

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

Stephan Werth,¹ Martin Horsch,¹ Jadran Vrabec,^{2, a)} and Hans Hasse¹

¹⁾ *University of Kaiserslautern, Laboratory of Engineering Thermodynamics,
Erwin-Schrödinger Str. 44, D-67663 Kaiserslautern, Germany*

²⁾ *University of Paderborn, Laboratory of Thermodynamics and Energy Technology,
Warburger Str. 100, D-33098 Paderborn, Germany*

^{a)} Corresponding author; jadran.vrabec@upb.de; phone: +49-5251 / 60-2421; fax: +49-5251 / 60-3522.

1 In a recent article, Goujon et al.¹ compared several molecular models for the description of
2 vapor-liquid equilibrium (VLE) properties of argon. They concluded with the claim: *Some*
3 *40 years after the first direct simulations of the surface tension of argon, we have achieved a*
4 *reconciliation between the simulation and experiment by including the three-body interactions*
5 *in the simulation.*

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

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

16 Goujon et al.¹ took parameters for the Lennard-Jones model from prior work of our
17 group² that reproduce the saturated liquid density and the vapor pressure within 0.8 % and
18 2.1 %, respectively³. The surface tension, which is off the experimental data by 17 % and
19 more, is strictly predictive in this case.

20 Goujon et al.¹ carried out molecular simulations in the canonical ensemble where the coex-
21 isting phases are in direct contact. Simulations with such a density gradient, which can reach
22 several orders of magnitude, require a proper treatment of the long range interactions^{4,5}.
23 Goujon et al.¹ initially considered using the method by Janeček⁵, which is known to yield
24 results for the thermodynamic properties that do not depend on the cutoff radius⁵⁻⁷.

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

31 The results for the Lennard-Jones model can be directly compared with literature data
32 from molecular simulation and equations of state. Figure 1 shows the relative deviations
33 of the simulation data by Goujon et al.¹ from correlations by Lotfi et al.⁸ for the saturated
34 liquid density and the vapor pressure and by Werth et al.⁶ for the surface tension. The
35 simulation results for the saturated liquid density by Lotfi et al.⁸ as well as by Potoff and
36 Panagiotopoulos⁹ generally agree with the correlation by Lotfi et al.⁸ within their statistical
37 uncertainties. The results from three equations of the state by Johnson et al.¹⁰, Kolafa and
38 Nezbeda¹¹ as well as Mecke et al.¹² also coincide well with the correlation by Lotfi et al.⁸.
39 The simulation results by Goujon et al.¹, however, exhibit significant deviations from these
40 reference data for the saturated liquid density, which they underestimated between about
41 0.5 % to 2 %. The vapor pressure correlation by Lotfi et al.⁸ is in good agreement with the
42 reference data and the equations of state. The simulation data by Kofke¹³ are only slightly
43 below the reference data, while the simulation results by Goujon et al.¹ overestimate the
44 vapor pressure by about 10 % at low temperatures and underestimate it by about 20 %
45 at higher temperatures. The simulation results for the surface tension by Goujon et al.¹,
46 however, are in good agreement with the results of Werth et al.⁶.

47 The systematic deviations of the simulation results by Goujon et al.¹ for the Lennard-
48 Jones model seem to be due to the employed potential truncation at $r_c = 18 \text{ \AA}$. These

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

51 We want to point out that the Lennard-Jones potential is indeed a crude simplification
52 of the intermolecular interactions, which needs to be superseded. However, an adjustment
53 of the potential parameters may improve the description of the surface tension as discussed
54 by Stöbener et al.^{14,15}. Nonetheless, careful simulations are required to come to definitive
55 conclusions. A more general approach has to be followed that also considers the physically
56 inappropriate repulsive term ($\sim r^{-12}$) of the Lennard-Jones potential^{16,17} as well as the
57 higher-order dispersion terms ($\sim r^{-8}$, $\sim r^{-10}$). Additionally the effect of capillary waves has
58 to be considered¹⁸, which has a large influence on the surface tension results in the density
59 functional theory¹⁹.

60 REFERENCES

- 61 ¹F. Goujon, P. Malfreyt, and D.-J. Tildesley. *J. Chem. Phys.*, 140:244710, 2014.
- 62 ²J. Vrabec, J. Stoll, and H. Hasse. *J. Phys. Chem. B*, 105:12126, 2001.
- 63 ³J. Stoll. *Molecular Models for the Prediction of Thermophysical Properties of Pure Fluids*
64 *and Mixtures*. PhD thesis, University of Stuttgart, 2004.
- 65 ⁴M. Mecke, J. Winkelmann, and J. Fischer. *J. Chem. Phys.*, 107:9264, 1997.
- 66 ⁵J. Janeček. *J. Phys. Chem. B*, 110:6264, 2006.
- 67 ⁶S. Werth, S. V. Lishchuk, M. Horsch, and H. Hasse. *Physica A*, 392:2359, 2013.
- 68 ⁷V. K. Shen, R. D. Mountain, and J. R. Errington. *J. Phys. Chem. B*, 111:6198, 2007.
- 69 ⁸A. Lofti, J. Vrabec, and J. Fischer. *Mol. Phys.*, 76:233, 1992.
- 70 ⁹J. J. Potoff and A. Z. Panagiotopoulos. *J. Chem. Phys.*, 112:6411, 2000.
- 71 ¹⁰J. K. Johnson, J. A. Zollweg, and K. E. Gubbins. *Mol. Phys.*, 78:591, 1993.

