

Melting point and phase diagram of methanol as obtained from computer simulations of the OPLS model

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In this work, the melting point and the phase diagram of methanol is determined via computer simulations using the OPLS model. The three different solid structures that are found experimentally were considered. By computing the free energies of both the fluid phase and the three different solid structures (α , β , γ), the initial solid-solid and fluid-solid coexistence points were determined. By performing Gibbs–Duhem integration, the complete coexistence lines were evaluated. In this way, it was possible to compute, for the first time, the complete phase diagram for a potential model of methanol. It is found that the optimized potential model for liquid simulations (OPLS) provides reasonable predictions for the densities of the three solid polymorphs, although they tend to be somewhat low when compared with the experiment. Overall the model provides a qualitatively correct description of the phase diagram of methanol. The β solid, which is thermodynamically stable in the experimental phase diagram of methanol, is found to be metastable in the phase diagram of the model. The α phase is stable at low pressures and the γ phase is stable at high pressures, in agreement with experiment. Thus, the model is able to predict the existence of the γ solid at high pressure. From free energy calculations we found that the melting point of the model at room pressure is 215 K. That was further confirmed by direct coexistence simulations. Thus, the model presents a melting point about 40 K above the experimental value of 175 K. Thus the OPLS model provides a reasonable description of the phase diagram of methanol, but it could probably be modified to improve the phase diagram predictions. © 2010 American Institute of Physics. [doi:10.1063/1.3328667]

I. INTRODUCTION

The current development of algorithms and computer power allows one to perform simulations of almost any system from simple fluids such as argon to systems as complex as proteins in solution.¹ The results obtained by computer simulation describe the properties of the proposed Hamiltonian describing the interaction between molecules. Unfortunately, it happens quite often that the simulation results do not reproduce quantitatively (sometimes even qualitatively), the experimental results. The reason of this is that the potential model used may not describe properly the true potential energy surface (PES) of the system considered. The interaction potential between molecules can be obtained in principle by two different approaches. The first is to use first principles calculations to obtain the PES. This route has been quite successful for simple fluids and small molecules and there is no doubt that it will be used more and more in the future.^{2–5} However, even for a molecule as relatively simple as water, the success of first principles calculations to describe condensed matter properties quantitatively is limited.^{3,4} The second approach to obtain a potential interaction between molecules is to propose a functional form for the interaction and obtain some of the parameters of the potential by forcing the model to reproduce experimental properties,^{6,7} such as the experimental density and the vaporization enthalpy at room

temperature. This second approach has been relatively successful in providing a first estimate for the interaction potential. However, quite often, one is interested in studying a system far from room temperature and pressure conditions and there is no guarantee that the performance of the model will be good for these conditions, far from where the parameters were obtained. A possible route of improving the performance is to increase the number of parameters of the model and force the model to reproduce experimental properties in a broader range of temperatures and pressures. The possibility of directly determining the vapor-liquid equilibria of a potential model, by using the Gibbs ensemble simulations, first proposed by Panagiotopoulos⁸ is particularly interesting. In fact, it seems a good idea to obtain the parameters of the potential model by forcing the model to reproduce experimental values of the vapor pressure curve, coexistence properties, and critical conditions. For instance, for methanol several potential models has been proposed in this way.^{9–12} The lesson is that phase equilibria can help to determine the parameters of potential models. However, vapor-liquid equilibria is not the only phase equilibria which a pure fluid exhibits. A pure compound will also present fluid-solid and quite often solid-solid equilibria. Although fluid-solid and solid-solid equilibria can be obtained via computer simulations they are not computed as often. There is no technical reason for this since free energy calculations can be performed for solid phases using the Einstein crystal

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methodology, proposed by Frenkel and Ladd,¹³ allowing fluid-solid equilibria to be obtained. Besides this, Gibbs–Duhem integration¹⁴ allows one to determine the complete coexistence curve. The study of the fluid-solid equilibria can be of interest *per se*, for instance, to design separation processes or to study solid nucleation¹⁵ (the equilibrium conditions of the model should be known in advance before attempting a nucleation study), phase diagram and polymorph predictions. Besides, the study of fluid-solid and solid-solid equilibria can be quite useful to improve the current potential models. The phase diagram of a molecule is a macroscopic signature of the microscopic interaction potential. Therefore, one could use this information to improve current potential models.

We have recently shown, for water, how phase diagram calculations can help in improving the potential model. In fact, after computing the phase diagram for two popular water models,¹⁶ TIP4P and SPC/E, it was found that one of them (TIP4P) provided a much better description of the phase diagram. Both models yielded rather low melting points.¹⁷ For this reason, it was clear that the TIP4P could be slightly modified to still predict a correct phase diagram but improve the description of the melting point. In this way, we proposed a new model,¹⁸ TIP4P/2005 with the same geometry as TIP4P, but with a significant improvement in the phase diagram prediction, melting point, and prediction of the density maximum of water. Quite recently we have compared the performance of this model to other potential models for ten different properties and found that the model does indeed represent an improvement over the previous potentials.¹⁹ Thus, TIP4P/2005 is an example (probably one of the first) of a potential model inspired by phase diagram calculations involving solid phases. We believe that a similar approach can be used for other molecules. Obviously, before presenting a new model, it is necessary to compute the phase diagram for at least a potential model.

After water, methanol is probably one of the most interesting molecules to consider. It is often used as a pressure transmitting medium in ultrahigh pressure measurements.²⁰ Also it is commonly used as cosolvent to stabilize nanoparticles at interfaces²¹ and in natural gas pipelines to avoid the formation of methane hydrates.²² It is relatively simple and common, its physics is dominated by hydrogen bonding, and it has the interesting feature (not present in water) of forming a glass phase rather easily. In fact, the formation of the glass phase of methanol has been studied by computer simulation in a number of cases.^{23–25} Somewhat surprisingly in these studies of glass formation, the melting point of the model was unknown. Another interesting feature of methanol is its amphiphilic character with a polar group and an apolar head, so it can be considered to be one of the simplest amphiphilic molecules. The study of methanol-water mixtures^{26,27} and in particular, of the excess properties,^{28,29} is also of interest. Several potential models have been proposed for methanol, but probably the most popular one is that proposed by Jorgensen,³⁰ denoted as optimized potential model for liquid simulations (OPLS). In this work, we compute the melting point of the OPLS model of methanol and obtain its phase diagram. The ability of the model to describe the properties

of the different solid phases will also be considered. The phase diagram of methanol is not as complex as that of water, but still it exhibits three different solid structures, denoted as α , β , and γ . As it will be shown, the model predicts a rather high melting temperature and melting enthalpy when compared with the experimental value. This in itself indicates that there is probably room for improvement. Our aim here is twofold. First, to provide the melting point of the model for those researchers who use this model when describing methanol. The second goal is more general, since it intends to illustrate that melting points and phase diagram calculations can now be performed for molecular fluids.³¹ In our view, such phase diagram calculations could be performed for other molecules and the information obtained could be useful in provided revised version of current potential models.

