Response to "Comment on 'The gas-liquid surface tension of argon: A reconciliation between experiment and simulation"' [J. Chem. Phys. 142, 107101 (2015)]

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In a recent article,[1] we calculated the vapor-liquid equilibrium (VLE) properties of argon using direct Monte Carlo simulations of the liquid-vapor interface. We have shown that both the VLE properties and the surface tension can be calculated accurately when considering a real two-body potential coupled with an explicit three-body term. We have developed a methodology to calculate the three-body contribution of the surface tension and its long-range correction, leading to good agreement between the simulation and experiment. As a consequence, we concluded as follows: *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*.

In a recent Comment, Werth *et al.*[2] have questioned our methodology by comparing one of our results performed with an effective two-body potential (the Lennard-Jones (LJ) potential) with various simulation results and equations of state of the Lennard-Jones fluid. They state that the simulations performed without long-range corrections to the energy exhibit large systematic deviations for the saturated liquid density and the vapor pressure, due to the truncation of the potential at $r_c = 18$ Å. They also suggest that effective two-body potentials may be able to reproduce both the VLE properties and surface tension of argon.

In our paper, we only use a LJ potential with parameters developed by Vrabec *et al.*[3] as a model to test the proposition that a cutoff distance of $r_c = 18$ Å without a z-dependent long range correction to the potential energy allows for an accurate calculation of the surface tension. We clearly show that this is the case in the paper. There are systematic deviations for the saturated liquid density and vapor pressure for the LJ potential with $r_c = 18$ Å as noted in our article but they are irrelevant to our conclusions.

The real potentials of interest in our paper are the accurate two-body potentials of Barker-Fischer-Watts (BFW)[4] and Nasrabad-Laghaei-Deiters (NLD)[5] potentials, coupled with the Axilrod-Teller (AT) triple-dipole contribution. We found that the simulated results for the VLE properties obtained with the NLD+AT potential and $r_c = 18$ Å are very close to experiment. Werth *et al.* suggest in their Comment that if the long-range correction (LRC) to the energy had been included in the NLD calculations, then the calculated liquid densities and vapor pressure would have been shifted by the same significant amount found for the LJ potential and that this throws some doubt on our conclusions.

To make a definitive comment on this issue, we have performed simulations of the liquid-vapor interface of argon with the inclusion of long-range corrections to the energy in the Metropolis scheme. The LJ potential has been widely studied in this way, and the Janecek method[6] and the method of Guo and Lu (GL)[7] both give results independent of cutoff. To include the LRC with the NLD potential, we have followed the methodology developed by Guo and Lu,[7] which splits the local LRC contribution to the energy into two terms. The first term is proportional to the fluid density and has been shown to give good results for VLE and interfacial properties.[7–10] This term is straightforward to implement for any form of potential. The LRC energy for a single atom located at z is

$$u^{\mathrm{LRC}}(z) = 2\pi\rho(z)\int_{r_c}^{\infty} u^{2\mathrm{B}}(r) r^2 dr, \tag{1}$$

where $\rho(z)$ is the number density of the fluid at z. The integral is calculated numerically at the beginning of the simulation, and the energy profiles are updated every 5 MC cycles. The rest of the simulation methodology is identical to that described in our previous article.

Figure 1 shows the deviation of saturated liquid density, vapor pressure, and surface tension for the LJ and NLD potentials. The data for simulations without the LRC to the energy are taken from our previous work.[1]

Looking at the results for the LJ potential, we see that the expected deviations from experiment vanish, when the long range corrections are included in the simulation. The saturated liquid density and the vapor pressure are affected by the long range correction and the results with the long-range correction are much closer to experiment, giving relative deviations of less than 0.5% for liquid density and less than 5% for vapor pressure. The surface tension remains far from experiment with a relative deviation between 20% and 30% depending on temperature. The results for the NLD+AT potential, with the LRC included, exhibit much smaller changes compared to the simulations without the LRC. The agreement with experiment is again excellent, with relative deviations smaller than 0.2% for liquid density, 5% for vapor pressure, and 1% for surface tension. These results confirm that the use of a cutoff radius

