Communication: long range corrections in liquid-vapor interface simulations.

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Long range corrections in liquid-vapor interface simulations

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Abstract

Long range corrections (lrc) for the potential energy and for the force in planar liquid-vapor interface simulations are considered for spherically symmetric interactions. First, it is stated that for the Lennard-Jones (LJ) fluid the lrc for the energy Δu of Janeček [J. Phys. Chem. B **110**, 6264 (2006)] is the same as that of Lotfi et al. [Mol. Simul. **5,** 233 (1990)]. Second, we present the lrc for the force $\Delta \boldsymbol{F}$ for any spherically symmetric interaction as a derivative of Δu plus a surface integral over the cut-off sphere by using the extended Leibniz rule of Flanders [Am. Math. Monthly **80**, 615 (1973)]. This $\Delta \boldsymbol{F}$ corrects the incomplete lrc $\Delta_1 \boldsymbol{F}$ of Lotfi et al. and agrees with the result of Janeček obtained by direct averaging of the forces. Third, we show that the molecular dynamics (MD) results for the surface tension γ of the LJ fluid with size parameter σ obtained by Werth et al. [Physica A **392**, 2359 (2013)] with the lrc $\Delta \boldsymbol{F}$ of Janeček and a cut-off radius $r_c = 3\sigma$ agree with the results of Mecke et al. [J. Chem. Phys. **107**, 9264 (1997)] obtained with the lrc $\Delta_1 \boldsymbol{F}$ of Lotfi et al. and $r_c = 6.5\sigma$ within -0.4 to +1.6 %. Moreover, using only the MD results for γ of Werth et al. we obtain for the LJ fluid a new surface tension correlation which also represents the γ-values of Mecke et al. within $\pm$ 0.7%. The critical temperature resulting from the correlation is $T_c = 1.31766$ and is in very good agreement with $T_{c,ref} = 1.32$ of the reference equation of state for the LJ fluid given by Thol et al. [J. Phys. Chem. Ref. Data **45**, 023101 (2016)].

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I. INTRODUCTION

Early studies[1-6] of the planar liquid-vapor interface of the Lennard-Jones (LJ) fluid were concerned with the structure of the interface and presented also results[1,2,4,5,6] for the surface tension γ. In the simulation studies[2-5] the long range parts of the energies or forces were neglected beyond a cut-off radius r_c as is usually done in simulations of homogeneous systems; in Ref. 4 and 5 the cut-off radius is explicitly given as $r_c = 2.5\sigma$ with σ being the LJ size parameter. It was, however, pointed out in a Monte Carlo study of adsorption by Rowley, Nicholson and Parsonage[7] that for inhomogeneous systems the effects of the long range interactions do not cancel out but can be included by appropriate corrections. For the LJ liquid- vapor interface it was found by Lotfi, Vrabec and Fischer[8] that the dew densities from interface simulations with $r_c = 2.5\sigma$ are mostly too high by a factor of 3 in comparison with those obtained via bulk fluid simulations.

Hence, in Ref. 8 a long range correction (lrc) for the energy Δu was derived for the liquid-vapor interface and therefrom a lrc for the force $\Delta_1 F = \nabla \Delta u$ was obtained by differentiation of Δu. By using the force correction $\Delta_1 F$ and enlarging r_c up to 5.0σ direct MD simulations of the LJ liquid-vapor interface with 1,372 particles brought the orthobaric densities close to those obtained from bulk fluid simulations.[8] In a subsequent article by Mecke, Winkelmann, and Fischer[9] MD simulations were made for the LJ liquid-vapor interface using $\Delta_1 F$ in order to obtain improved orthobaric densities and also the surface tensions γ including a tail correction γ_{tail}. In that article[9] three set-ups with different particle numbers N and cut-off radii r_c were used: a) $N = 1,372$, $r_c = 2.5\sigma$, b) $N = 1,372$, $r_c = 5.0\sigma$, and c) $N = 2,048$, $r_c = 6.5\sigma$. It was found that for the low temperature $T = 0.7$ (reduced by k_B/ε with k_B being the Boltzmann constant and ε the LJ energy parameter) the surface tension γ increased by 7.6% in going from a) to b) and by 0.5% in going from b) to c). For the high temperature $T = 1.10$ the surface