II. METHODOLOGY

In this work we shall use the OPLS model of methanol.³⁰ In this model, one Lennard-Jones (LJ) center is located on the position of the carbon atom (to represent the CH₃ group). Another LJ is located on the position of the oxygen atom. Three charges are located on the position of the C, O, and H atoms. Thus, the hydrogen atom is represented by a charge without any LJ center associated (as it is done in water models). The dipole moment of the model is of 2.20 D, compared to the dipole moment of the molecule in the gas phase which amounts to 1.70 D. To compute the fluid-solid equilibria of methanol with the OPLS model, we consider three possible solid structures α , β , and γ , which are found in the experimental phase diagram. The space groups are α - $P2_12_1$, β -Cmcm, and γ - $P\bar{1}$, respectively, the unit cell being orthorhombic in the first two structures and triclinic in the last one. These features have been determined experimentally from diffraction studies. The initial configuration used in the simulations was obtained from the experimental data (after adjusting slightly the bond lengths and angles to the values of the OPLS model).

The equation of state (EOS) of the solid was obtained from anisotropic NpT Monte Carlo (MC) simulations. In anisotropic NpT simulations, both the volume of the system and the shape of the simulation box fluctuate along the run.^{32,33} The use of the anisotropic version of the NpT ensemble is absolutely required to simulate solid phases. It guarantees that the shape of the simulation box (and therefore that of the unit cell of the solid) is the equilibrium one. It also guarantees that the solid is under hydrostatic pressure and free of stress (the pressure tensor will then be diagonal with the three components being identical to the thermodynamic pressure). For the solid phases α , β , and γ , we used 300, 320, and 270 molecules, respectively. The EOS of the fluid was obtained from isotropic NpT simulations using a cubic box containing 300 molecules. We typically used 20 000 cycles for equilibration followed by about 40 000 cycles to obtain thermodynamic averages for α and β phases and 60 000 cycles in both cases for the γ phase (we defined a cycle as a trial move per particle plus an attempt to change the volume of the system).

In our MC simulations, the LJ site-site interactions were truncated at 10 Å (except for the γ solid for which we truncated at 9.0 Å). Standard long range corrections to the LJ energy were added. Ewald summation technique has been employed for the calculation of the long range electrostatic forces. Ewald sums are especially convenient to deal with solid phases. The real space contribution of the Ewald sum was truncated at the same values of the LJ interaction. The screening parameter and the number of vectors of reciprocal space considered had to be carefully selected for each crystal phase.^{1,34} The number of molecules for each solid phase was chosen so as to fit at least twice the cutoff distance in each direction.

To compute phase equilibria, besides the EOS (which is obtained from NpT simulations) the evaluation of the chemical potential is required. Therefore free energy calculations are needed. Let us describe briefly how the free energy was obtained for the fluid and for the solid phases. The free energy of the methanol in the liquid phase was obtained by thermodynamic integration. Thermodynamic integration allows one to obtain the free energy at any thermodynamic state provided that the free energy at a reference state is known and that no phase transition is crossed along the integration. Formulae to describe the change in the residual part of the free energy change along isotherms, isobars, and isochores have been given elsewhere.³¹ We used 1 bar and 298 K as the reference state for which the density of the OPLS model is 0.762 g/cm³. To obtain the free energy at this reference state, we started from an ideal gas at zero pressure and $T=800$ K (a supercritical temperature), and integrate along the isotherm to the reference density. Then we integrate along the isochore up to the reference temperature of 298 K. In this way, no phase transition was crossed. Once the residual free energy of the liquid is obtained at a certain thermodynamic state, the total free energy is obtained by adding the ideal term given by

$$\frac{A(\rho, T)}{Nk_B T} = \ln(\rho\Lambda^3) - 1. \quad (1)$$

In this calculation the rotational, vibrational, and electronic contributions to the partition function were set to one (they are certainly not one, but its exact value does not affect phase equilibria since for a rigid molecule treated by classical mechanics these contributions will be identical for the two co-existence phases). In this work, we shall assign the thermal de Broglie wavelength to be $\Lambda=1$ Å both for the liquid and the solid phases. This is an arbitrary choice but again it does not affect phase equilibria (see Ref. 31 for further details).

Let us now describe briefly the procedure used to compute the free energy of the solid phase. We shall use the Einstein molecule³⁵ as extended to rigid nonlinear molecules in Refs. 31 and 36. The Einstein molecule, is a small modification of the well known Einstein crystal method proposed by Frenkel and Ladd.¹³ In Einstein molecule method, the reference point of one of the molecules of the system remains fixed instead of fixing the location of the center of mass. Another interesting procedure to obtain free energies of solids has been proposed recently by Radu *et al.*³⁷ We have shown recently that the Einstein molecule method pro-

vides free energies identical to those of the Einstein crystal method. Since all details about the implementation of the Einstein molecule can be found elsewhere,^{31,36} we give here just a brief summary.

In the Einstein molecule approach, the free energy of a given solid is estimated by designing a path from the ideal Einstein crystal to the real solid following the next three steps procedure. In the first step, the difference in free energy between the ideal Einstein crystal and the ideal Einstein molecule, which is equal to the former except that molecule 1 is fixed, is evaluated. This contribution is computed analytically and takes the value of $k_B T \ln(V/\Lambda^3)$. In the second step, the difference between the free energy of the ideal Einstein molecule and the real solid with molecule 1 fixed is calculated. Finally, in the last step, the constraint over molecule 1 in the real solid is removed; the change in free energy in this step is $-k_B T \ln(V/\Lambda^3)$. Since contributions in the first and three step cancels out, it is only necessary to evaluate the free energy of the ideal Einstein molecule and its change in a path connecting it with the real solid with molecule 1 fixed.

