PHYSICAL REVIEW E **67**, 061203 (2003)

Direct excess entropy calculation for a Lennard-Jones fluid by the integral equation method

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(Received 15 May 2002; published 27 June 2003)

The present work is devoted to the calculation of excess entropy by means of correlation functions, in the framework of integral equation theory. The tangent linear method is set up to get exact thermodynamic derivatives of the pair-correlation function, essential for the calculation of the physical quantities, as well as to carry out an optimization process for the achievement of thermodynamic consistency. The two-body entropy of the Lennard-Jones fluid is in very good agreement with the available molecular dynamics results, attesting the high degree of accuracy of the integral equation scheme. It is shown that an accurate prediction of the excess entropy and the resulting residual multiparticle entropy relies on the correct evaluation of the excess chemical potential, especially at high density. Two independent routes to calculate the latter are compared, and the consequences are discussed.

DOI: 10.1103/PhysRevE.67.061203 PACS number(s): 61.20.Gy, 05.70.Ce, 05.20.Jj

One of the most demanding tasks in the theory of liquids is the evaluation of the excess entropy S^{ex}, which is representative of the number of accessible configurations to the system. It is well known that related entropic quantities play a preponderant role, not only in the description of phase transitions of complex fluids [1] but also in the relation between the thermodynamic properties and dynamics [2–5]. In this context, the prediction of the excess entropy and related quantities such as the residual multiparticle entropy (RMPE) in terms of correlation functions, without thermodynamic integration, is of primary importance.

Within the theory of distribution functions of classical statistical physics, the integral equation method is one of the most powerful schemes to calculate the correlation functions of a fluid. It is based on the exact Ornstein-Zernike (OZ) equation, which has to be solved together with an approximate closure relation, involving the so-called bridge function. When appropriate versions of it are used [6,7], a high degree of accuracy, comparable to simulation results without the need of large computer power, can be achieved for the structural and thermodynamic properties [8] of various classes of fluids [9], including liquid metals [10,11].

In evaluating entropic properties, the key quantity to be determined is the chemical potential. Two independent rigorous ways exist, namely, the classical formula of Kirkwood [12] on the one hand, and that based on the activity [7] on the other hand. In order to perform a numerical evaluation, the former demands, for integration purpose, numerous calculations of the pair-correlation function with different values of the charging parameter, while the latter is more straightforward, but its local formulation is an approximation in terms of the bridge function. Nevertheless, Kjellander and Sarman [13], and later Lee [14] derived a direct expression within Kirkwood's formula which is also convenient and local. Moreover, very recently, Sarkisov [15] has shown that the two local formulations are formally equivalent, provided that the correlation functions are linear with respect to the charging parameter. However, to our best knowledge, these were never compared numerically.

The aim of the present work is to analyze the different routes to calculate the excess entropy in terms of the correlation functions for a Lennard-Jones (LJ) fluid. We use the integral equation proposed by Vompe and Martynov (VM) [16]. The latter as well as various forms of it [17,15] have both proved to be successful in calculating correlation functions as well as the resulting thermodynamic properties. In order to keep the accuracy at the highest possible level, tangent linear differentiation is applied to the integral equation code in order to get the exact numerical thermodynamic derivatives and to achieve thermodynamic consistency [8,18]. The chemical potential appears to be the crucial quantity in determining the excess entropy, and the two abovementioned formulations are carefully examined over a wide range of densities and different temperatures. Both theoretical results are compared to available molecular dynamics simulation data [19,21] that serve as a reference.

Let us consider a fluid of density ρ and temperature T, whose atoms or molecules, separated by a distance r from each other, interact via the Lennard-Jones pair potential

$$u(r)=4\epsilon\{(\sigma/r)^{12}-(\sigma/r)^{6}\}, \tag{1}$$

σ being the position of the node and ϵ the well depth. The LJ potential is designed in principle to model realistic simple fluids such as noble gases; however, it has been applied successfully to more complex systems including molecular liquids such as methanol [22,23], organic liquids [24], and fullerenes [9]. Therefore, the results presented with the LJ potential can be regarded as widely applicable, in addition to being a convenient benchmark to test liquid state theories.