tension increased by 78% in going from a) to b) and decreased by 1.35% in going from b) to c). The strong variation of the results in going from $r_c = 2.5\sigma$ to $r_c = 5.0\sigma$ is somewhat surprising and indicates an only weak effect of the lrc $\Delta_1\boldsymbol{F}$. Hence, in Ref. 9 it was concluded "In order to obtain reliable values for the surface tension, cut-off radii of at least 5 molecular diameters supplemented by a tail correction are required". It will be shown below, that the results for γ obtained in Ref. 9 with N = 2048 and $r_c = 6.5\sigma$ including γ_{tail} agree within -0.4 to +1.6 % with recent MD results obtained by Werth, Lishchuk, Horsch, and Hasse[10] which we believe to be presently the most reliable simulation results for the LJ liquid-vapor interface. It should still be mentioned that Mecke, Winkelmann, and Fischer[11] also performed MD simulations for liquid-vapor interfaces of the LJ mixture argon + methane. In view of the weak effect of the lrc $\Delta_1\boldsymbol{F}$ in Ref. 9 such a correction was not used anymore in the mixture simulations[11] but a rather large cut-off radius $r_c = 7.0\ \sigma_{Ar} = 6.38\ \sigma_{CH4}$ was used for all interactions.

Several years after Ref. 8 and 9 had appeared Janeček published an interesting article[12] on lrcs for the energy and the force in inhomogeneous simulations. The lrc for the energy given in Ref. 12 is the same as was already given in Ref. 8 which was overlooked by Janeček and subsequent authors. The merit of Janeček[12] is that he derived a lrc for the force $\Delta\boldsymbol{F}$ by directly averaging over the forces from outside the cut-off sphere. Based on his result for $\Delta\boldsymbol{F}$ Janeček pointed out that the lrc for the force $\Delta_1\boldsymbol{F} = \nabla\Delta u$ derived in Ref. 8 and used in Ref. 8 and 9 is incomplete. From the physical point of view this becomes immediately evident by looking at the upper part of Fig. 1 in Ref. 12.

The present paper is organized such that in Section II the lrcs for the energy and for the force as given by Lotfi, Vrabec and Fischer[8] and by Janeček[12] are discussed in detail. In particular, we explore the mathematical reason for the incomplete lrc $\Delta_1\boldsymbol{F}$ given in Ref. 8 by

using an extended version of the Leibniz rule for a three-dimensional integral with a parameter.[13-16] In Sec. III we compare the MD results for the surface tension γ obtained by Mecke, Winkelmann and Fischer[9] with the recent MD results obtained by Werth, Lishchuk, Horsch, and Hasse.[10] Moreover, we suggest for the LJ fluid an improved correlation for the surface tension based only on the MD data of Ref. 10 and compare the critical temperature T_c with the value from the recent reference equation of state of the LJ fluid.[20]

II. LONG RANGE CORRECTIONS

We consider only spherically symmetric intermolecular potentials and a planar liquid-vapor interface. If not stated otherwise we use the LJ potential $u(r)$ with the energy parameter ε, the size parameter σ, and r being the intermolecular distance

$$u(r) = 4\varepsilon\big[(\sigma/r)^{12} - (\sigma/r)^6\big]. \qquad (1)$$

Henceforth the following reduced quantities are used: intermolecular distance $r^* = r/\sigma$, spatial coordinate perpendicular to the interface $z^* = z/\sigma$, energy $u^* = u/\varepsilon$, force component $F_z^* = F_z/(\varepsilon/\sigma)$, temperature $T^* = k_B T/\varepsilon$, density $\rho^* = \rho\sigma^3$, and surface tension $\gamma^* = \gamma\sigma^2/\varepsilon$. For convenience, the stars are omitted where no confusion can occur.