In the ideal Einstein molecule, the molecules (without any intermolecular interactions) vibrate around a harmonic external field forcing the molecules to be around the equilibrium positions and orientations. The calculation of the free energy of the ideal Einstein molecule $A_{\text{Ein-mol-id}}$ (here in after A_0) is easily obtained^{31,36} once the translational and the orientational contributions are defined for the specific model. For OPLS methanol, the external field has the following contributions. The translational term ($U_{\text{Ein-mol-id},t}$) is given by

$$U_{\text{Ein-mol-id},t} = \sum_{i=2}^N [\Lambda_E(\mathbf{r}_i - \mathbf{r}_{io})^2], \quad (2)$$

where $\mathbf{r}_{io}$ is the position of the reference point of molecule i in the reference Einstein solid, while $\mathbf{r}_i$ represents its position in the current configuration. As can be seen in Eq. (2), all the particles except particle 1 (which is fixed) are attached to their lattice positions by harmonic springs. We used the oxygen atom as the reference point. An orientational field ($U_{\text{Ein,or}}$) that forces the particles to adopt the right orientation is also included (this field acts over all the particles of the system, including particle 1). The orientational contribution is given by

$$U_{\text{Ein,or}} = \sum_{i=1}^N \left[\Lambda_{E,a} \left(\frac{\psi_{a,i}}{\pi} \right)^2 + \Lambda_{E,b} \left(\frac{\psi_{b,i}}{\pi} \right)^2 \right]. \quad (3)$$

The angles $\psi_{a,i}$ and $\psi_{b,i}$ are defined in terms of two unit vectors, $\vec{a}$ and $\vec{b}$, that specify the orientation of the molecule. $\psi_{a,i}$ is the angle formed by the unit vector $\vec{a}$ of molecule i in a given configuration ($\vec{a}_i$) and the unit vector ($\vec{a}_{io}$) of that molecule in the reference lattice. The angle $\psi_{b,i}$ is defined analogously but with vector $\vec{b}$. The definition of vectors $\vec{a}$ and $\vec{b}$ used here for a rigid triatomic molecule as methanol is similar to that used previously for another triatomic molecule (water).³¹ Vector $\vec{b}$ goes along the C–O–H bisector (it was calculated using two unit vectors, one in the OH direction and the other in the OC direction), and vector $\vec{a}$ is perpendicular to $\vec{b}$ and located in the plane of the molecule (that

formed by the C, O, and H atoms). The reference lattice, i.e., the values of $\mathbf{r}_{io}$, $(\vec{a}_{io})$, and $(\vec{b}_{io})$, were obtained from the final configuration in an annealing run which consists in consecutive NVT simulations of the real solid (with molecule 1 fixed) decreasing the temperature slowly, while keeping the shape of the simulation box constant.

Once the free energy of the ideal Einstein molecule A_0 is evaluated, the free energy of the real solid A_{sol} is calculated following the next expression:

$$A_{\text{sol}} = A_0 + \Delta A_1 + \Delta A_2, \quad (4)$$

where $\Delta A_1 + \Delta A_2$ represents the change in free energy between the ideal Einstein molecule and the real solid with molecule 1 fixed. The first term ΔA_1 is the change of free energy between the ideal Einstein molecule and the interacting Einstein molecule, in which both the springs and the intermolecular potential are present with molecule 1 fixed. This quantity is obtained in a perturbative approach

$$\Delta A_1 = U_{\text{lattice}} - k_B T \ln \langle \exp[-\beta(U_{\text{sol}} - U_{\text{lattice}})] \rangle_{\text{Ein-mol-id}}, \quad (5)$$

where U_{sol} is the energy of the solid calculated with the intermolecular potential and U_{lattice} is the energy of the frozen lattice, i.e., the energy of the reference lattice. The brackets with the subscript Ein-mol-id indicates that the average is evaluated by sampling configurations in the ideal Einstein molecule (only the external field is present) within the NVT ensemble. The second quantity ΔA_2 represents the change in free energy between the interacting Einstein molecule and the real solid with molecule 1 fixed. This calculation is made by slowly turning off the springs, according to the following expression:

$$U(\lambda) = \lambda U_{\text{sol}} + (1 - \lambda)(U_{\text{Ein-mol-id}} + U_{\text{sol}}), \quad (6)$$

where λ is a parameter that takes values between 0 and 1. The free energy change corresponding to this transformation can be estimated by numerically evaluating the following integral:

$$\Delta A_2 = - \int_0^{\Lambda_E} \frac{\langle U_{\text{Ein-mol-id}} \rangle_{N,V,T,\lambda}}{\Lambda_E} d(\lambda \Lambda_E). \quad (7)$$

This integral is usually performed by using a Gauss–Legendre quadrature formula. For that purpose, the integrand of this expression must be evaluated at several values of $\lambda \Lambda_E$, which can be done by performing NVT MC simulations for those values of the coupling parameter (in our case, we use ten values of λ).

The shape of the box is the same for all the NVT simulations of Einstein molecule method used for the evaluation of the free energy of a real solid at a specific thermodynamic state. This was the equilibrium one obtained from a NpT anisotropic simulation of the real solid (no particle is fixed) at the specific thermodynamic state. Length of the runs used in the free energy calculations were similar to those used in the NpT runs. In this work, we used $\Lambda_E/(k_B T/\text{\AA}^2) = \Lambda_{E,a}/(k_B T) = \Lambda_{E,b}/(k_B T) = 25\,000$. The value of Λ_E must be chosen not too small because in this case extremely long runs would be required to evaluate ΔA_1 accurately, and not

too high since then many values of $\lambda \Lambda_E$ should be evaluated to determine the integral appearing in Eq. (7) accurately. A common recipe (used in this work) is to set this value such as the difference between ΔA_1 and U_{lattice} would be around $0.03NkT$.

Once the Helmholtz free energy of the solid A is obtained for a certain reference state, the free energy for other states can be obtained through thermodynamic integration. The chemical potential μ is obtained as

$$\mu/kT = (G/NkT) = (A/NkT) + (pV/(NkT)), \quad (8)$$

so that once the EOS and the Helmholtz free energy are known, then it is straightforward to obtain the chemical potential. Coexistence between two phases is obtained from the condition of identical chemical potential at a certain pressure and temperature. It is worth noting that the free energies computed for the fluid and solid phases correspond to that of the model under consideration (OPLS in this case). To evaluate its free energy the Hamiltonian is changed from the model of interest to that of a reference system, but the computed free energies correspond to those of the potential under consideration.

