



Accurate potential energy curve for helium dimer retrieved from viscosity coefficient data at very low temperatures



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HIGHLIGHTS

- Long-range potential determined directly from viscosity data at very low temperatures.
- Cross section sensitivity matrix was calculated by the close coupled equations.
- Non-linear problem was rewritten as a linear Fredholm integral equation of first order.
- Predicted viscosity from the inverted potential is within experimental error.

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ABSTRACT

The long range potential of helium–helium interaction, which requires accurate *ab initio* calculation, due to the small value of the potential depth, approximately 11 K (9.5×10^{-4} eV = 0.091 kJ/mol) at 2.96 Å, will be obtained in this study by an alternative technique. This work presents a robust and consistent procedure that provides the long range potential directly from experimental data. However, it is difficult to obtain experimental data containing information regarding such a small potential depth. Thereby, sensitivity analysis will be used to circumvent this difficulty, from which viscosity data at lower temperatures (<5 K) were chosen as appropriate data to be used to retrieve the potential function between 3 and 4 Å. The linear relationship between the potential energy function and the viscosity coefficient will be established under quantum assumptions and the Bose–Einstein statistics. The use of quantum theory is essential, since the temperatures are below 5 K. The potential obtained in this study describes the viscosity with an average error of 1.7% that is less than the experimental error (5%), with the results being similar to those obtained for recent *ab initio* potentials.

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1. Introduction

Potential energy functions play a central role in chemistry, and from these functions, the properties of a system can, in principle, be determined. Often, the potential energy function is obtained from *ab initio* methods, but it can also be determined from experimental data using inverse techniques. Inverse problems theory to handle experimental data has been applied to refine potential energy functions from the second virial coefficient [1,2], differential cross-sections [3,4], phase shifts [5] and from spectroscopic data [6,7].

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The helium diatomic system at low temperatures has received considerable attention in recent years due to quantum and relativistic effects in their thermodynamics and transport properties [8]. The theoretical interpretation of the results has been performed with the *ab initio* potential function [9]. The helium dimer has a very small potential well depth, measuring approximately 11 K [10,11], consequently, highly accurate calculations are required to obtain the potential energy function [10,11].

The present paper presents an alternative way to refine the helium potential energy function from viscosity coefficient data at low temperatures. Few studies have been conducted along this line and often at high temperatures [12], limit in which classical theory is valid, and in parametric form, usually for a Lennard-Jones potential energy curve [13].

To gain insight into this problem, an investigation into the sensitivity [2,3] of the viscosity coefficient to the potential energy function is conducted, and an adequate temperature range for experimental data was observed. The present study shows a higher sensitivity for long range potential in the temperature range below 5 K. Since it is necessary to use viscosity coefficient data at low temperatures in an inverse procedure, a quantum strategy to refine the potential energy curve is necessary and will be presented in this study.

The inverse problem was divided into two parts: in the first part, the cross-section is obtained from the viscosity coefficient, whereas in the second part, the potential energy function is determined from the cross-section. The solution to the first part was determined using the Tikhonov regularization under a Laplace integral equation formulation. In the second part, the relationship between the potential energy and the total cross-section, which is nonlinear, was linearized by a sensitivity analysis algorithm [2].

The cross-section sensitivity matrix established has an approximate linear relation between the potential energy and total cross-section. In a previous study [5], the functional derivative of the quantum phase shift with respect to the potential energy function was established and coupled with the variable phase equation. For the first time, this set of coupled differential equations was used to establish the cross-section sensitivity matrix within exact quantum theory. This problem is ill-posed, since sensitivity matrix elements possess values that are close to zero. In an attempt to circumvent this problem in a tractable way, the Tikhonov regularization procedure was used again.

The result obtained by the inverse technique was compared with recent *ab initio* potentials [10,14] and exhibited excellent agreement. The present work presents a general strategy to obtain an accurate inverted potential, comparable in quality with high level potential energy models and calculations.

2. Theoretical background

2.1. General formalism of the direct problem

Chapman–Enskog theory [15,16] provides a well-established perturbation method to calculate the viscosity coefficient η of a non-ideal gas from the collision integral $\Omega^{(2,2)}$. In a first order approach, the viscosity coefficient is given by

$$\eta(T) = \frac{5(\pi m k_B T)^{1/2}}{16\pi \Omega^{(2,2)}}, \quad (1)$$

in which m is the mass of the system, and k_B is Boltzmann's constant. The collision integral of interest to determine the viscosity coefficient is set in the form

$$\Omega^{(2,2)}(T) = \frac{1}{4\pi(k_B T)^4} \int_0^\infty \exp(-E/k_B T) E^3 Q^{(2)} dE, \quad (2)$$

with T the temperature and E the collision energy.

The transport cross-section $Q^{(2)}$ in classical statistical mechanics is directly related to the scattering angle, but in quantum assumptions and for the Bose–Einstein statistics, the cross-section is associated with the phase shift [16], as follow

$$Q^{(2)}(\kappa) = \frac{8\pi}{\kappa^2} \sum_{l \text{ even}}^{\infty} \frac{(l+1)(l+2)}{(2l+3)} \sin^2[\delta_{l+2}(\kappa) - \delta_l(\kappa)], \quad (3)$$

with $\kappa = 2\pi\sqrt{2mE}/h$ the wave number, h Planck's constant and l the angular moment. The phase shift δ_l is obtained from Calogero's equation,

$$\frac{d\delta_l(R; \kappa)}{dR} = -\frac{1}{\kappa} U_{\text{eff}}(R) \sin^2[\kappa R + \delta_l(R; \kappa)], \quad (4)$$

when $R \rightarrow \infty$, in which $U_{\text{eff}}(R) = \frac{8\pi^2\mu}{h^2} E_p(R) + \frac{l(l+1)}{R^2}$ and R is the interatomic distance and μ is the system reduced mass. Calogero's equation can be obtained, for spherical potential fields, substituting the free particle wavefunction $\phi_\rho(R) = \alpha \sin[kR + \delta(\rho)]$ into the radial Schrödinger's equation. A first order differential equation for the phase [17] is then obtained, which is known as Calogero's equation, and the phase is constructed as the coordinate ρ is moved to infinity. The equation is general and can be applied to other diatomic systems, if the potential is provided. More details about the Calogero's equation can be found in the published works of Morse and Allis [18], Calogero [19], and Braga and Murrell [20]. The viscosity coefficient as a function of the temperature is determined by solving these equations, obeying the sequence (4), (3), (2) and (1).

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