In molecular simulations a cut-off radius r_c has to be introduced beyond which the potential or the force are set equal to zero. Hence, in order to obtain the interface properties of the liquid- vapor interface of the LJ fluid with the full potential given in Eq. (1), Lotfi, Vrabec and Fischer[8] derived lrcs for the potential energy and the force. Assuming a cylindrical coordinate system with the z-axis being perpendicular to the interface they obtained the lrc Δu to the potential energy at a point $\mathbf{r_1}$ as

$$\Delta u(\mathbf{r_1}) = \int_{r_{12} > r_c} u(r_{12})\, \rho(\mathbf{r_2})\, d\mathbf{r_2}, \qquad (2)$$

where $u(r_{12})$ is the intermolecular potential between particles at $\mathbf{r}_1 = (x_1, y_1, z_1)$ and $\mathbf{r}_2 = (x_2, y_2, z_2)$ with $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$, $r_{12} = |\mathbf{r}_{12}|$ and $z_{12} = z_2 - z_1$. For the special case of the LJ potential Eq. (2) yielded[8] for the lrc $\Delta u(z_1)$ at a position z_1

$$\Delta u(z_1)/8\pi = \int_{-\infty}^{-r_c} dz_{12}\, \rho(z_2)(z_{12}^{-10}/10 - z_{12}^{-4}/4) + \int_{-r_c}^{r_c} dz_{12}\, \rho(z_2)(r_c^{-10}/10 - r_c^{-4}/4)$$

$$+ \int_{r_c}^{\infty} dz_{12}\rho(z_2)(z_{12}^{-10}/10 - z_{12}^{-4}/4). \tag{3}$$

Therefrom, these authors[8] obtained by differentiation of Eq, (3) on the basis of the usual one-dimensional Leibniz rule for the lrc of the z-component of the force $\Delta_1 F_z(z_1)$ as

$$\Delta_1 F_z(z_1)/8\pi = -\int_{-\infty}^{-r_c} dz_{12}\rho(z_2)(z_{12}^{-11} - z_{12}^{-5}) - \int_{r_c}^{\infty} dz_{12}\rho(z_2)(z_{12}^{-11} - z_{12}^{-5}), \tag{4}$$

which was used in Ref. 8 and 9.

Several years later Janeček[12] also derived lrcs for the potential energy and the force. Let us first consider his lrc for the potential energy given in his Eqs. (11) and (12). The only difference between his formulas and lrc for the potential energy of Ref. 8, given above as Eq. (3), is that Eq. (3) presents the lrc as one-dimensional integrals whilst Janeček[12] uses summations over strips. But this formal difference should not have a relevant impact on the results. A point of concern, however, is that Janeček[12] did not mention the correct lrc for the energy from Ref. 8, the above Eq. (3), but has given a lrc for the potential energy in his Eq. (16) in which the upper line, $w(\xi) = 0$ for $\xi \le r_c$, is wrong. He claims that this lrc for the energy in Monte Carlo simulations is equivalent to the lrc for the force in Ref. 9. Unfortunately, this statement together with the caption of Fig. 2 in Ref. 12 can be misunderstood in the sense that the wrong Eq. (16) in Ref. 12 is due to Mecke, Winkelmann, and Fischer[9] which definitely is not the case.

The merit of Janeček,[12] as already mentioned, is that he also gave a lrc for the force. We remind that in Ref. 8 the lrc for the force was derived from Δu by interchanging differentiation and integration following the usual Leibniz rule for a one-dimensional integral with a parameter. Janeček, however, used a different route. He first derived from the LJ potential $u(r)$ the full force in z-direction $F_z(z_1)$ at a position z_1 resulting in the algebraic expression

$$F_z(z_1) = -24(z_2 - z_1)(2r_{12}^{-14} - r_{12}^{-8}). \tag{5}$$

Thereafter, he averaged the long range contributions of the forces similar as it is done in the above Eq. (2) for the potential energy, so that he avoided the interchange of differentiation and integration. Thus he obtained for the lrc for the force

$$\Delta F_z(z_1) = \Delta_1 F_z(z_1) + \Delta_2 F_z(z_1), \tag{6}$$

with $\Delta_1 F_z(z_1)$ given by the present Eq. (4). The second term $\Delta_2 F_z(z_1)$ was given by Janeček[12] in his Eq. (13) and in the first line of Eq. (14) (for the case $\xi \le r_c$) and can be written in integral form as

$$\Delta_2 F_z(z_1) = -2\pi u(r_c) \int_{-r_c}^{r_c} dz_{12} \rho(z_2) z_{12}, \tag{7}$$

where $u(r_c)$ is the LJ potential at $r = r_c$.

