waals well is too shallow. This holds even when we completely refrain from damping the dispersion attractions. In principle, this discrepancy can be explained by the dispersion attraction being too weak or by the overlap repulsion being too strong. (A change of the quadrupole moment by any reasonable amount made very little difference to the second virial coefficient.) We believe, however, that the long range dispersion efficients C_6, C_8, and C_{10} are fairly accurate, since the *ab initio* value for C_6 agrees well with the accurate semiempirical value[14] and since the dispersion attraction as a whole is stronger already than it is in the BvdA potential. We think, therefore, that the exchange repulsion is too strong by about 20%, which actually amounts to a shift in the "repulsive wall" of about $0.1a_0$ only. There may be two reasons for our overestimate of the exchange repulsion.

(i) Formula (7), used to evaluate the exchange repulsion, does not take into account the so-called exchange-induction effects, which may reduce the exchange repulsion by an outward polarization of the molecular charge clouds. We have estimated this effect by performing converged self-consistent field calculations on the N_2–N_2 dimer. The resulting energy lowering was largely due to the basis set superposition error,[18] however, and the net effect was considerably too small to explain the observed discrepancy. (For instance, for the structure with $\theta_A = \theta_B = 90°$, $\theta_A = 0°$ and $R = 4$ Å the energy lowering amounts to 6% of the exchange repulsion, 4% of which is due to the basis set superposition error.)

(ii) By the use of Hartree-fock wave functions ψ_0^A and ψ_0^B in formula (7) we have neglected the effect of the intra-

TABLE III. Second virial coefficient[a] (in $cm^3\ mol^{-1}$).

T(K)	B_{clas}	$B_R^{(1)}$	$B_{A_{rot}}^{(1)}$	$B_{A_{cor}}^{(1)}$	B_{total}	B_{expt}
75	− 280.2	4.70	2.58	0.12	− 272.8	− 275 ± 8
80	− 247.0	3.82	2.09	0.10	− 241.0	− 243 ± 7
90	− 196.8	2.68	1.44	0.07	− 192.7	− 197 ± 5
100	− 161.0	1.98	1.05	0.05	− 157.9	− 160 ± 3
110	− 134.1	1.53	0.80	0.04	− 131.7	− 132 ± 2
125	− 104.4	1.11	0.57	0.03	− 102.7	− 104 ± 2
150	− 71.77	0.72	0.36	0.02	− 70.68	− 71.5 ± 2
200	− 35.79	0.39	0.19	0.009	− 35.20	− 35.2 ± 1
250	− 16.58	0.25	0.12	0.006	− 16.20	− 16.2 ± 1
300	− 4.75	0.18	0.08	0.004	− 4.48	− 4.2 ± 0.5
400	8.86	0.11	0.05	0.003	9.02	9.0 ± 0.5
500	16.30	0.08	0.04	0.002	16.41	16.9 ± 0.5
600	20.87	0.06	0.03	0.001	20.96	21.3 ± 0.5
700	23.90	0.05	0.02	0.001	23.97	24.0 ± 0.5

[a] Calculated values with the potential parameters from Tables I and II.

TABLE IV. Properties of α-nitrogen ($T = 0$ K, $p = 0$).

		Experiment	Calculated			
		Refs. 28–33	BvdA potential		Present potential	
Lattice constant (Å)	a	5.644	5.644[a]	5.699[b]	5.644[a]	5.614[b]
Cohesion energy (kJ/mol)		6.9	5.89	5.92	6.86	6.87
Compressibility $\chi_T(10^{-10}\ N^{-1}\ m^2)$		4.6		5.07		4.69
Phonon frequencies (cm^{-1})						
	$\Gamma(0,0,0)$					
Librations	E_g	32.3	32.8	31.0	32.6	33.8
	T_g	36.3	43.4	41.0	37.7	38.9
	T_g	59.7	71.5	68.0	57.4	59.1
Transl. vibrations	A_u	46.8	50.6	47.2	49.0	51.0
	T_u	48.4	52.7	48.8	51.8	54.1
	E_u	54.0	60.2	55.6	56.8	59.4
	T_u	69.4	79.4	73.1	76.0	79.7
	$M\left(\frac{\pi}{a},\frac{\pi}{a},0\right)$					
Mixed	M_{12}	27.8	28.8	27.6	27.3	28.0
	M_{12}	37.9	41.5	39.1	39.4	40.7
	M_{12}	46.8	53.3	50.2	46.9	48.7
	M_{12}	54.9	63.7	59.1	58.1	60.7
	M_{12}	62.5	72.0	66.5	66.3	69.6
	$R\left(\frac{\pi}{a},\frac{\pi}{a},\frac{\pi}{a}\right)$					
Transl. vibrations	R_1^-	33.9	37.0	34.4	35.9	37.4
	R_{23}^-	34.7	38.4	35.8	36.9	38.4
	R_{23}^-	68.6	78.4	72.3	75.3	79.1
Librations	R_1^+	43.6	50.7	47.9	43.0	44.5
	R_{23}^+	47.2	53.6	50.8	44.5	45.9
rmsd transl.			6.5	2.1	4.2	6.8
rmsd libr.			7.5	5.0	1.7	1.5
rmsd all			6.7	3.4	3.1	5.0

