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Many-body and quantum effects in the surface tension and surface energy of liquid neon and argon using the Fowler's approximation

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ABSTRACT

The Fowler's expression for calculation of the reduced surface tension and surface energy has been used with Lennard–Jones (LJ) and two-body Hartree–Fock dispersion (HFD)-like potentials for neon and argon, respectively. The required radial distribution functions (RDFs) have been used from two recently determined expressions in the literature and a new equation proposed in this work. Quantum corrections for neon system have been considered using the Feynman–Hibbs (FH) and Wigner–Kirkwood (WK) approaches. To take many-body forces into account for argon system, the simple three-body potentials of Wang and Sadus (2006) [33] and Hauschild and Prausnitz (1993) [30] used with the HFD-like potential without requiring an expensive three-body calculation. The results show that the quantum and three-body effects improve the prediction of the surface tension of liquid neon and argon using the Fowler's expression.

1. Introduction

The surface tension is a key fluid property in applications such as coatings, adhesives, and surfactants. It is also of fundamental importance in wetting phenomena, hydrophobic effects, and probing interactions between solids and fluids [1].

Using statistical mechanics methods, the surface tension and surface energy can be obtained from the intermolecular potential and the radial distribution function (RDF) in the liquid–vapor interface [2–4]. The main difficulty arises in the calculation of those functions, and the problem has usually been solved by considering the RDF of the liquid phase for a Lennard–Jones (LJ) fluid. In particular, the simplest approximation which proposed by Fowler [5] is considered in the calculation of the surface tension. It is a step transition from liquid to vapor phases with no interfacial zone (and hence with no interfacial thickness).

The Fowler's approximation has been used by several authors [2,6–10] and some of these theoretical calculations showed a certain degree of agreement with experimental data but none of them considered the quantum or many-body effects in this approximation.

The statistical mechanics calculation of the surface tension was thoroughly reviewed by Lekner and Henderson [2] from a purely theoretical point of view (i.e. without direct comparison with computer simulations or experimental results). They also showed that it is necessary to account for the contribution of the vapor density to improve the results obtained via the Fowler's approximation.

While neon does not display dramatic quantum effects of helium, these effects cannot be ignored and the neglect of the quantum effects can be a source of irreducible discrepancy when the experimental data and classical results are compared [11,12].

Sinha et al. [13] have considered the quantum effects on the temperature dependence of the surface tension of simple liquids. Frish and Nielaba [14] have computed the quantum corrections for the surface tension of neon using a scaled particle theory. They found that the quantum effects lower the surface tension in better agreement with the experimental values.

Two approaches have been proposed to consider the quantum effects, the Wigner–Kirkwood (WK) and the Feynman–Hibbs (FH) potentials. The WK potential arises from an expansion in powers of $\hbar$ and $(1/kT)$ of the partition function [15,16] which has been used in the literature to estimate the quantum corrections on different properties (except the surface tension and surface energy) [17,18]. This potential is more useful at sufficiently high temperatures.

The FH potential is obtained from the Feynman–Hibbs variational estimate of the quantum partition function [8], used in the present work, leads to a pair potential depends on temperature and easy to implement in a standard molecular dynamics (MD) or Monte Carlo (MC) simulation code [3].

The FH potential has been studied by different authors [11,12,19,20] to calculate the thermodynamic and structural properties of the systems such as helium and neon but no one used the FH potential for considering the quantum effects in the calculation of the surface tension in the Fowler's approximation.

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Besides the two-body interactions, it is also well known [21–23] that three-body interactions can make a small but significant contribution to the energy of fluids. To obtain a quantitative agreement with the experiment, pair potentials must be used in conjunction with three-body interactions [24].

Miyazaki et al. [25] have calculated the surface tension of argon using two-body BFW potential plus the three-body interactions using a new MC method. They found that the effect of the three-body potentials on the surface tension can be quite important.

Grant and Desai [26] have derived a general statistical mechanical expression for the surface tension of a fluid with an arbitrary many body interaction potential. Zhou et al. [27] have used a density functional theory to study the surface tension of argon using the two-body and three-body interactions.

There are many contributions to the three-body interactions but evidences [28] indicated that the triple-dipole term of Axilrod and Teller [29] alone is an excellent approximation. Nonetheless, the need for the three-body calculations in addition to pair calculations represents a considerable computational impediment [24].

Hauschild and Prausnitz [30] have proposed a three-body correction term to the true two-body potential to evaluate phase behavior of the fluids such as methane and argon using simulation without requiring an expensive three-body calculation. Recently, Abbaspour et al. [31,32] used a two-body HFD-like potential with the three-body potential of Hauschild and Prausnitz to simulate the different properties of oxygen and methane.