The integral equation method is based on the exact Ornstein-Zernike equation

$$h(r)=c(r)+\rho\int h(r')c(|\mathbf{r}-\mathbf{r}'|)d\mathbf{r}'=c(r)+\gamma(r). \tag{2}$$

To determine the total correlation function $h(r)[=g(r)-1]$, the direct correlation function $c(r)$, and the indirect correlation function $\gamma(r)$, the OZ equation is solved together with a closure relation written in the formally exact expression

$$h(r)=\exp[-\beta u(r)+\gamma(r)+B(r)]-1, \tag{3}$$

where $\beta=1/k_BT$, k_B being Boltzmann's constant. Equation (3) depends on the so-called bridge function $B(r)$ which represents an infinite sum of elementary bridge diagrams [7]. As the latter is very slowly convergent, it has to be approximated to find a concrete solution of the system formed by Eqs. (2) and (3). Here we use the one proposed by Vompe and Martynov [16]:

$$\begin{aligned}B(r)=\frac{1}{2A}(\{1+4A[\gamma(r)-\beta u_2(r)]\}^{1/2}\\ -1-2A[\gamma(r)-\beta u_2(r)]),\end{aligned} \tag{4}$$

where $u_2(r)$ is the attractive part of the pair potential according to the Weeks, Chandler, and Andersen (WCA) splitting [25]. The parameter A is fixed for each thermodynamic state on a physical ground by imposing the consistency between independent thermodynamic routes, namely, the virial and compressibility routes on the one hand, and the virial and energy routes on the other hand [8].

Once the pair-correlation function $g(r)$ is obtained, the thermodynamic quantities of interest can easily be calculated, e.g., the excess internal energy per particle

$$\frac{U^{\text{ex}}}{\langle N\rangle}=2\pi\rho\int u(r)g(r)r^2dr, \tag{5}$$

the pressure P from the virial equation of states

$$P=\rho k_BT-\frac{2\pi\rho^2}{3}\int r\frac{du(r)}{dr}g(r)r^2dr, \tag{6}$$

and the isothermal compressibility χ_T through the compressibility route

$$\frac{1}{\chi_T}=\rho k_BT\left[1-4\pi\rho\int c(r)r^2dr\right]. \tag{7}$$

The Gibbs-Duhem (GD) relation that links the chemical potential to the pressure via the compressibility route provides the following expression for the excess chemical potential [26]:

$$\beta\mu^{\text{ex}}=-4\pi\int_0^\rho d\rho'\int c(r,\rho')r^2dr, \tag{8}$$

which can be calculated only by a thermodynamic integration this way. A local formulation of $\beta\mu^{\text{ex}}$ is therefore highly desirable in terms of correlation functions and we consider the two following approximate direct formulas: first, that given by Lee [14],

$$\begin{aligned}\beta\mu^{\text{ex},L}=4\pi\rho\int\Bigg(\gamma(r)+B(r)-h(r)+\frac{1}{2}h(r)\gamma(r)\\ +h(r)B(r)-\frac{h(r)}{\gamma^*(r)}\int_{-\beta u_2(r)}^{\gamma^*(r)}B(\gamma')d\gamma'\Bigg)r^2dr,\end{aligned} \tag{9}$$

in which it is assumed that $B(r)$ can be expressed as a unique function of the indirect correlation function $\gamma(r)$ or a renormalized version of it, $\gamma^*(r)=\gamma(r)-\beta u_2(r)$ as proposed by Lee *et al.* [33], and secondly, that propounded by Kiselyov and Martynov [27] and explored recently by Schmidt [28] and Sarkisov [15],

$$\begin{aligned}\beta\mu^{\text{ex,KM}}=4\pi\rho\int\Bigg[\gamma(r)+B(r)-h(r)\\ +\frac{1}{2}h(r)\left(\gamma(r)+\frac{4}{3}B(r)\right)\Bigg]r^2dr.\end{aligned} \tag{10}$$