Once an initial coexistence point between two phases is known, the rest of the coexistence curve can be obtained by performing Gibbs–Duhem integration. The Gibbs–Duhem integration, first proposed by Kofke in 1993 is a numerical integration of the Clapeyron equation.^{14,38,39} The Clapeyron equation between two coexistence phases (labeled as I and II) can be written as

$$\frac{dp}{dT} = \frac{s_{\text{II}} - s_{\text{I}}}{v_{\text{II}} - v_{\text{I}}} = \frac{h_{\text{II}} - h_{\text{I}}}{T(v_{\text{II}} - v_{\text{I}})}, \quad (9)$$

where we use lower case for thermodynamic properties per mole (or per particle). Since the difference in enthalpy and volume between two phases can be determined easily (at a certain T and p) the equation can be integrated numerically. When implementing the Gibbs–Duhem integration one obtains the coexistence pressure for the selected temperatures (the temperature acting as the independent variable). This is quite convenient when the coexistence line does not present a large slope in the p – T plane. Some times it is more convenient to integrate the Clapeyron equation in a different way: $dT/dp = T\Delta v/\Delta h$. We used a fourth order Runge–Kutta algorithm to integrate the Clapeyron equation. In the Gibbs–Duhem simulations anisotropic NpT simulations were used for the solid phases, whereas isotropic NpT simulations were used for the liquid.

Finally we have also computed fluid–solid equilibria by direct coexistence. In this method, the fluid and the solid phases are introduced into the simulation box, and simulations are performed to achieve equilibrium between the two coexistence phases.^{40–42} The method can be applied in several ways. One of the possible implementations is to perform simulations in the NpT ensemble, for several temperatures, at a given fixed pressure. If the temperature is above the melting temperature the solid will melt (i.e., the total energy of the system will increase) on the contrary, if the temperature is below the melting temperature the fluid will freeze (i.e., the total energy will decrease). In this way, it is possible to

establish a lower and upper limit to the melting temperature. We have performed direct coexistence simulations to determine the melting point of the α phase of methanol at room pressure. A total number of 826 molecules were introduced in a simulation box. About half of them occupying the left hand side of the simulation box were in the solid state (α solid) whereas the rest (in fluid phase) occupied the right hand side of the simulation box. The approximate size of the simulation box was of about $60 \times 28 \times 28 \text{ \AA}^3$. The x axis was perpendicular to the fluid-solid interface. Simulations were performed at the following temperatures 200, 220, 225, 230, and 240 K. Simulations typically lasted about 100 ns, although longer runs were used for some selected temperatures. To perform the direct coexistence simulations, molecular dynamics (MD) calculations were performed using GROMACS (version 3.3).⁴³ The time step used in the simulations was 2 fs. The temperature is kept constant by using a Nose-Hoover^{44,45} thermostat with a relaxation time of 2 ps. To keep the pressure constant, a Parrinello-Rahman barostat^{46,47} was used. The relaxation time of the barostat was 2 ps. The pressure of the barostat has been set to 1 bar in all the simulations. The three sides of the simulations box were allowed to change independently. The geometry of the methanol molecules was enforced using constraints.^{48,49} The LJ part of the potential was truncated at 10 $\text{\AA}$ and usual LJ long range corrections were used. Ewald sums are used to deal with the electrostatic interactions. The real part of the Coulombic potential is truncated at 10 $\text{\AA}$. The Fourier part of the Ewald sums are evaluated by using the particle mesh Ewald method of Essmann *et al.*⁵⁰ The width of the mesh is set equal to 1 $\text{\AA}$ and fourth-order interpolation is used. As can be seen, the conditions used in the direct coexistence simulations are similar to those used in the NpT and NVT MC simulations used to determine the EOS and free energies of the different phases of methanol.

III. RESULTS

The simulation results of the EOS for both the fluid phase and solid phases of methanol are given in Tables I–III. Densities obtained from simulation for the fluid phase at 298 K and 1 bar (0.762 g/cm^3), for α phase at 160 K and 1 bar (0.994 g/cm^3), for β phase at 170 K and 1 bar (0.991 g/cm^3), and for γ phase at 298 K and 40 000 bar (1.276 g/cm^3) were compared to their experimental counterparts (0.7864 g/cm^3), (1.0147 g/cm^3), (0.9921 g/cm^3), and (1.3526 g/cm^3). The experimental densities for α and β phases were obtained from Torrie *et al.*,⁵¹ whereas for the γ phase it was taken from Allan *et al.*⁵² As can be seen, the OPLS model provides good values for the orthorhombic phases (especially for the β phase) and reasonable predictions for the triclinic one. In all the cases, the model underestimates the experimental densities.

The free energy for methanol fluid at the reference state A (298 K, 1 bar) was -12.18 (in NkT units) as calculated from thermodynamic integration using the simulated EOS along the 800 K isotherm and the 0.762 g/cm^3 isochore. On the other hand, the free energy A of α , β , and γ solid phases at the reference states are shown in Table IV. As was men-

TABLE I. Density ρ and residual internal energy U as a function of temperature T and pressure p for methanol in the fluid phase. Only some representative points were included. Uncertainties are given in parenthesis.

p/bar	T/K	$\rho/(\text{g/cm}^3)$	$U/(\text{kJ/mol})$
1	150	0.897(3)	-43.31(3)
1	175	0.880(2)	-42.37(4)
1	200	0.861(4)	-41.38(3)
1	225	0.835(3)	-40.07(3)
1	250	0.809(1)	-38.55(1)
1	275	0.784(3)	-37.03(2)
1	298	0.762(2)	-35.75(2)
1	800	0.000 488(1)	-0.018(2)
10	800	0.00 484(1)	-0.165(3)
50	800	0.0246(1)	-0.833(5)
100	800	0.0505(4)	-1.67(3)
250	800	0.133(1)	-4.19(2)
500	800	0.260(1)	-7.71(3)
1000	800	0.417(3)	-11.77(8)
2000	800	0.559(2)	-15.21(5)
3000	800	0.636(2)	-17.01(3)
4000	800	0.690(5)	-18.14(1)
5000	800	0.731(4)	-18.95(3)
6000	800	0.766(2)	-19.61(2)
7000	800	0.793(1)	-20.02(2)

tioned in Sec. II, before computing the free energy, the solid structure must be relaxed to equilibrium. We shall report here the unit cell dimensions at 100 K and 1 bar: The lengths of the edges for the α phase were $a=23.44 \text{ \AA}$, $b=24.63 \text{ \AA}$, and $c=27.02 \text{ \AA}$; for the β phase $a=24.15 \text{ \AA}$, $b=27.96 \text{ \AA}$, and $c=24.63 \text{ \AA}$; and for the γ phase $a=28.30 \text{ \AA}$, $b=22.25 \text{ \AA}$, and $c=22.60 \text{ \AA}$, the angles of the unit cell for the γ phase are $\hat{b}c=89.68^\circ$, $\hat{a}c=100.85^\circ$, and $\hat{b}a=94.64^\circ$. As a check of consistency, we evaluated the free energy for the α and β phases at 150 K and 1 bar and for the γ phase at 100 K and 40 000 bar by means of the thermodynamic integration technique using the value at 100 K and 1 bar as reference point. For α , β , and γ phases, we obtained the values (in NkT units) of -29.55 , -29.44 , and -35.22 , respectively, which coincide extremely well with the values of Table IV.