Wang and Sadus [33] showed that there is a simple and accurate relationship between the two-body and three-body interactions that allows us to obtain the three-body effect in a simulation without any additional computational cost. Recently, Goharshadi and her co-workers [19,20,34] used the two-body HFD-like potential with the Wang and Sadus relation to simulate the thermodynamic properties of helium, neon, argon, krypton, and xenon with good agreement with the experimental and other theoretical data.

In this work, the Fowler's expression for calculation of the reduced surface tension and surface energy has been used using the LJ and two-body HFD-like potentials for neon and argon, respectively. The required RDFs have been used from two recently determined expressions in the literature and a new equation proposed in this work.

For the first time, the quantum corrections for neon system have been considered using the FH and WK approaches in the Fowler's expression. The simple three-body expression of Wang and Sadus [33] and the three-body potential of Hauschild and Prausnitz [30] have been also used with the HFD-like potential without requiring an expensive three-body calculation.

2. Theory

2.1. The Fowler's approximation

The expression for calculation of the surface tension, γ, and surface energy, E, of fluids according to the Fowler's approximation [5], but also considering the contribution of the vapor density [2], is given by [3,4]:

$$\gamma = \frac{\pi(\rho_L - \rho_V)^2}{8} \int_0^\infty r^4 \frac{\partial U(r)}{\partial r} g(r)\, dr \tag{1}$$

$$E = \frac{\pi(\rho_L - \rho_V)^2}{2} \int_0^\infty r^3 U(r) g(r) dr \tag{2}$$

where r is the intermolecular distance, ρ_L and ρ_V are the coexisting densities of the liquid and vapor phases, respectively, $U(r)$ is the intermolecular potential, and $g(r)$ is the RDF.

2.2. Neon system

2.2.1. Intermolecular potentials of neon

Systems of spherical molecules, such as the rare gases, have been intensively studied over a broad range of temperatures and densities using pair interactions of LJ type. Therefore, the reduced LJ potential has been used as a classical potential for neon:

$$U^*_{\text{class}}(x) = 4\left[x^{-12} - x^{-6}\right] \tag{3}$$

where $x = r/\sigma$ and $U^*_{\text{class}} = U_{\text{class}}/\varepsilon$ (σ is distance at which the LJ potential has zero value and ε is well depth of the potential). The value of the parameters of the LJ potential for neon has been given in Table 1.

Two approaches have been proposed to consider the quantum effects, the Wigner–Kirkwood (WK) and Feynman–Hibbs (FH) potentials which are considered in this work.

The WK quantum effective potential was selected as a consequence of its good performance for a variety of simple nearly classical liquids [35–39]. The WK potential arises from an asymptotic expansion of the partition function in powers of $\hbar$ [15,16]:

$$U^*_{WK}(x) = U^*_{\text{class}}(x) - T^* \times \log\left[1 - \frac{\hbar^2}{24 T^{*2} \mu\sigma^2\varepsilon}\left(U^{*\prime\prime}_{\text{class}} + \frac{2U^{*\prime}_{\text{class}}}{x} - \frac{U^{*\prime 2}_{\text{class}}}{2T^*}\right)\right] \tag{4}$$

where $\mu = m/2$, m being the mass of the atom and T^* is the reduced temperature ($T^* = kT/\varepsilon$). $U^*_{\text{class}}(x)$ is the classical reduced LJ potential (Eq. (3)), and $U^{*\prime}_{\text{class}}$ and $U^{*\prime\prime}_{\text{class}}$ are the corresponding first and second derivatives.

Recently, Tchouar et al. [11] showed that the quantum corrections for the neon system using the FH potential which has been obtained from quantum partition function (without exchange) for a canonical ensemble of atoms is superior than the WK potential and is able to correct the discrepancy existing between the experiment and classical simulation both for the thermodynamic quantities and transport coefficients. Therefore, the FH potential has been also used with the classical reduced LJ potential as:

$$U^*_{\text{FH}}(x) = U^*_{\text{class}}(x) + \frac{\hbar^2}{24\, T^* \mu\sigma^2\varepsilon}\left[U''_{class}(r) + 2\frac{U'_{\text{class}}(r)}{r}\right] \tag{5}$$

As Eqs. (4) and (5) show, the quantum WK and FH potentials appear as the sum of the classical potential and a quantum correction term that depends on the mass and the temperature.

2.2.2. RDFs of neon

The main difficulty in the computation of surface tension and surface energy using the Fowler's approximation arises in the calculation of RDF [9].

Table 1
The potentials of neon and argon used in this work.

Potential	Parameters
LJ [11]	σ (Å) = 2.789 ε/k (K) = 36.82
HFD-like [34, 44]	σ (Å) = 3.3527 ε/k (K) = 143.224 A^* = 99744.4 α^* = 11.9196 $C^*_6 = 0.651991$ $C^*_8 = 3.68594$ $C_{10}* = -2.99307$ D = 1.36 α = 0.1563 ρ_c (kg/m^3) [46] = 535.599