[a] Fixed at experimental value.

[b] Calculated by minimization of the free energy.

molecular electron correlation on the intermolecular exchange repulsion. Very recent calculations by Böhm and Ahlrichs[30] have shown that this effect may substantially lower the repulsive part of the potential. It was not possible to extract this part explicitly from their results, however, because their "supermolecule" approach does not permit a quantitative separation of the intramolecular correlation effects from the intermolecular correlation, which yields the dispersion attraction. Neither could we subtract the results of Visser *et al.*[13] for the dispersion attraction, because the attraction that is implicitly included in the results of Böhm *et al.*[30] is substantially underestimated, as is evident from their van der Waals well being too shallow. Moreover, these authors have only considered a few specific orientations of the N_2 molecules in their *ab initio* calculations. Therefore, we have presently improved our N_2–N_2 potential by introducing two empirical scaling parameters which change the size and the slope of the repulsive overlap term (8) and, via the relations (13) and (14), also the slope of the damping functions. We write

$$\begin{aligned} F^{L_A,L_B,L} &= X F^{L_A,L_B,L}_{ab\ initio}\,, \\ \alpha^{L_A,L_B,L} &= Z \alpha^{L_A,L_B,L}_{ab\ initio}\,, \\ \beta^{L_A,L_B,L} &= Z^2 \beta^{L_A,L_B,L}_{ab\ initio} \end{aligned} \tag{17}$$

adopting the same scaling constants X and Z for the isotropic $L_A = L_B = L = 0$ term and all anisotropic L_A, L_B, L terms in the potential. The condition that the second virial coefficient should lie well within the experimental error bars over the entire temperature range, see Table III, appeared to be sufficient to determine both these scaling parameters. The resulting values are $X = 1.50$ and $Z = 1.0509$. A scaling factor of 1.5 may seem large, but one must realize that a small change in the exponent of the exchange repulsion causes a large change in the preexponential factor.

B. Solid state properties

In the condensed phases three- and more-body interactions between the molecules may be nonnegligible, but such interactions between neutral nondipolar molecules are relatively weak. Probably they contribute less than 10% to the cohesion energy. All practical lattice dynamics calculations are based on (sometimes effective) pair potentials. The pair potential for nitrogen which we have obtained in the preceding sections has been employed to calculate several properties of solid nitrogen. We have concentrated on the ordered α and γ phases since most experimental data pertain to these phases. In the computation of the solid state properties from the pair potential we have used the recently developed lattice dynamics method of Briels *et al.*[10] which is appropriate for harmonic as well as strongly anharmonic large amplitude motions of the molecules. The lattice free energy, which at $T = 0$ equals the sublimation energy, has been calculated under inclusion of the lattice vibrations at the mean field level. The lattice constants have been obtained by minimizing the free energy, at a given pressure and temperature. For calculations at nonzero pressure this was done as described in Ref. 10. From these results we have also calculated the isothermal compressibility:

$$\chi_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T, \tag{18}$$

where v is the molar volume. We have also checked whether the new potential correctly predicts the α–γ phase transition taking place at $p = 4$ kbar, for $T = 0$. This transition depends on a very subtle balance between the attractive and repulsive forces at different relative orientations of the N_2 molecules and none of the available, mostly empirical, potentials has given any transition at all. With the present potential we correctly find the α phase to be slightly more sta-

TABLE V. Properties of γ-nitrogen ($T = 0$ K, $p = 4$ kbar).