The chemical potential of the α and β solid phases was

TABLE II. Residual internal energy U along the isochore 0.762 g/cm^3 as a function of temperature T for methanol in the fluid phase. Only some representative points were included. Uncertainties are given in parenthesis.

T/K	$U/(\text{kJ/mol})$
298	-35.75(2)
350	-33.37(2)
400	-31.14(2)
450	-29.08(5)
500	-27.08(3)
550	-25.41(3)
600	-23.89(2)
650	-22.68(4)
700	-21.49(3)
750	-20.48(2)
800	-19.52(1)

TABLE III. Density ρ and residual internal energy U as a function of temperature T and pressure p for the α , β , and γ solid phases of methanol. Only some representative points were included. At 225 K and 1 bar the γ phase is mechanically unstable and melts so no value is reported. Uncertainties were estimated to be within 0.001 g/cm³ for the densities and within 0.01 kJ/mol for the energies.

p/bar	T/K	α $\rho/(\text{g}/\text{cm}^3)$	β $\rho/(\text{g}/\text{cm}^3)$	γ $\rho/(\text{g}/\text{cm}^3)$	α $U/(\text{kJ}/\text{mol})$	β $U/(\text{kJ}/\text{mol})$	γ $U/(\text{kJ}/\text{mol})$
1	75	1.035	1.034	1.043	-50.01	-49.88	-47.52
1	100	1.024	1.024	1.032	-49.32	-49.19	-46.81
1	125	1.012	1.013	1.019	-48.59	-48.47	-46.07
1	150	0.999	1.001	1.007	-47.82	-47.73	-45.30
1	175	0.986	0.989	0.993	-47.05	-46.95	-44.50
1	200	0.972	0.976	0.977	-46.22	-46.13	-43.62
1	225	0.958	0.960	...	-45.38	-45.23	...
1	100	1.023	1.024	1.032	-49.30	-49.18	-46.84
2000	100	1.056	1.056	1.064	-49.48	-49.33	-46.99
6000	100	1.103	1.104	1.112	-49.34	-49.19	-46.85
10 000	100	1.138	1.140	1.147	-48.91	-48.74	-46.40
30 000	100	1.252	1.253	1.264	-44.98	-44.87	-42.41
50 000	100	1.324	1.325	1.339	-39.98	-39.88	-37.40
70 000	100	1.381	1.381	1.395	-34.47	-34.46	-32.05
80 000	100	1.405	1.405	1.419	-31.67	-31.67	-29.30
90 000	100	1.427	1.427	1.441	-28.86	-28.87	-26.55
100 000	100	1.447	1.447	1.461	-26.06	-26.09	-23.81
110 000	100	1.466	1.465	1.479	-23.27	-23.29	-21.04
120 000	100	1.483	1.483	1.497	-20.48	-20.47	-18.24
130 000	100	1.499	1.499	1.513	-17.67	-17.64	-15.45

obtained along the 1 bar isobar using 100 K and 1 bar as the reference state. In Fig. 1, their values are plotted compared to those of methanol fluid. As can be seen, the chemical potential of the β phase is always higher than that of the α phase which indicates that the last is the most stable phase at 1 bar between the solid ones (the γ phase was excluded of Fig. 1 since its chemical potential is significantly higher than the other ones as can be inferred from Table IV). When the chemical potential of the fluid phase is compared to that of the α phase, it is clear that this one is more stable for temperatures below 215 K, whereas the situation is the opposite at higher temperatures. Therefore, a coexistence point appears at 215 K, which is the melting point of the OPLS model. For the β solid the melting temperature is 209 K, which is a consequence of the lower stability of this phase. These results point out that the only stable phases at the pressure of 1 bar are the α solid for temperatures below 215 K and the liquid for temperatures above this value (being the β solid a thermodynamically metastable phase at this pressure).

We have also used direct coexistence simulations (MD) to obtain the melting point of the model in a totally different way (details were provided in Sec. II). In Fig. 2, the evolution of the potential energy of the system with time at several temperatures is shown. As can be seen, at 240 K, the energy increases with time reaching a plateau which corresponds (and confirmed by visual inspection) to the complete melting of the solid. The same behavior is found at 230 and 225 K, although the time required to melt the solid completely increases as the temperature decreases (in fact, it changes from about 3 ns at 240 K to more than 100 ns at 225 K). The energy of the final plateau is different for the different temperatures considered, reflecting the variation of the internal energy of liquid methanol with temperature (at room pressure). For the temperature of 200 K the energy of the system decreases with time, and visual inspection reveals the slow growth of the solid (which freezes completely in about 140 ns). It is interesting to note that the rate of growth of the α solid of methanol seems to be smaller than that found for ice I_h in water simulations. Obviously the growth rate is a prop-

TABLE IV. Free energies (A_{sol}) for the α , β , and γ solid phases of methanol, as well as their contributions (A_0 , ΔA_1 , and ΔA_2) for several thermodynamic states. In all these simulations, $\Lambda_E/(k_B T/\text{\AA}^2) = \Lambda_{E,d}/(k_B T) = \Lambda_{E,b}/(k_B T) = 25\,000$. Uncertainty in the free energies was estimated in $0.01NkT$.

