

Consistent anisotropic repulsions for simple molecules

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(Received 10 February 2000; revised manuscript received 26 April 2000)

We extract atom-atom potentials from the effective spherical potentials that successfully model Hugoniot experiments on molecular fluids, e.g., O₂ and N₂. In the case of O₂ the resulting potentials compare very well with the atom-atom potentials used in studies of solid-state properties, while for N₂ they are considerably softer at short distances. Ground-state ($T=0$ K) and room-temperature calculations performed with the N-N potential resolve the previous discrepancy between experimental and theoretical results.

In recent years there has been an increasing interest in the high-pressure properties of liquids and solids.¹ As experimental research focused on the “extreme” states of matter, it also forced us to refine our knowledge of the relevant intermolecular interactions. In many instances, including the study of thermodynamic properties, such interactions can be described by effective two-body potentials. Because even simple molecular systems such as N₂ or O₂ can reveal bewildering complexity at high pressures, developing reliable potentials has proved to be a laborious task. A further difficulty is that the intermolecular interactions are in most cases anisotropic. Taking into account the anisotropy is essential for an accurate description of solid phases. In general, site-interaction models (commonly referred to as atom-atom potentials), describing the intermolecular interaction as a sum of the interactions between atoms residing on different molecules, have proved to be a successful approach.

Quantum mechanical calculations have been used to provide information on the intermolecular atom-atom potentials, which are further adjusted to reproduce measured quantities such as virial coefficients, sublimation energy, melting point at room temperature, low-pressure crystal structures, etc.^{2,3} These experimental data are mainly suitable to constrain the potential in the attractive region. There are also abundant high-temperature and high-pressure data which could provide information on the short-range anisotropic repulsion. However, they have been mostly interpreted assuming a spherical short-range repulsion, with the addition of a long-range van der Waals attractive tail.^{4–6} The main reason is that the statistical mechanical theory of particles interacting with spherical potentials is well developed, and reliable and efficient computational tools are available. In contrast, such theories for anisotropic interactions are cumbersome, requiring approximations that are hard to justify and generally limited in their applicability.⁷

The fact that the spherical short-range repulsions employed by earlier workers can successfully explain high-density, high-temperature experimental data of molecular fluids suggests that the sphericalization of the anisotropic repulsion is reasonable in the high-density, high-temperature environment. In this work we set out to investigate to what extent one can extract the anisotropic interactions, in particular at short range, from such spherical interactions. Considering the extensive database of spherical intermolecular potentials for both like and unlike pairs, the atom-atom

potentials so extracted could provide a unified description of pure and mixed molecular solids under a variety of pressure and temperature conditions.¹

Physically, the spherical potentials extracted from experimental data for anisotropic systems are effective interactions, resulting from “averaging” the anisotropy at high temperatures. A great deal of effort has gone into justifying and finding procedures to construct such effective spherical interactions. In this regard, the so-called “median” potential of Shaw, Johnson, and Holian⁸ represents one outstanding contribution. Subsequently, Lebowitz and Percus⁹ clarified the main ideas behind this approximation, which we now summarize for the slightly more general case of a mixture.

If $\phi^{ij}(r, \Omega_1, \Omega_2)$ is an anisotropic potential between molecules of type i and j , and $\phi_0^{ij}(r)$ is the corresponding effective spherical potential, a perturbation potential

$$\phi_\gamma^{ij}(r, \Omega_1, \Omega_2) = \phi_0^{ij}(r) + \Delta_\gamma[\phi^{ij}, \phi_0^{ij}] \quad (1)$$