The difference between the result of Ref. 12 and the result of Ref. 8 is in the additional term $\Delta_2 F_z(z_1)$ which accounts for the lrc contribution at z_1 from those particles which are outside the cut-off radius r_c and have a z-coordinate z_2 with $-r_c \le z_{12} \le r_c$ (see upper part of Fig. 1 in Ref. 12). As these particles have to contribute to the lrc for the force, the statement of Janeček that the lrc for the force used in Ref. 9 (taken from Ref. 8) is incomplete, is definitely correct.

When it became clear that the lrc for the force derived in Ref. 8 is incomplete, the challenge arose to understand the difference between $\Delta_1 F_z(z_1)$ from Ref. 8 and $\Delta F_z(z_1)$ from Ref. 12. For that purpose, we use the generalization of the Leibniz rule to the case of a three-dimensional space in the form given by Flanders.[13] He considers a fluid flowing through a region of space. The Euler description gives the velocity $\mathbf{v}(\mathbf{x},t)$ at time t at position $\mathbf{x}$. Suppose now a domain D_t that moves with the flow and a function $G(\mathbf{x},t)$ on the region of flow. For that case, Flanders[13,14] proved the following formula which was already known in continuum mechanics[15,16]

$$\frac{d}{dt}\iiint_{D_t} G(\boldsymbol{x},t)dxdydz = \iint_{\partial D_t} G\boldsymbol{v} \cdot d\boldsymbol{\sigma} + \iiint_{D_t} \frac{dG}{dt}dxdydz. \qquad (8)$$

Here $d\boldsymbol{\sigma} = \mathbf{n}\, d\sigma = (n_x, n_y, n_z)\, d\sigma$ is the outward directed vectorial area element on the closed surface ∂D_t of the domain D_t. Graphical representations of the considered situation are given in Ref. 13 and in Ref. 14. Moreover we mention that in these references the function $G(\mathbf{x},t)$ is called $F(\mathbf{x},t)$ which we changed in order to avoid confusion with the force terms in the present paper.

If we apply now Eq. (8) to our case with planar geometry and any spherically symmetric interaction $u(r_{12})$, , then $G(\mathbf{x},t)$ is $u(r_{12})\rho(\mathbf{r}_2)$ with $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$, $\mathbf{r}_1 = (x_1 = 0, y_1 = 0, z_1)$, and $\mathbf{r}_2 = (x_2, y_2, z_2)$, $t = z_1$, $\mathbf{x} = \mathbf{r}_2$, the domain D_t is given by $r_{12} > r_c$, and the velocity $\mathbf{v}$ is the unit vector in the z-direction $\mathbf{v} = \mathbf{e}_z$. Therewith $\mathbf{v} \cdot d\boldsymbol{\sigma} = n_z\, d\sigma$ and in these notations the Leibniz rule takes the form

$$\frac{\partial}{\partial z_1}\int_{r_{12}>r_c} u(r_{12})\rho(\boldsymbol{r}_2)d\boldsymbol{r}_2 = \int_{r_{12}>r_c} \frac{\partial u(r_{12})}{\partial z_1}\rho(\boldsymbol{r}_2)d\boldsymbol{r}_2 + \int_{r_{12}=r_c} u(r_c)\rho(\boldsymbol{r}_2)n_z d\sigma. \quad (9)$$

Let us first discuss the meaning of this equation for the LJ fluid. The expression on the lhs corresponds to the negative lrc $-\Delta_1 F_z(z_1)$ from Ref. 8 given in the present Eq. (4), whilst the