Solid	p/bar	T/K	$\rho/(\text{g}/\text{cm}^3)$	A_0/NkT	$\Delta A_1/NkT$	$\Delta A_2/NkT$	A_{sol}/NkT
α	1	100	1.024	28.17	-62.18	-15.08	-49.09
α	1	150	0.999	28.17	-41.24	-16.47	-29.55
β	1	100	1.024	28.17	-62.02	-15.08	-48.93
β	1	150	1.001	28.17	-41.15	-16.46	-29.44
γ	1	100	1.032	28.16	-58.98	-15.04	-45.86
γ	40 000	100	1.305	28.16	-50.62	-12.76	-35.22

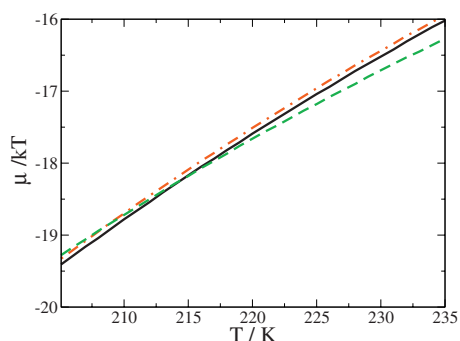


FIG. 1. Chemical potential μ as a function of temperature T at 1 bar for fluid phase (dashed) and for α (solid) and β (dashed-dotted) solid phases of methanol.

erty which depends on the substance, on the degree of supercooling, on the solid considered and on the plane considered.⁵³ At 220 K, the energy seems to be stable for the longest considered run (of about 100 ns). Inspection of the final configuration reveals that both the fluid and solid phases are present in approximately the same amount. Thus, from these MD simulations, it is obvious that the melting point should be between 225 and 200 K, and that in fact, it should not be far from 220 K for which the interface is stable for more than 100 ns. In summary, these MD runs suggest again a melting point around 220(5) K, in excellent agreement with the results obtained from free energy calculations 215(4) K. We have found previously for water models that melting point temperatures estimated from free energy calculations and from direct coexistence simulations were mutually consistent.⁵⁴ The same is found here for methanol.

Once we have computed the melting point of methanol by free energy calculations, the reader may wonder why it was not obtained from NpT simulations by simply heating the solid at constant pressure (in NpT simulations) and checking the temperature at which the solid melts. In Fig. 3, the evolution of the potential energy with temperature (at room pressure) is shown. The simulations were performed for the α solid starting at low temperatures and using the final configuration of a run as the input configuration of the

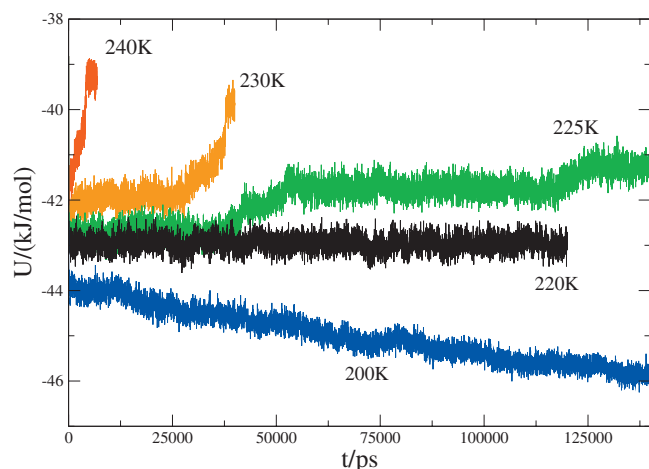


FIG. 2. Evolution of the potential energy with time in direct coexistence simulations of the OPLS model of methanol at 1 bar. The number of molecules was of 826.

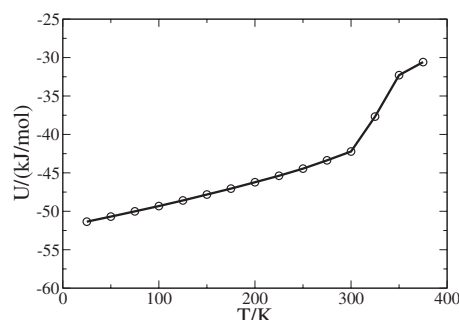


FIG. 3. Internal energy of the α solid phase as a function of temperature. The jump observed around 325 K corresponds to the spontaneous melting of the solid (i.e., the lost of mechanical stability). The true melting point of the α solid obtained from free energy calculations corresponds to 215 K.

next run (at the next higher temperature). As can be seen there is a jump in the internal energy and at the temperature of 350 K, the solid has melted completely. Since the true melting point of the model is 215 K it can be seen that the α solid can be superheated in NpT simulations by about 110 K, and therefore this technique cannot be used to determine the melting point. This behavior is similar to that found for water where it was found that ices could be superheated by about 80 K above the true melting temperature.⁵⁵ It appears that solid methanol can be superheated even more (about 110 K). For the β solid we found similar behavior and the solid melted spontaneously at the same temperature than the α solid. This is consistent with the quite similar free energies found for the α and β solids.

In order to find coexistence points between solid phases, their chemical potentials were obtained along the isotherm of 100 K between 1 and 150 000 bar by means of the thermodynamic integration technique, using as reference their values at 100 K and 1 bar. Results are shown in Fig. 4. It has been found that the β phase is always less stable than the α for all the studied pressures. The competition between α and γ had the following results: for pressures lower than 115 047 bar the first one is the most stable whereas that for higher pressures the most stable is the second one. Thus, 115 047 bar and 100 K is a coexistence point between the α and γ phases.

The complete phase diagram was determined using Gibbs–Duhem integration starting from the melting point and the coexistence point at high pressure obtained between the α and γ phase. Some representative results of this pro-

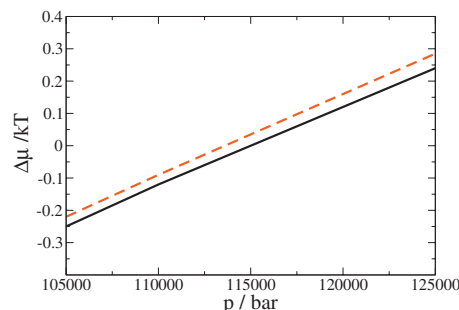


FIG. 4. Difference between the chemical potential of α or β solid phases and that of γ solid phase of methanol plotted against pressure p at 100 K. α - γ (solid line) and β - γ (dashed line).