It is worth mentioning that the latter expression seems to be more convenient than the one given by Eq. (9) since it does not require any renormalization of $\gamma(r)$ involving a splitting of the pair potential [29], such as the WCA one. Moreover, it does not require any analytic expression of $B(r)$ as a function of $\gamma(r)$ or $\gamma^*(r)$ as it is the case in Eq. (9), where the integral of $B(r)$ is needed. It is interesting to note that these expressions of the excess chemical potential are grounded in two independent routes. While the former is derived from the formula given by Kirkwood [12] in which the charging parameter accounts for an insertion of a particle in the fluid, the latter is based on the activity in which $\beta\mu^{\text{ex}}$ is expressed in terms of the one-particle direct correlation function [7].

The excess entropy can be obtained in the framework of the grand canonical ensemble as a multiparticle expansion as proposed by Nettleton and Green [30] as well as by Ravaché [31] later on:

$$S^{\text{ex}}=\sum_{n=2}^{\infty}S_n, \tag{11}$$

which is expressed here in units of k_B per particle. S^{ex} depends on n-body correlation functions and, for instance, the two-body term is written in terms of the pair-correlation function as

$$S_2=-2\pi\rho\int[g(r)\ln g(r)-g(r)+1]r^2dr. \tag{12}$$

As shown by Baranyai and Evans [19] using molecular dynamics simulation on the Lennard-Jones fluid, S_2 represents from 85% to 95% of the excess entropy. Therefore, S_2 provides a simple and good estimate of the excess entropy especially near the melting point [2], and requires only the knowledge of the pair-correlation function. As a matter of fact, these authors [20], who also computed S_3, the three-body term, were the first to show that the expansion is ensemble independent. This is very important regarding the

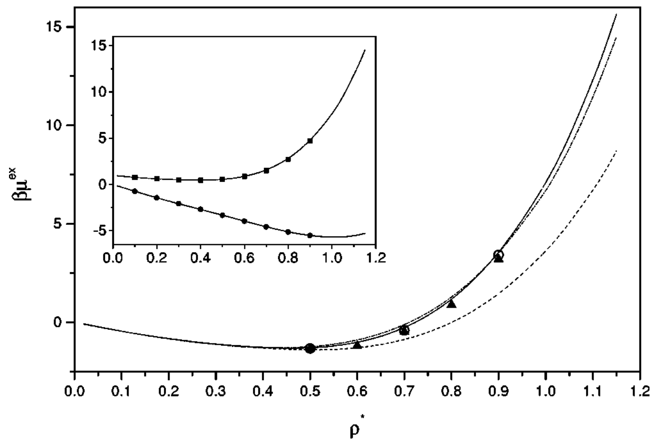

FIG. 1. Excess chemical potential as a function of density along the $T^*=1.5$ isotherm calculated with the VM integral equation. The full line represents the results coming from Eq. (10), the dashed line is those obtained by using Eq. (9), and the dot-dashed line is extracted from the Gibbs-Duhem equation (8). The symbols belong to the simulation data [33] (triangles) and the equation of state [35] (open circles). The solid lines in the inset represent the calculations of the excess internal energy (bottom curve) and compressibility factor (upper curve), which are compared to the equation of state [34] for the excess internal energy (filled circles) and compressibility factor (squares).

consistency between different thermodynamic routes prescribed by the integral equation used in the present work. On the other hand, from the macroscopic point of view, S^{ex} can be expressed in terms of the excess internal energy U^{ex}, pressure P, and excess chemical potential μ^{ex} as follows:

$$S^{ex}=\frac{\beta P}{\rho}-1+\frac{\beta U^{ex}}{\langle N\rangle}-\beta\mu^{ex}. \qquad (13)$$

Finally, since all the thermodynamic quantities in the right hand side of Eq. (13) can be calculated by means of the pair-correlation function, it is also the case for S^{ex} and the residual multiparticle entropy $\Delta S=S^{ex}-S_2$.