- 72 ¹¹J. Kolafa and I. Nezbeda. *Fluid Phase Equilib.*, 100:1, 1994.
- 73 ¹²M. Mecke, A. Müller, A. Winkelmann, J. Vrabec, J. Fischer, R. Span, and W. Wagner.
74 *Int. J. Thermophys.*, 17:391, 1996. and 19:1493, 1998.
- 75 ¹³D. A. Kofke. *J. Chem. Phys.*, 98:4149, 1993.
- 76 ¹⁴K. Stöbener, P. Klein, S. Reiser, M. Horsch, K.-H. Küfer, and H. Hasse. *Fluid Phase*
77 *Equilib.*, 373:100, 2014.
- 78 ¹⁵S. Werth, K. Stöbener, P. Klein, K.-H. Küfer, M. Horsch, and H. Hasse. *Chem. Eng. Sci.*,
79 DOI: 10.1016/j.ces.2014.08.035, 2014. in press.
- 80 ¹⁶J. J. Potoff and D. A. Bernard-Brunel. *J. Phys. Chem. B*, 113:14725, 2009.
- 81 ¹⁷C. Avendaño, T. Lafitte, A. Galindo, C. S. Adjiman, G. Jackson, and E. A. Müller. *J.*
82 *Phys. Chem. B*, 115:11154, 2011.
- 83 ¹⁸F. Schmitz, P. Virnau, and K. Binder. *Phys. Rev. E*, 90:012128, 2014.
- 84 ¹⁹J. Gross. *J. Chem. Phys.*, 131:204705, 2009.

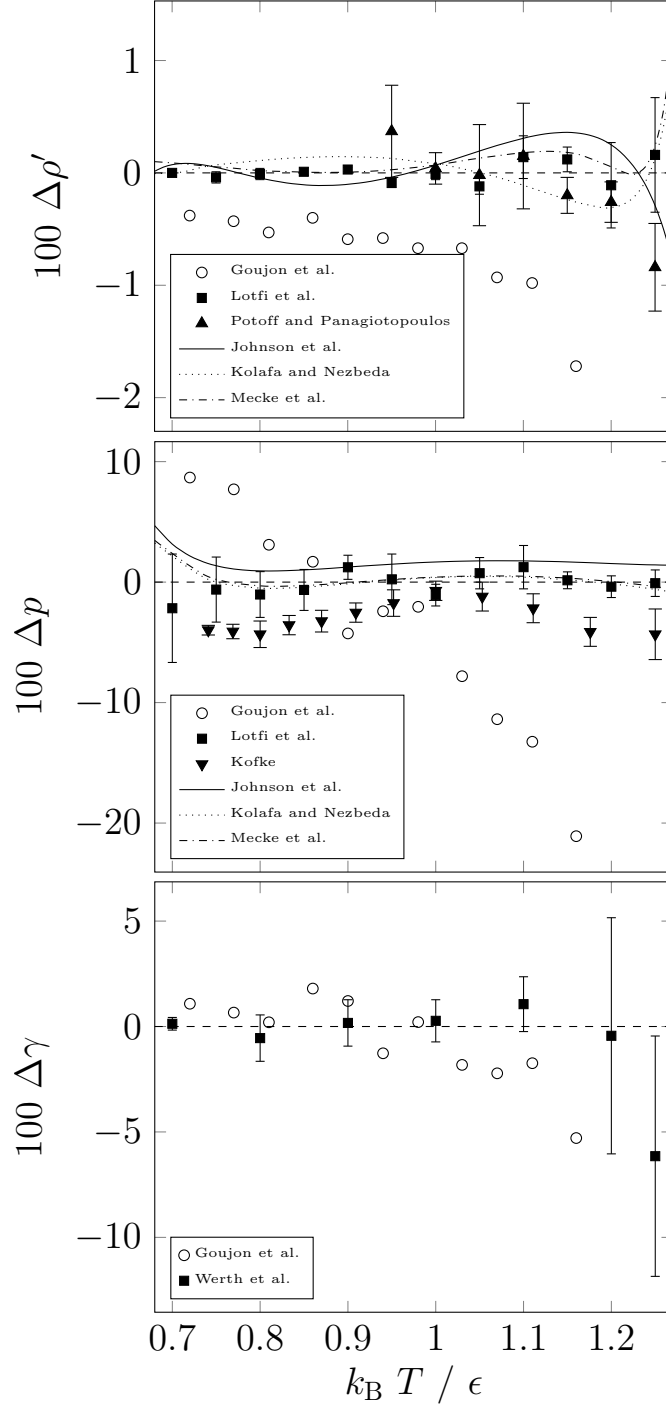


FIG. 1. Relative deviation $\Delta X = (X_i - X_{\text{corr}})/X_{\text{corr}}$ of simulation results and equations of state for the Lennard-Jones model from correlations by Lotfi et al.⁸ for saturated liquid density (top) and vapor pressure (center) as well as by Werth et al.⁶ for surface tension (bottom).