is constructed to connect $\phi_0^{ij}(r)$ at $\gamma=0$ to $\phi^{ij}(r, \Omega_1, \Omega_2)$ at $\gamma=1$ with $0 \leq \gamma \leq 1$, $\Delta_0[\phi^{ij}, \phi_0^{ij}] = 0$, and $\Delta_1[\phi^{ij}, \phi_0^{ij}] = \phi^{ij} - \phi_0^{ij}$. The first-order Helmholtz free energy correction along this path is $\Delta F = \gamma(\partial F / \partial \gamma)|_0$ and is proportional to $\sum_{ij} x_i x_j \int g_{ij}^0(\mathbf{r}_1, \mathbf{r}_2) (\partial \Delta_\gamma^{ij} / \partial \gamma)|_0 d\mathbf{r}_1 d\mathbf{r}_2 d\Omega_1 d\Omega_2$, where g_{ij}^0 's are the pair correlation functions of the sphericalized system and x_i 's are the concentrations ($\sum_i x_i = 1$). It is easy to see that ΔF can be annulled, independent of all g_{ij}^0 's, by requiring

$$\int (\partial \Delta_\gamma^{ij} / \partial \gamma)|_0 d\Omega_1 d\Omega_2 = 0 \quad (2)$$

for all pairs.

The disadvantage of Eq. (2) as a definition for spherical potentials is that $(\partial \Delta_\gamma^{ij} / \partial \gamma)|_0$ is, to a large extent, arbitrary. The median is defined by $(\partial \Delta_\gamma^{ij} / \partial \gamma)|_0 = \text{sgn}(\phi^{ij} - \phi_0^{ij})$ and minimizes the integral of absolute potential deviations, $\int |\phi^{ij} - \phi_0^{ij}| d\Omega_1 d\Omega_2$.¹¹ We also note that, as a consequence of the Gibbs-Bogoliubov inequalities, for the common case $\Delta_\gamma[\phi^{ij}, \phi_0^{ij}] = \gamma[\phi^{ij} - \phi_0^{ij}]$ the first-order perturbation theory provides a rigorous upper bound on the free energy of the system of interest.⁷ While for the general case that we consider here only approximate inequalities hold,¹⁰ they do lead to useful heuristic variational principles.

One of the main advantages of the median potential over other effective spherical potentials¹¹ is that it is independent of density and temperature (and also concentrations in the case of mixtures^{12,13}). Despite its essentially heuristic basis,^{9,14} this appears to be an optimal choice for the thermodynamics of simple fluids such as N₂ and CO₂ at high pressures and temperatures,⁸ where the repulsive interactions make dominant contributions. Hence, we treat the spherical potentials derived from experimental data (such as Hugoniot data for N₂ and O₂) as median potentials and develop a procedure to invert them to extract the corresponding anisotropic potentials.

To illustrate the basic idea behind such an inversion process, consider first a simpler system of dumbbells consisting of two hard spheres (with diameter R) with their centers fixed at length L apart. In this case the equivalent problem is to determine R by inverting an effective hard-sphere potential (with diameter R_m). The median definition of R_m is $\int \text{sgn}(R_{12} - R_m) d\Omega_1 d\Omega_2 = 0$,¹⁵ where R_{12} is the distance of closest approach between two dumbbells oriented at solid angles Ω_1 and Ω_2 . It is fairly simple to show that this equation has a unique solution R .

Potentials that are used to model the thermodynamics of high-pressure, high-temperature fluids are more complicated than pure hard cores. The most successful one is the so-called exponential-6 (“exp-6”) potential

$$v(r) = \frac{\epsilon}{\alpha - 6} \left\{ 6 \exp \left[\alpha \left(1 - \frac{r}{r_0} \right) \right] - \alpha \left(\frac{r_0}{r} \right)^6 \right\}, \quad (3)$$