TABLE V. Coexistence properties along the fluid- α coexistence curve. Densities ρ and molar enthalpies h are given for each coexistence point. Only some representative points were included. Uncertainties were estimated to be within 0.002 g/cm³ for the densities and within 0.02 kJ/mol for the enthalpies. The asterisk indicates the melting point of the OPLS methanol, which was used as the initial point in the Gibbs–Duhem integration. The uncertainty in the melting point was estimated in 4 K.

p/bar	T/K	Fluid $\rho/(\text{g}/\text{cm}^3)$	α $\rho/(\text{g}/\text{cm}^3)$	Fluid $h/(\text{kJ}/\text{mol})$	α $h/(\text{kJ}/\text{mol})$
1	*215	0.844	0.964	−40.51	−45.71
250	219.7	0.852	0.967	−39.56	−44.79
1000	232.6	0.876	0.980	−36.70	−42.21
3000	259.7	0.931	1.008	−29.57	−35.61
5000	280.0	0.963	1.032	−22.46	−29.28
7000	296.6	0.991	1.053	−16.20	−23.13
10 000	318.1	1.025	1.081	−6.19	−14.19
14 000	340.7	1.071	1.112	5.05	−2.57
18 000	359.3	1.101	1.138	17.19	8.63
22 000	374.6	1.129	1.162	28.20	19.52
28 000	393.8	1.164	1.193	44.52	35.44
34 000	409.1	1.196	1.221	60.25	50.90
40 000	422.3	1.225	1.245	75.19	66.11
52 000	442.4	1.272	1.288	105.19	95.58
64 000	456.1	1.313	1.324	133.94	124.23
79 000	467.6	1.357	1.364	167.88	158.96
94 000	472.4	1.397	1.399	201.73	192.76
106 000	473.4	1.426	1.424	226.80	219.12
115 000	471.0	1.445	1.442	245.97	238.54
124 000	468.2	1.462	1.459	265.23	257.68
130 000	466.0	1.474	1.470	277.78	270.40

cedure are shown in Tables V–VII, whereas the complete phase diagram is plotted in Fig. 5 compared with the experimental diagram. As stated before the OPLS model overestimates the melting temperature by about 40 K, which is a reasonable result taking into account that it was not optimized to reproduce the melting point. It should be mentioned that the model underestimates the critical temperature by about 30 K (Ref. 56) (thus the critical temperature is underestimated and the melting temperature is overestimated). The melting enthalpy Δh of the OPLS model at room pressure is 5.2 kJ/mol, which is too high when compared with the experimental value (3.215 kJ/mol).⁵⁷ It is likely that reducing the strength of the hydrogen bond in the model could reduce

both the melting temperature and the melting enthalpy to bring the results in closer agreement with experiment. The OPLS model is able to predict correctly the existence of the α , γ and fluid phases within the phase diagram of methanol. However the β phase is missing in the computed phase diagram whereas it appears in the experimental one. Notice that experimentally when methanol is cooled at room pressure it freezes into the β solid, which is stable for about 15 K and then transforms into the α phase. Thus the stability range of the β solid is quite small. It follows then that the properties of the α and β solids must be quite similar (as an example, the density of these two solids is quite similar and it will be shown later that the same is true for the structure). For this

TABLE VI. Coexistence properties along the α - γ coexistence curve. Densities ρ and molar enthalpies h are given for each coexistence point. Only some representative points were included. Uncertainties were estimated to be within 0.002 g/cm³ for the densities and within 0.02 kJ/mol for the enthalpies. The asterisk indicates the coexistence pressure between α and γ solids used as initial point in the Gibbs–Duhem integration. Its uncertainty was estimated in 1500 bar.

p/bar	T/K	α $\rho/(\text{g}/\text{cm}^3)$	γ $\rho/(\text{g}/\text{cm}^3)$	α $h/(\text{kJ}/\text{mol})$	γ $h/(\text{kJ}/\text{mol})$
*115 047	100	1.474	1.489	228.12	228.06
117 083	150	1.474	1.488	233.83	233.69
119 831	210	1.474	1.488	241.34	241.16
122 705	270	1.474	1.488	249.16	248.84
125 824	330	1.474	1.488	257.49	257.18
128 614	390	1.474	1.488	265.18	264.85
131 414	450	1.474	1.488	272.87	272.36
133 152	490	1.473	1.487	277.72	277.32
133 964	510	1.473	1.488	280.08	279.54

TABLE VII. Coexistence properties along the fluid- γ coexistence curve. Densities ρ and molar enthalpies h are given for each coexistence point. Only some representative points were included. Uncertainties were estimated to be within 0.002 g/cm³ for the densities and within 0.02 kJ/mol for the enthalpies. The asterisk indicates the α - γ -fluid triple point which was used as the initial point in the Gibbs–Duhem integration. Its uncertainty was estimated in 2000 bar.

p/bar	T/K	Fluid $\rho/(\text{g}/\text{cm}^3)$	γ $\rho/(\text{g}/\text{cm}^3)$	Fluid $h/(\text{kJ}/\text{mol})$	γ $h/(\text{kJ}/\text{mol})$
*131 120	465.1	1.474	1.486	281.13	272.24
136 523	470.0	1.485	1.495	292.12	283.75
142 655	475.0	1.494	1.504	305.56	296.64
148 955	480.0	1.505	1.514	318.16	309.86
156 754	485.0	1.518	1.526	334.34	325.94
165 102	490.0	1.531	1.537	351.04	343.15
174 620	495.0	1.545	1.551	370.43	362.66
185 318	500.0	1.559	1.565	392.05	384.30
197 312	505.0	1.575	1.579	416.52	408.43
211 705	510.0	1.593	1.597	444.86	437.11

reason the disappearance of the β phase in the calculated phase diagram, although not pleasant, cannot be regarded as a important failure, since only an extremely accurate potential could capture the small free energy differences that exists between the α and the β structures. From a quantitative point of view the pressure at which the γ phase appears within the phase diagram of the OPLS model is too high. Although the experimental α - γ coexistence curve has not been reported the γ phase has been found experimentally at pressures of about 35 000 bar, whereas for the model it appears at pressures above 100 000 bar. Even for water it has been difficult to reproduce quantitatively the high pressure part of the phase diagram. It seems that the same is true for methanol. This may be connected with the fact that the repulsive part of the potential (which becomes increasingly important at high pressures) is not well described the LJ potentials.

