Comment on "The gas-liquid surface tension of argon: A reconciliation between experiment and simulation" [J. Chem. Phys. 140, 244710] (2014)

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In a recent article, Goujon et al.[1] compared several molecular models for the description of vapor-liquid equilibrium (VLE) properties of argon. They concluded with the claim: *Some 40 years after the first direct simulations of the surface tension of argon, we have achieved a reconciliation between the simulation and experiment by including the three-body interactions in the simulation.*

The results presented by Goujon et al.[1] do not support that claim because of two reasons: First, their simulation data exhibit large systematic deviations to other sources which puts doubt on their simulation methodology. Second, they have exclusively focused on the three-body interaction, neglecting other features of the molecular interactions.

The base case chosen by Goujon et al.[1] is a simple Lennard-Jones model, the other two cases are based on pair potentials with additional three-body interactions. They studied the VLE in terms of the saturated densities, the vapor pressure and the surface tension. One of the two discussed molecular models with three-body interactions (NLD + AT) was found to be superior to the Lennard-Jones model for all of these three VLE properties, while the other one (BFW + AT) was found to be inferior.

Goujon et al.[1] took parameters for the Lennard-Jones model from prior work of our group[2] that reproduce the saturated liquid density and the vapor pressure within 0.8 % and 2.1 %, respectively[3]. The surface tension, which is off the experimental data by 17 % at low temperatures, is strictly predictive in this case.

Goujon et al.[1] carried out molecular simulations in the canonical ensemble where the coexisting phases are in direct contact. In such simulations, large density gradient are present, which require a proper treatment of the long range interactions[4,5]. Goujon et al.[1] initially considered using the method by Janeček[5], which is known to yield results for the thermodynamic properties that do not dependend on the cutoff radius[5–7]. They compared

this method with a truncated potential, extended by a correction term for the surface tension only. From the simulation results for the surface tension, Goujon et al.[1] concluded that a cutoff radius of $r_c = 18$ Å is sufficient to relinquish Janeček's method. However, that truncation of the pair potential leads to an underestimation of the saturated liquid density by 0.4 % and an overestimation of the saturated vapor pressure by 15 % at a temperature of 90 K, cf. Figure 2 in the publication by Goujon et al.[1].

The results for the Lennard-Jones model can be directly compared with literature data from molecular simulation and equations of state. Figure 1 shows the relative deviations of the simulation data by Goujon et al.[1] from correlations by Lotfi et al.[8] for the saturated liquid density and the vapor pressure and by Werth et al.[6] for the surface tension. The simulation results for the saturated liquid density by Lotfi et al.[8] as well as by Potoff and Panagiotopoulos[9] generally agree with the correlation by Lotfi et al.[8] within their statistical uncertainties. The results from three equations of the state by Johnson et al.[10], Kolafa and Nezbeda[11] as well as Mecke et al.[12] also coincide well with the correlation by Lotfi et al.[8]. The simulation results by Goujon et al.[1], however, exhibit significant deviations from these reference data for the saturated liquid density, which they underestimated between about 0.5 % to 2 %. The vapor pressure correlation by Lotfi et al.[8] is in good agreement with the reference data and the equations of state. The simulation data by Kofke[13] are only slightly below the reference data, while the simulation results by Goujon et al.[1] overestimate the vapor pressure by about 10 % at low temperatures and underestimate it by about 20 % at higher temperatures. The simulation results for the surface tension by Goujon et al.[1], however, are in good agreement with the results of Werth et al.[6].

The systematic deviations of the simulation results by Goujon et al.[1] for the Lennard-Jones model seem to be due to the employed potential truncation at $r_c = 18$ Å. These

deviations put doubt on the simulations results that are based on three-body interaction models, for which it can be assumed that they are affected by the same systematic error.