which combines the short-range exponential repulsion found in early quantum-theory calculations¹⁶ with a truncated dispersive interaction¹⁷ that accounts for the attraction at longer distances. This functional form has been found to provide a good representation of the experimental Hugoniots of N₂, O₂, and other small molecules,⁴⁻⁶ while satisfying to a large extent the “law of corresponding states.”⁴ In this work we use the potential parameters for nitrogen, $\epsilon^{N_2}/k_B = 101.9$ K, $r_0^{N_2} = 4.09$ Å, and $\alpha^{N_2} = 13.2$, obtained by Ross and Ree,^{4,5} and the oxygen parameters $\epsilon^{O_2}/k_B = 125$ K, $r_0^{O_2} = 3.86$ Å, and $\alpha^{O_2} = 13.2$, which have been also successfully used to model the molecular dissociation under shock compression.^{5,6} As experimental Hugoniots are excellent probes of the short-range repulsive interactions, such potential parameters are perhaps the best representation of the repulsive region under the spherical approximation. We also note that the well position r_0 and depth ϵ of the above potentials are in very good agreement with the ones obtained in molecular beam scattering experiments.¹⁸

The present inversion process derives an anisotropic potential $\phi(r, \Omega_1, \Omega_2)$ that maps into $v(r)$ (with the exp-6 potential parameters described above) through the median construction

$$\int \text{sgn}[\phi(r, \Omega_1, \Omega_2) - v(r)] d\Omega_1 d\Omega_2 = 0 \quad (4)$$

at all intermolecular distances r , where $\phi(r, \Omega_1, \Omega_2)$ is the sum of interactions $\varphi(r_{ij})$ between atoms i and j residing on different molecules,

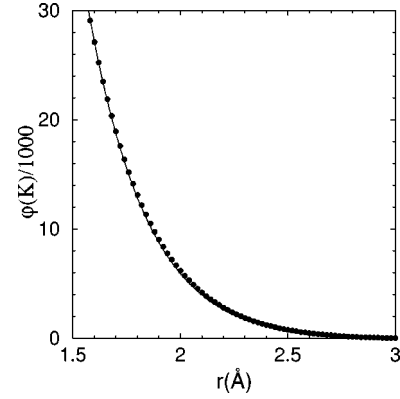


FIG. 1. Repulsive region comparison between the present O-O potential (circles) and that of Ref. 2 (solid line).

$$\phi(r, \Omega_1, \Omega_2) = \sum_{ij} \varphi(r_{ij}). \quad (5)$$

We also use an exp-6 form to represent $\varphi(r)$ in Eq. (5) and recast Eq. (4) as a χ^2 minimization.

To elaborate, for a given set of exp-6 parameters (ϵ, r_0, α) of $\varphi(r)$ [thereby a given $\phi(r, \Omega_1, \Omega_2)$] we calculate the spherical potential $\phi^0(r; \epsilon, r_0, \alpha)$ that satisfies the median condition, Eq. (4), at a large number of intermolecular separations (≈ 100), between r_{min} and a large cutoff separation (r_{max}) beyond which the potential can be neglected. In practice we choose $r_{min} = 2$ Å, [$v(r_{min})/k_B \approx 10^5$ K] and $r_{max} = 7$ Å, which is sufficient to cover the relevant potential region up to very high densities and temperatures. We then minimize the function $\chi^2(\epsilon, r_0, \alpha) = \sum_i [v(r_i) - \phi^0(r_i; \epsilon, r_0, \alpha)]^2 / [v(r_i)^2 + \epsilon_*^2]$ to determine the exp-6 parameters of $\varphi(r)$, where ϵ_* is the well depth of $v(r)$.¹⁹

We carried out such minimizations for O₂ and N₂, with fixed gas-phase bond lengths of $l_{O_2} = 1.20741$ Å and $l_{N_2} = 1.097685$ Å. The resulting potential parameters are the following.

- (i) O-O potential: $\epsilon/k_B = 45.64$ K, $\alpha = 12.52$, and $r_0 = 3.480$ Å.
- (ii) N-N potential: $\epsilon/k_B = 34.42$ K, $\alpha = 12.59$, and $r_0 = 3.773$ Å.