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first integral on the rhs corresponds to the negative lrc $-\Delta F_z(z_1)$ from Ref. 12 given in the present Eq. (6). The difference between the two lrcs obtained in Ref 8 and Ref. 12 is represented by the second integral on the rhs of Eq. (9). This can still be rewritten in simpler form where we have to keep in mind that the integration is made outside the cut-off sphere and hence the vector **n** is directed inside the cut-off sphere yielding $n_z = -\ z_{12}/r_c$. Therewith one obtains

$$\int_{r_{12}=r_c} u(r_c)\rho(\boldsymbol{r}_2)n_z d\sigma = -u(r_c)\int_{r_{12}=r_c} \rho(\boldsymbol{r}_2)\frac{z_{12}}{r_c}d\sigma. \quad (10)$$

Finally, changing the integration over the surface area $d\sigma$ to the integration over z_2 by using $d\sigma = 2\pi\, r_c\, dz_2$ and replacing dz_2 by dz_{12} yields

$$-u(r_c)\int_{r_{12}=r_c} \rho(\boldsymbol{r}_2)\frac{z_{12}}{r_c}d\sigma = -2\pi u(r_c)\int_{-r_c}^{r_c} dz_{12}\,\rho(z_2)z_{12}, \quad (11)$$

which corresponds to the term $\Delta_2 F_z(z_1)$ obtained by Janeček[12] for the LJ-fluid and is given above in Eq. (7). Summarizing, we obtain from Eq. (9) after rearranging the sequence of the terms

$$-\int_{r_{12}>r_c}\frac{\partial u(r_{12})}{\partial z_1}\rho(\boldsymbol{r}_2)d\boldsymbol{r}_2 = -\frac{\partial}{\partial z_1}\int_{r_{12}>r_c} u(r_{12})\rho(\boldsymbol{r}_2)d\boldsymbol{r}_2 - 2\pi u(r_c)\int_{-r_c}^{r_c} dz_{12}\,\rho(z_2)z_{12}. \quad (12)$$

We emphasize that Eq. (12) is valid for all spherically symmetric interactions $u(r)$ and planar interfaces. It means that the lrc for the force can be obtained as negative derivative of the lrc for the potential energy plus a term with an integral over the cut-off sphere.

Application of Eq. (12) to the LJ fluid yields the lrc for the force $\Delta F_z(z_1)$ in integral form as

$$\Delta F_z(z_1)/2\pi = -4\int_{-\infty}^{-r_c} dz_{12}\rho(z_2)(z_{12}^{-11} - z_{12}^{-5}) - u(r_c)\int_{-r_c}^{r_c} dz_{12}\rho(z_2)z_{12}$$

$$- 4\int_{r_c}^{\infty} dz_{12}\rho(z_2)(z_{12}^{-11} - z_{12}^{-5}), \tag{13}$$

which is in agreement with Eq. (6) in combination with Eqs. (4) and (6).

Eq. (12) can e.g.also be used to get the lrc for the force in integral form for the Mie n-m potentials which were considered recently in Ref. 17.

III. SURFACE TENSION EQUATION FOR THE LENNARD-JONES FLUID

After the disagreement between $\Delta_1 F_z(z_1)$ from Ref. 8 and $\Delta F_z(z_1)$ from Ref. 12 has been clarified in the previous Section, it seems interesting to compare representative MD results for the LJ fluid obtained with either lrc for the force. The one source is the publication of Mecke, Winkelmann and Fischer[9] from which we take the results obtained with 2,048 particles, the lrc $\Delta_1 F_z(z_1)$ and $r_c = 6.5\sigma$. The other source is the publication of Werth, Lishchuk, Horsch, and Hasse[10] from which we take the results obtained with 300,000 particles, the lrc $\Delta F_z(z_1)$ and $r_c = 3.0\sigma$.

The simulation results are compiled in Table I. Column 2 shows the simulation results γ_{S1} from Ref. 9 and column 3 shows the simulation results γ_{S2} from Ref. 10. Direct comparison can be made for the temperatures $T = 0.70$ and $T = 1.10$. The relative differences $\Delta\gamma_S = (\gamma_{S1}/\gamma_{S2} - 1)$ x100 are shown in column 4 and amount -0.4% at the low temperature and 1.6% at the high temperature which is quite satisfactory in view of the uncertainties of other simulation results.