We want to point out that the Lennard-Jones potential is indeed a simplification of the intermolecular interactions. However, an adjustment of the potential parameters may improve the description of the surface tension as discussed by Stöbener et al.[14,15]. Nonetheless, careful simulations are required to come to definitive conclusions. A more general approach has to be followed that also considers the physically inappropriate repulsive term ($\sim r^{-12}$) of the Lennard-Jones potential[16,17] as well as the higher-order dispersion terms ($\sim r^{-8}$, $\sim r^{-10}$). Additionally, the effect of capillary waves has to be considered[18], which has a large influence on the surface tension results in the density functional theory[19].

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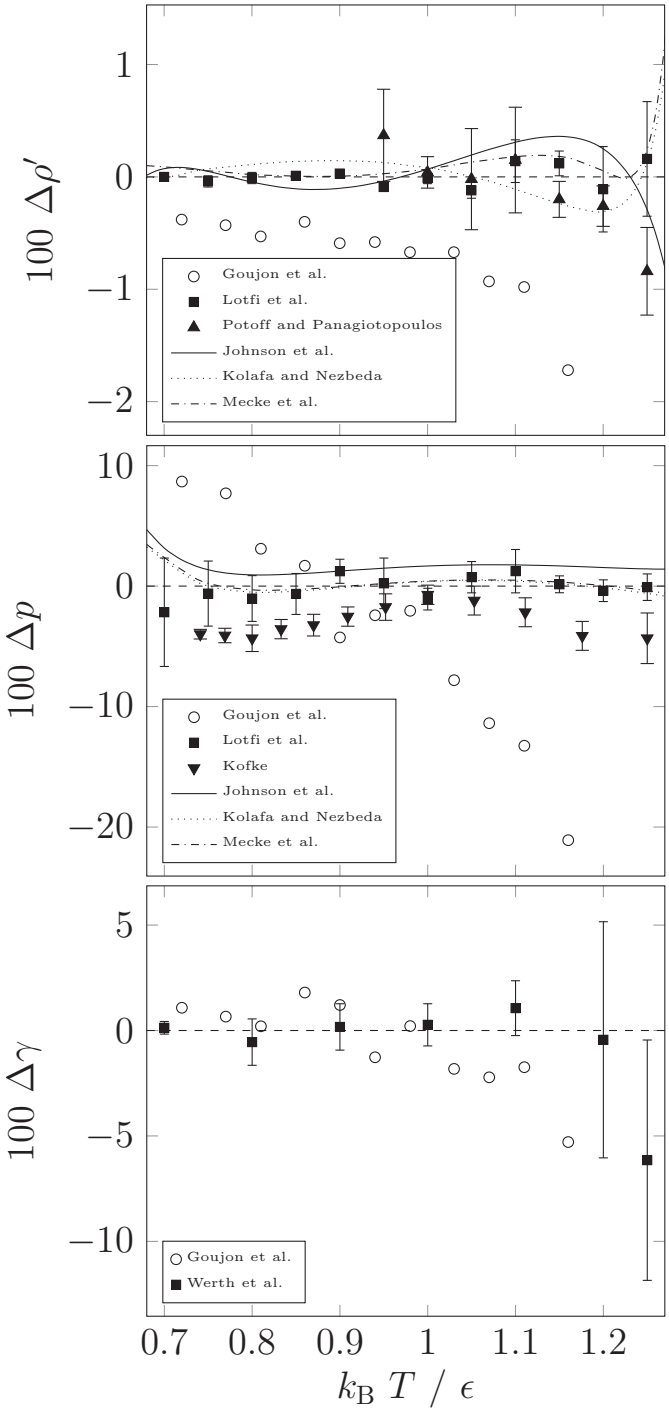

FIG. 1. Relative deviation $\Delta X = (X_i - X_{\mathrm{corr}})/X_{\mathrm{corr}}$ of simulation results and equations of state (X_i) for the Lennard-Jones model from correlations (X_{corr}) by Lotfi et al.[8] for saturated liquid density ρ' (top) and vapor pressure p (center) as well as by Werth et al.[6] for surface tension γ (bottom).