The results presented here are obtained by solving numerically the VM integral equation given by Eq. (4) together with the OZ equation using the algorithm of Labik *et al.* [32] which combines the Newton-Raphson (NR) method and the traditional iterative technique. A good compromise between accuracy and rapidity is to represent the functions by a grid size of 1024 with a mesh of 0.02. The number of 80 equations are treated by the NR method, which guarantees a good and rapid convergence in all cases. The tangent linear differentiation method is applied twice to the code, the first time to yield exact thermodynamic derivatives of $g(r)$ and the second time with respect to the parameter A for the optimization process by the gradient method [18], in order to get a thermodynamically consistent value of A for each thermodynamic state. We refer the reader to Refs. [8] and [18] for the technical details of this procedure. The physical quantities are expressed in Lennard-Jones units, for instance, the reduced temperature is $T^*\equiv k_BT/\epsilon$ and the reduced density is $\rho^*\equiv\rho\sigma^3$.

In Fig. 1, we display the excess chemical potential calculated through either Eqs. (9) or (10) along the isotherm $T^*=1.5$. Up to $\rho^*=0.5$, both expressions give results that are very close to each other, while significant differences can be seen at higher densities. In order to judge whether the agree-

TABLE I. Excess internal energy $U^{ex}/N\varepsilon$, compressibility factor $\beta P/\rho$, and excess entropy S^{ex} of the Lennard-Jones fluid calculated with the VM integral equation. The superscripts L, KM, GD, and HV correspond, respectively, to results obtained by using Eqs. (9), (10), and (8), and simulation data from Hansen and Verlet (HV) [37] while the subscript MD stems from molecular dynamics simulation data from Refs. [19] (a) and [21] (b).

T^*	ρ^*	$U^{ex}/N\varepsilon$	$U^{ex}_{MD}/N\varepsilon$	$\beta P/\rho$	$\beta P_{MD}/\rho$	$S^{ex,L}$	$S^{ex,KM}$	$S^{ex,GD}$	$S^{ex,HV}$
1.15	0.5	−3.4519	−3.499(a)	−0.2046		−1.3129	−1.4778	−1.4778	−1.457
1.15	0.6	−4.1093	−4.130(a)	0.0274		−1.5113	−1.8530	−1.9213	−1.815
1.15	0.65	−4.4461	−4.458(a)	0.2619		−1.5741	−2.0929	−2.1955	−2.037
1.15	0.75	−5.1001	−5.108(b)	1.1721	1.161(b)	−1.5828	−2.6565	−2.7759	−2.556
1.15	0.85	−5.6666	−5.665(b)	2.8675	2.865(b)	−1.3355	−3.3462	−3.3920	−3.150
1.15	0.92	−5.9678	−5.953(b)	4.6702	4.719(b)	−0.9380	−3.9193	−3.8318	−3.625
1.15	0.93	−6.0023	−5.986(b)	4.9768	5.022(b)	−0.8626	−4.0081	−3.8943	−3.671
1.15	0.94	−6.0342	−6.013(b)	5.2967	5.364(b)	−0.7821	−4.0988	−3.9564	−3.739
1.15	0.95	−6.0637	−6.039(b)	5.6303	5.711(b)	−0.6963	−4.1912	−4.0182	−3.810
1.15	0.96	−6.0904	−6.063(b)	5.9779	6.069(b)	−0.6051	−4.2854	−4.0795	−3.882
1.15	0.97	−6.1144	−6.082(b)	6.3400	6.450(b)	−0.5083	−4.3817	−4.1404	−3.953
0.75	0.7	−5.0457	−5.076(a)	−1.6179	−0.812(a)	−1.5125	−2.7760	−2.7760	−2.595
0.75	0.8	−5.7530	−5.772(a)	−0.3555	−0.294(a)	−1.1773	−3.5719	−3.5430	−3.226
0.75	0.84	−6.0152	−6.024(b)	0.4973	0.441(b)	−0.9257	−3.9389	−3.8465	−3.441
0.75	0.85	−6.0777	−6.084(b)	0.7466	0.692(b)	−0.8502	−4.0351	−3.9217	−3.516
0.75	0.86	−6.1389	−6.134(b)	1.0112	0.952(b)	−0.7693	−4.1330	−3.9967	−3.581
0.75	0.87	−6.1984	−6.192(b)	1.2918	1.244(b)	−0.6830	−4.2325	−4.0709	−3.659