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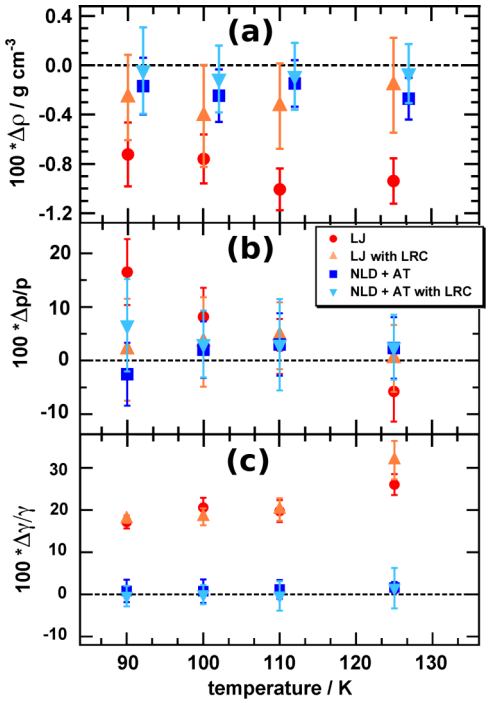

FIG. 1. Comparison between the LJ and NLD+AT potentials with and without the inclusion of long-range corrections to the energy during the simulation. (a) Absolute deviation of the liquid density: the NLD+AT symbols are shifted by 2 K along x-axis for clarity. (b) Relative deviation of the vapor pressure. (c) Relative deviation of the surface tension. The deviations are calculated using experiment[11,12] as a reference.

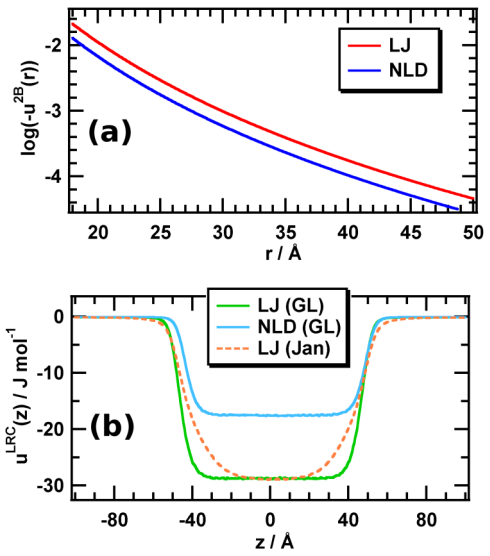

FIG. 2. (a) Comparison between the two-body energy $\log(-u^{2B})$ at long range for the LJ and NLD potentials. (b) Local long-range correction to the energy at $T = 125$ K using the first term of the Guo and Lu method[7] (GL) and the Janecek method[6] (Jan).

$r_c = 18$ Å without at LRC is sufficient for simulations using the NLD+AT potential. In this case, the use of two-body LRC does not make any significant difference to the VLE properties. Note that, in the case of the NLD+AT simulations, each contribution to the surface tension (two-body, three-body, and their respective LRCs) must be calculated to obtain the correct results.

The relatively small increase in the saturated liquid density when adding energy corrections to the NLD potential can be explained by looking at the expression of the potential. Figure 2(a) shows both LJ and NLD potentials for values of $r > r_c$. The use of $\log(-u(r))$ emphasises the difference between the two curves for every value of r. For large distances, the NLD potential is much smaller than the LJ potential. This gives rise to smaller long-range corrections as the potentials are integrated to infinity. This behaviour also appears in the calculation of the LRC for the surface tension, as shown in our original article (see Table I in Ref. 1).

Figure 2(b) shows the profile of the LRC energy used in the simulations for both the LJ and NLD potentials. As the LRC is calculated using the method of GL, we have plotted the energy profile of the GL method for the LJ potential as a comparison. The corrections applied to the NLD potential are much smaller in intensity, leading obviously to a smaller influence on the simulated liquid density and vapor pressure.

Although the properties of effective Lennard-Jones potential were outside the scope of our original paper, we note that the recent work of Stöbener,[13] cited in the Comment, does not provide LJ parameters for argon that can simultaneously reproduce both the VLE properties and surface tension (the deviation from experiment is still about 10%).

To summarize, no systematic errors arise in the simulations of the surface tension for the NLD+AT potential reported in our original paper by avoiding the LRC correction to the potential energy, using a cutoff of $r_c = 18$ Å contrary to the speculation in Werth *et al.* This is due to the very small contribution of the long-range two-body energy of the NLD potential. The values obtained for VLE properties and surface tension in the case of simulations with LRC are in very good agreement with experiment. Additionally, even a very recent parameterisation of an effective LJ potential still fails to produce both the VLE and surface tension accurately. As we have shown that the NLD+AT potential is able to predict accurately the surface tension of argon, we stand by the statements made in our original paper.

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