In Fig. 1 we compare the O-O potential with a potential that is used to study the solid-state properties of molecular oxygen.² The agreement is satisfactory, in particular, at short distances. In Fig. 2 we make a similar comparison between the N-N potential and the so-called Eters potential,³ which is widely used for the study of molecular nitrogen. Figure 2 also shows another potential,²⁰ which was recently used for the study of small N₂ clusters.²¹ It is clear that the potential that we extracted by inverting the median is much softer at small separations than either of these two, the main difference being attributable to the exp-6 parameter α that mediates the stiffness of the repulsion.

Solid nitrogen has been the subject of numerous experimental and theoretical studies in the last decades, leading to a good understanding of its phase diagram at lower pressures.^{3,22-25} However, questions remain regarding its high-pressure behavior, i.e., above ≈ 20 –30 GPa. Some of these questions concern the crystal symmetry and thermodynamics of the high-pressure phases and others the stability of

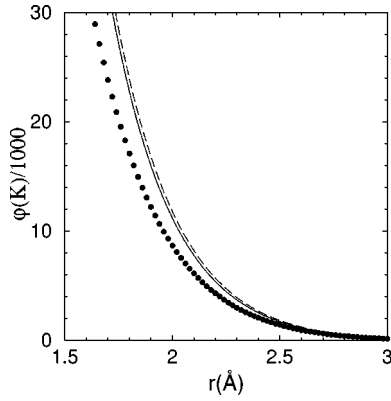


FIG. 2. Repulsive region comparison between the present N-N potential (circles) and that of Ref. 3 (solid line) and Ref. 20 (dashed line).

molecular nitrogen with respect to atomic dissociation and its possible transition to a metallic state. But ultimately all these questions appear to be related to each other.^{23,26} X-ray diffraction and Raman spectroscopy studies of solid molecular nitrogen have revealed an increasing complexity of the phase diagram with pressure, e.g., the ϵ -N₂ phase, which is apparently a high-pressure distortion of the $Pm\bar{3}n$ cubic lattice of δ -N₂.³ Calculations using a site-interaction model such as the Etters potential have successfully described the low-pressure part of the phase diagram. However, they show a sharp disagreement with the experimental data at high pressure,²⁷ which in addition to a high sensitivity of the high-pressure structures to the intermolecular potential,²⁸ emphasizes the need for more reliable interactions. To test the N-N potential obtained in this work, we first calculate the 0 K pressure of ϵ -N₂ (rhombohedral $R\bar{3}c$) by minimizing at fixed density the energy with respect to distortions of the $Pm\bar{3}n$ structure consistent with the $R\bar{3}c$ symmetry.^{3,29} Because experimental data are available only at room temperature, we correct the 0 K pressure $p(\rho,0)$ by adding the thermal contribution $3\gamma\rho k_B T$ at each molecular density ρ (γ is the Grüneisen parameter).²⁷ In addition, we performed isothermal molecular dynamics simulations at room tempera-

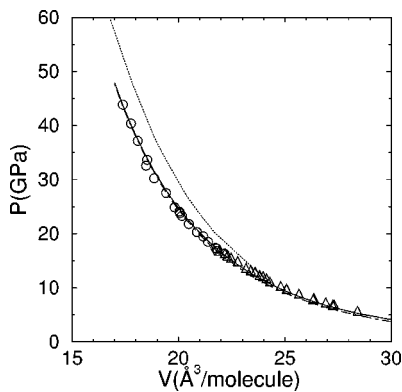


FIG. 3. Room-temperature isotherm of N₂: molecular dynamics (solid line) and energy minimization (dot-dashed line) results obtained with the N-N potential of this work, Etters potential calculations from Ref. 30 (dotted line), and experimental data of Ref. 27 (circles, ϵ -N₂; triangles, δ -N₂).