ment can be attributed to the integral equation given by Eq. (4) or to the specific formulation of the chemical potential, we calculated $\beta\mu^{\mathrm{ex}}$ from Eq. (8). This is done by fitting the values of $\int c(r,\rho')r^2dr$ in the range $0\leqslant\rho^*\leqslant1.15$ by a polynomial of order 3 in density which can then be integrated analytically to get $\beta\mu^{\mathrm{ex}}$ as a function of ρ^*. Surprisingly, the chemical potential obtained in this manner compares favorably to the simulation results of Lee *et al.* [33] and the equation of state of Johnson *et al.* [34], attesting to the quality of the VM integral equation. These results are also very close to those coming from Eq. (10), and small discrepancies appear only at very high densities above $\rho^*=1.0$, in the supercooled metastable region. It appears that Eq. (10) is more accurate than Eq. (9), and this reveals the difficulties encountered for the direct calculation of $\beta\mu^{\mathrm{ex}}$ in our previous work [8]. The inset of Fig. 1 shows the curves of the excess internal energy and compressibility factor as a function of density, which compare favorably with the results from the equations of state [35].

In Table I, we gather the excess internal energy and compressibility factor, which are compared with the molecular dynamics (MD) data of Baranyai and Evans [19] and Giaquinta *et al.* [21], for isotherms $T^*=1.5$, 1.15, and 0.75, corresponding to states in the supercritical region, the subcritical region, and the vicinity of the triple point, respectively. Very good results are obtained since the values calculated with the VM integral equation depart from the MD ones by no more than 1–2 % in the majority of cases. A deviation of 3–50 % is seen in the compressibility factor at $T^*=0.75$; however, since the values obtained with both the VM integral equation and the MD are close to zero, the absolute departure is not large. The excess entropy can therefore be calculated with confidence from the excess internal energy and compressibility factor. The results of S^{ex} presented in Table I depend also on the excess chemical potential that are calculated directly by using either Eq. (9) or Eq. (10). Taking the values extracted from the MD simulation data of Hansen and Verlet [37] as a reference, it appears that S^{ex} calculated on the basis of Eq. (10) gives the best predictions. At the lowest temperature and highest densities, the discrepancies are more significant due to the approximate values of $\beta\mu^{\mathrm{ex}}$. However, these do not overestimate the MD data by more than 16%. Obviously, the results of S^{ex} calculated by using Eq. (9) do not yield correct values except at $T^*=1.15$ for the two lowest densities.

As for the chemical potential, S^{ex} can be calculated from Eq. (8) by a thermodynamic integration. Taking the value of the chemical potential given by Eq. (10) as a reference, namely, $\beta\mu^{\mathrm{ex}}(\rho^*=0.7)=-6.569\,49$ at $T^*=0.75$ and $\beta\mu^{\mathrm{ex}}(\rho^*=0.5)=-2.728\,43$ at $T^*=1.15$, the results are in good agreement with those coming from Eq. (10). It is worth noticing that the agreement improves slightly in nearly all the cases with respect to the MD data, essentially revealing the approximate nature of the direct formula given by Eq. (10). Nevertheless, one can conclude that Eq. (10) leads to accurate predictions of S^{ex}, even at very high densities. It is worth mentioning that the thermodynamic consistency that is obtained by an optimization of the parameter A is very important in the present scheme. This confirms the statement of Schmidt [28] who attributed the discrepancies of his results at high density to the thermodynamic inconsistency of the closure he used.