		Experiment	Calculated			
		Refs. 28–33	BvdA potential		Present potential	
Lattice constants (Å)	a	3.957	3.957[a]	3.961[b]	3.957[a]	4.010[b]
	c	5.109	5.109[a]	5.104[b]	5.109[a]	5.160[b]
Cohesion energy (kJ/mol)		···	5.29	5.30	6.39	6.64
Phonon frequencies (cm^{-1})						
	$\Gamma(0, 0, 0)$					
	E_g	55.0	67.5	67.6	55.3	51.0
Librations	B_{1g}	98.1	104.2	103.3	95.0	86.4
	A_{2g}	···	125.1	124.4	107.7	98.6
Transl. vibrations	E_u	65.0	65.0	65.2	67.8	62.5
	B_{1u}	···	115.8	114.9	111.9	101.6
rmsd			8.0	7.9	2.4	7.3

[a] Fixed at experimental values.
[b] Calculated at $p = 4$ kbar.

ble than the γ phase at zero pressure, but, if we increase the pressure, the free energy curves of both phases run nearly parallel and we do not find a crossing at any reasonable pressure. The phonon frequencies for α and γ nitrogen have been calculated by means of the time-dependent Hartree or random phase approximation, described in Refs. 8–10.

From the results, which are collected in Tables IV and V, we can draw the following conclusions. The lattice constants are close to the experimental ones[31] with the α phase, at $p = 0$, being slightly too dense and the γ phase, at $p = 4$ kbar, being somewhat too open. The lattice cohesion energy, or sublimation energy,[32] at $T = 0$ K is reproduced much better by the new potential than by the BvdA potential. The agreement is actually better than it could be expected since we have neglected the three-body interactions. Also the isothermal compressibility of α nitrogen at $p = 0$ and $T = 0$ is in very good agreement with experiment,[33] much better than the value (3.39×10^{-10} $\mathrm{N}^{-1}\,\mathrm{m}^2$) calculated by Ling and Rigby.[3] The phonon frequencies calculated at the experimental structure are even closer to the infrared,[34] Raman,[35] and neutron scattering[36] data than the frequencies obtained from the BvdA potential which were already very good. Especially the results for the pure librational modes are remarkably good, which indicates that the anisotropy of the new potential is of high quality. The agreement with experiment becomes slightly worse, especially for the translational phonons, when we relax the lattice structure to its theoretical optimum. The frequencies in the α phase become generally too high, those in the γ phase too low. This is in line with the results for the lattice constants. The observation that the lattice constants are too small for the zero pressure α phase and too large for the γ phase at $p = 4$ kbar might indicate that the repulsive part of the potential is slightly too steep, for those orientations of the molecules which occur in the closely packed α and γ phases.

IV. CONCLUSION

In Secs. II and III we have constructed a new intermolecular potential for nitrogen, which is based on new *ab initio* calculations for the short range overlap terms and on the recent *ab initio* results of Visser *et al.*[13] for the long range dispersion attractions, corrected for overlap effects via the damping functions of Tang and Toennies.[15] Although our calculations and those of Visser *et al.* are intrinsically better than those of Berns and van der Avoird[1] and those of Mulder *et al.*[12] which have been used to construct the BvdA potential, the new potential which emerges directly from the *ab initio* calculations yields results of lesser quality for several experimental quantities. Among the various possibilities which might explain this discrepancy, we think that the overestimate of the short range exchange repulsion by the neglect of intramolecular correlation effects is the main reason. (By using a slightly smaller basis, but mainly by a more approximate analytic representation of the short range interactions Berns and van der Avoird fortuitously obtained a weaker repulsion.) We have corrected the short range part of the potential for this discrepancy by introducing two scaling parameters which, when optimized, yield a very good result for the second virial coefficient of nitrogen over a wide temperature range. The new, scaled potential has been tested by calculating several properties of solid nitrogen. We conclude that it is superior to the earlier potentials especially in reproducing the sublimation energy and the isothermal compressibility and in its orientational dependence, as manifested by the librational phonon frequencies. Further theoretical studies directed to the explicit evaluation of the role of intramolecular correlation effects both on the long range dispersion attraction[37,38] and on the short range repulsion are in progress.

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