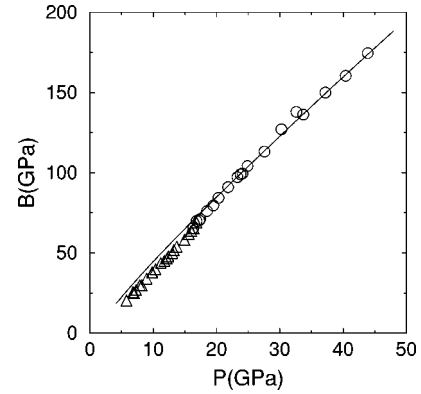


FIG. 4. Bulk modulus B of N₂ extracted from molecular dynamics results obtained with the N-N potential of this work (solid line) and experimental data of Ref. 27 (circles, ϵ -N₂; triangles, δ -N₂).

Figure 3 compares these results with the experimental data of Ref. 27 and the results obtained with the Etters potential.³⁰ The overall agreement is remarkably good, given the fact that the N-N potential has not been adjusted at all and is a significant improvement over the Etters potential calculations. This demonstrates the crucial contribution of the short-range repulsion to close-packed high-pressure structures. Our 0 K energy minimizations do not show any significant relaxation of the $R\bar{3}c$ structure to a lower symmetry, higher-pressure $R3c$ lattice.²⁹ This may be due to the fact that we are only considering structures with eight molecules per unit cell and also without inclusion of the quadrupole-quadrupole interaction. However, such a transformation is believed to occur at a still higher pressure and low temperature.³¹

We further test the agreement of the experimental and theoretical results by looking at the isothermal bulk modulus $B = V(\partial P/\partial V)_T$. In order to extract B we fit both the experimental and theoretical results with a modified Birch equation that has been previously used to model the bulk modulus of nitrogen at pressures up to about 2 GPa:³²

$$P = P_0 + \frac{3B_0}{2}(y^7 - y^5)[1 - \xi(y^2 - 1)], \quad (6)$$

where $y = (V_0/V)^{1/3}$. The comparison shown in Fig. 4 yields

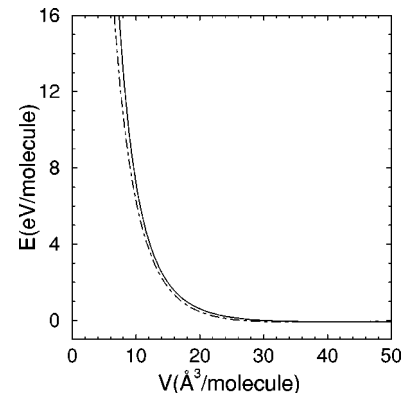


FIG. 5. 0 K energy calculations for α -N₂ with the N-N potential of this work (solid line) and the local-density-functional results of Ref. 25.

very satisfactory agreement.

Local-density-functional energy calculations²⁵ yield a reliable description of molecular nitrogen, but one that is limited to 0 K. In order to further assess the accuracy of our N-N potential we calculate the 0 K energy as a function of density for α -N₂. Figure 5 shows again good agreement between these data and the corresponding local-density-functional results.²⁵ The potential obtained in the present work gives a slightly steeper isotherm at high density, producing good agreement with experimental pressures in Fig. 3.

We conclude that the N-N and O-O potentials extracted from the median provide a good representation of the short-range repulsive region. Given the fact that classical molecular dynamics and Monte Carlo simulations are still the most accurate and efficient way of studying anisotropic molecular systems at finite temperatures, the need for reliable potentials for such simulations cannot be overstated. The present work has shown that the task of constructing such anisotropic interactions is greatly simplified by inverting a spherical po-

tential based on experimental data. The resulting potential is “transferable,” in that it can self-consistently describe material properties of different solid phases as well as liquid phases. If desired, one can refine the attractive part of the potential with inclusion of additional multipolar interactions.³ Such additional refinements that can effectively capture the effect of the long-range two- and three-body dispersive interactions may be necessary to describe properties at low pressures and temperatures. However, at very high pressures the structure and thermodynamics of the fluid are dominated by excluded volume effects well represented by two-body potentials^{4,33} that, as we show here, are also “transferable.”

We thank Andrew K. McMahan for kindly providing the results published in Ref. 25. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

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