TABLE II. Two-body contribution to the excess entropy S_2 and residual multiparticle entropy ΔS calculated with Eq. (10). The subscript MD for S_2 corresponds to molecular dynamics simulation data from Refs. [19] (a) and [21] (b), and subscripts GD and MD for ΔS correspond, respectively, to results obtained with Eq. (8) and molecular dynamics simulation data [37].

T^*	ρ^*	S_2	$S_{2,\mathrm{MD}}$	ΔS	ΔS_{GD}	ΔS_{MD}
1.5	0.1	−0.244	−0.240(a)	−0.015	−0.023	
1.5	0.2	−0.470	−0.466(a)	−0.048	−0.043	
1.5	0.3	−0.673	−0.660(a)	−0.100	−0.066	
1.5	0.4	−0.874	−0.876(a)	−0.161	−0.114	
1.5	0.5	−1.106	−1.115(a)	−0.237	−0.288	
1.5	0.6	−1.393	−1.401(a)	−0.329	−0.453	
1.5	0.7	−1.760	−1.757(a)	−0.420	−0.583	
1.5	0.8	−2.247	−2.234(a)	−0.487	−0.616	
1.5	0.9	−2.909	−2.871(a)	−0.497	−0.485	
1.5	1	−3.815		−0.418	−0.114	
1.5	1.01	−3.921		−0.404	−0.061	
1.5	1.02	−4.032		−0.389	−0.005	
1.5	1.03	−4.145		−0.372	0.054	
1.5	1.04	−4.262		−0.354	0.117	
1.5	1.11	−5.218		−0.016	0.854	
1.5	1.12	−5.369		0.026	0.959	
1.15	0.5	−1.203	−1.250(a)	−0.275	−0.275	−0.207(a)
1.15	0.6	−1.511	−1.540(a)	−0.342	−0.410	−0.275(a)
1.15	0.65	−1.700	−1.720(a)	−0.393	−0.495	−0.317(a)
1.15	0.75	−2.182	−2.203(b)	−0.474	−0.594	−0.376(b)
1.15	0.85	−2.859	−2.855(b)	−0.487	−0.533	−0.320(b)
1.15	0.92	−3.495	−3.462(b)	−0.425	−0.337	−0.195(b)
1.15	0.93	−3.599	−3.566(b)	−0.409	−0.295	−0.105(b)
1.15	0.94	−3.707	−3.668(b)	−0.392	−0.249	−0.071(b)
1.15	0.95	−3.819	−3.771(b)	−0.372	−0.199	−0.039(b)
1.15	0.96	−3.935	−3.882(b)	−0.351	−0.145	0.000(b)
1.15	0.97	−4.055	−3.993(b)	−0.327	−0.086	0.040(b)
1.15	0.98	−4.179		−0.301	−0.022	
1.15	0.99	−4.307		−0.273	0.047	
1.15	1.05	−5.174		−0.041	0.578	
1.15	1.06	−5.335		0.010	0.689	
0.75	0.7	−2.231	−2.310(a)	−0.544	−0.544	−0.285(a)
0.75	0.8	−2.967	−2.980(a)	−0.605	−0.576	−0.246(a)
0.75	0.84	−3.361	−3.378(b)	−0.578	−0.485	−0.063(b)
0.75	0.85	−3.470	−3.492(b)	−0.565	−0.451	−0.024(b)
0.75	0.86	−3.584	−3.599(b)	−0.549	−0.412	0.018(b)
0.75	0.87	−3.703	−3.711(b)	−0.529	−0.368	0.052(b)
0.75	0.92	−4.370		−0.361	−0.034	
0.75	0.93	−4.510		−0.302	0.068	
0.75	0.94	−4.656		−0.239	0.178	
0.75	0.95	−4.808		−0.171	0.301	
0.75	0.96	−4.951		−0.089	0.550	