TABLE I. Comparison of surface tensions γ for the LJ fluid from MD results[9,10] and from correlation equations. γ_{S1}: MD results from Ref. 9, γ_{S2}: MD results from Ref. 10, $\Delta\gamma_S$ (%) = $(\gamma_{S1}/\gamma_{S2} - 1)$x100, γ_{C1}: correlation results from Ref. 9, γ_{C2}: correlation results from Ref.10, γ_{C3}: results from the present correlation Eq. (13) based only on the MD results from Ref.10.

T	γ_{S1}	γ_{S2}	$\Delta\gamma_S$ (%)	γ_{C1}	γ_{C2}	γ_{C3}
0.70	1.1452 (194)	1.150(4)	- 0.42	1.1451	1.1515	1.1534
0.80		0.930(10)		0.9187	0.9249	0.9248
0.85	0.8096(162)			0.8096	0.8152	0.8144
0.90		0.707(8)		0.7034	0.7082	0.7070
1.00		0.502(5)		0.5012	0.5034	0.5021
1.10	0.3150 (122)	0.310 (4)	1.61	0.3150	0.3133	0.3129
1.20		0.144(8)		0.1500	0.1434	0.1450
1.25		0.075(4)		0.0787	0.0696	0.0726

Another point of interest are the correlation equations for the surface tension for which we use the equation given in the book of van der Waals and Kohnstamm[18]

$$\gamma_{Corr} = A(1 - T/T_c)^b. \qquad (14)$$

In Ref. 9 the parameters A, T_c and b were obtained by a fit to the available three simulation results which gave $A = 2.96019$, $T_c = 1.32521$, $b = 1.26415$. In Ref. 10 the parameter T_c was taken from an external source[19] as $T_c = 1.3126$ and A and b were obtained by a fit to the simulation results which gave $A = 2.94$ and $b = 1.23$. The surface tensions obtained from these two correlation equations are also contained in Table I as γ_{C1} (Ref. 9) and γ_{C2} (Ref. 10). Therefrom we learn that at the highest temperature $T= 1.25$ the correlation γ_{C2} yields a considerably too low value for the surface tension which can be attributed to the chosen critical temperature. Surprisingly, at that temperature the correlation γ_{C1} is closer to the simulation value γ_{S2} than γ_{C2}. As a consequence, we made a least square fit using only all

simulation data of Ref. 10, Table 1 and 2, for 300,000 particles and obtained as correlation equation

$$\gamma_{Corr} = 2.97504(1 - T/1.31766)^{1.25065}. \qquad (15)$$

The surface tensions obtained from this correlation equation are also contained in Table I as γ_{C3}. First, we see that this correlation reproduces the simulation results γ_{S2} from Ref. 10 very well and also represents the γ_{S1} values of Ref. 9 within ± 0.7%. Moreover, we note that the obtained critical temperature T_c = 1.31766 is in very good agreement with the critical temperature $T_{c,ref}$ = 1.32 in the reference equation of state for the Lennard-Jones fluid.[20]

IV. CONCLUSIONS

First, it was stated that for the LJ fluid the lrc for the energy in Ref. 12 is the same as that given earlier in Ref. 8. Second, by using the Leibniz rule for the three-dimensional integral given by Flanders[13] we detected the reason for the incomplete lrc for the force derived from the lrc for the energy in Ref. 8. Third, we found agreement between the surface tension results from Ref. 9 obtained with the incomplete force-lrc and a cut-off radius of 6.5σ and those from Ref. 10 with the correct force-lrc within -0.4 to +1.6 %. Finally, we obtained a correlation equation for the surface tension of the LJ fluid by taking only MD data from Ref. 10. This correlation reproduces also the MD results of Ref. 9 for the surface tension within ± 0.7%. Moreover, the critical temperature resulting from the correlation is in very good agreement with that from the recent reference equation of state for the LJ fluid in Ref. 20.

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