We come now to the calculation of the two-body entropy S_2 and the RMPE, namely, $\Delta S=S^{\mathrm{ex}}-S_2$, which are presented in Table II. Strikingly, the results for S_2, being obtained independently from S^{ex} by means of Eq. (12), are in excellent agreement with the MD data [19,2] in all the cases considered here, which means that the pair-correlation functions $g(r)$ obtained from the VM integral equation are correct for a wide region of the phase diagram. The RMPE is then determined from S^{ex}, which is obtained from the chemical potential calculated by using either Eq. (10) or Eq. (8). We have not considered the case with Eq. (9) since it leads to incorrect results. The quantity ΔS is always very small and is therefore very sensitive to the approximations made in the calculation of S^{ex}. As a result, the calculated ΔS take higher values than the MD ones whatever the formulation used; however those coming from the Gibbs-Duhem integration are seen to be in slightly better agreement.

As evidenced by Giaquinta *et al.* [2,21], the RMPE reflects the phase changes of the system despite its smallness, and a vanishing ΔS may correspond to the freezing of the liquid. It is seen that the zeros of ΔS we have obtained are shifted toward higher densities and, according to this criterion, the resulting freezing densities are somewhat higher than those of the simulation. The RMPE coming from the Gibbs-Duhem relation yields the best predictions, and it is worth mentioning that at $T^*=1.15$ and 0.75 our results are very similar to those obtained by Lomba *et al.* [36] with the reference hypernetted chain integral equation. Nevertheless, to calculate the excess entropy, these authors used a definition in terms of the excess free energy. They attributed the discrepancies to the evaluation of S_2, which represents the major source of errors. From our calculations, we find that the evaluation of S^{ex} represents the essential impediment for an accurate determination of the RMPE since in our integral equation scheme it relies on the evaluation of the chemical potential by an approximate direct formula.

By the light of our results, it appears that Eq. (9) is valid only at low and moderate densities i.e., below $\rho^*=0.5$, while Eq. (10) is reliable also at higher ones, small discrepancies appearing only near the freezing line. Sarkisov [15] has shown that Eqs. (9) and (10) are equivalent when bridge functions of the form given by Eq. (4) are used and with the assumption that the correlation functions satisfy linearity with respect to the charging parameter for the particle insertion of Kirkwood's formula. The present numerical results reveal that this is not the case at densities characteristic of the dense liquid. Therefore, it is likely that the linearity does not hold any more at high densities. Finally, for the purpose of determining small quantities such as the residual multiparticle entropy, further improvement will depend on a better formulation of the excess chemical potential as well as on a better expression of the bridge function on which it is based.

In conclusion, we have calculated the excess entropy directly in terms of correlation functions. In the present scheme, its evaluation relies on an accurate determination of the chemical potential. Within the integral equation of Vompe and Martynov [16], we have shown that the direct formulation proposed by Kiselyov and Martynov [27] gives correct predictions, while the direct formula of Lee [14] gives good results only at low and moderate densities. Therefore, both direct formulations of the chemical potential are reliable to obtain the liquid-gas coexistence curve as shown by Duh and Haymet [29]. This study opens the possibility of going toward the determination of phase diagrams for different types of potential by a formulation based only on correlation functions. In addition, we have also shown that the two-body entropy can be calculated with a high degree of accuracy and could be used for the determination of the self-diffusion coefficient by means of an universal scaling law such as that proposed by Dzugutov [4] for dense liquids. Work along these lines is in progress.

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