In Figs. 6–8, the C–C, O–O, and O–H radial distribution functions for α , β and γ methanol as obtained from computer simulations at 150 K and 1 bar are presented. The first peak of the O–H distribution function provides an idea of the number of molecules that form hydrogen bonds. As can be seen, the results for α and β phases are almost undistinguish-

able presenting a higher peak than the γ phase. In other words hydrogen bonding is more favorable in the α and β phases and that explains why these phases are more stable than the γ phase at low T and p . The results of α and β for the OH distribution function are different for distances larger than 4 Å. For the C–C distribution function the results of the α and β solids are almost indistinguishable (differences appears only at about 8 Å) but clearly different from those of the γ phase. For the O–O distribution function, α and β presents a similar first coordination layer, and they differ in the second coordination layer. In summary the structure of the α and β phases is quite similar at short distances, differences emerging at longer distances. That explains why their densities, internal energies, and free energies are so similar: they are due to the strong structural similarities between the two phases. To provide further evidence of that the fluid- α and fluid- β coexistence curves of the OPLS model are presented in Fig. 9. As can be seen both phases melt at quite similar temperatures (except at low pressures where the melting temperature of the α phase is slightly larger). Therefore the model is able to capture the similar free energies of those two phases. Notice the existence of re-entrant melting in the fluid- α (and fluid- β) coexistence curves. In the region where the slope of the melting curve is negative the solid becomes less dense than the fluid. Similar behavior was found at high pressures in the melting curves of several water models.¹⁶

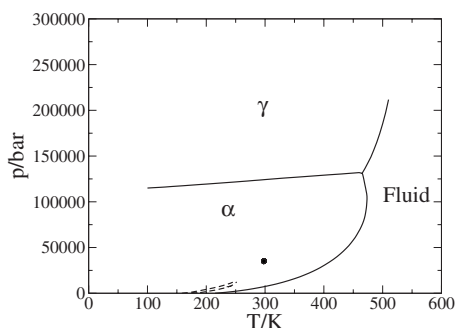


FIG. 5. Phase diagram of OPLS methanol (solid) compared to the experimental one (dashed). The experimental phase diagram was determined between 1 bar and 15 000 bar detecting two coexistence curves; going from low to high temperature, the first coexistence line represents the transition between the α solid phase to the β phase and the second defines the transition between the β phase and the fluid. The single point represents the only experimental thermodynamic state for which the existence of the γ phase has been reported.

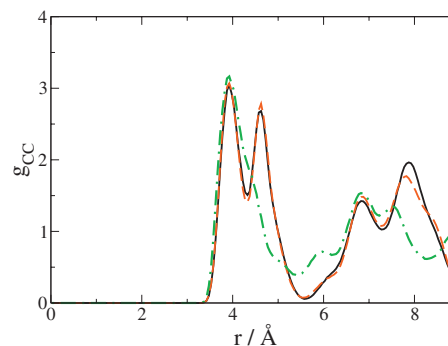


FIG. 6. C–C radial distribution function at 150 K and 1 bar. α (solid), β (dashed), and γ (dashed-dotted).

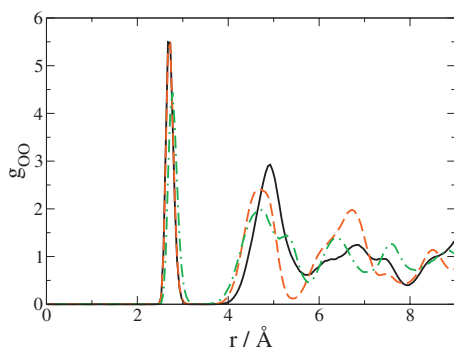


FIG. 7. O–O radial distribution function at 150 K and 1 bar. α (solid), β (dashed), and γ (dashed-dotted).

IV. CONCLUSIONS

By performing computer simulations, we have determined the phase diagram of the OPLS model of methanol. Free energy calculations were performed to locate initial coexistence points, and Gibbs–Duhem integration was used to determine the complete coexistence curves. The model provides a reasonable description of the densities of the solid phases of methanol. It also predicts correctly the appearance of the solid phases α and γ . Taking into account that the model was fitted to reproduce just the liquid density and vaporization enthalpy at room temperature the results can be considered to be satisfactory. However, it is clear that there is room for improvement of the model. The model predicts that the β solid phase is metastable within the phase diagram of the OPLS model of methanol. According to the OPLS model α and β solids have similar free energies, being that of the α phase always slightly lower. Experimentally this similarity must also occur since the stability range of the β phase is quite small. The model predicts a melting point temperature of about 215 K. This melting point was further confirmed by direct coexistence simulations. Taking into account that the experimental value of the melting point is 175 K, the model overestimates the melting temperature by about 20%. Similar deviations in the estimate of the melting point was found for popular models of water as SPC,⁵⁸ SPC/E,⁵⁹ or TIP4P.⁶ Taking just these two substances, water and methanol, it is clear that models fitted to reproduce the properties of the liquid at room temperature may have errors in the estimate of the melting point temperature as large as 20% (although for

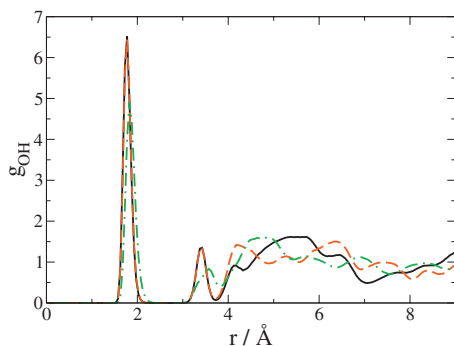


FIG. 8. O–H radial distribution function at 150 K and 1 bar. α (solid), β (dashed), and γ (dashed-dotted).

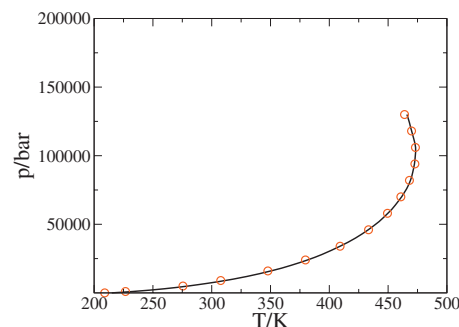


FIG. 9. Fluid- α (solid line) and fluid- β (open circles) coexistence lines for the OPLS model of methanol.

methanol it seems that the melting point temperature is overestimated whereas for water the models tend to underestimate the melting point).

This work shows that phase diagram calculations can be performed for realistic potentials of molecular fluids. Notice however that this methodology is not absent of significant sources of uncertainties.⁶⁰ In fact, the free energy of the fluid is evaluated from the ideal gas along a pathway that bypasses the critical point. Along such an integration path, errors accumulate rendering accurate computations of melting points extremely difficult. Additionally, coexistence lines are computed via Gibbs–Duhem integration, a second integration procedure, which is again prone to errors. Finally, the system sizes studies are rather small, producing another source of error.

Previous work on idealized molecular models have illustrated that it can be quite useful to understand the underlying physics of molecular systems^{61–68} The interest in this type of studies is twofold. First the knowledge of the melting point temperature is of interest to study nucleation phenomena and supercooled fluids.⁶⁹ Second the phase diagram calculations can help in improving and developing new potential models, not only for those researchers interested in solid phase properties, but also for those researchers interested in the fluid phase. The study of solid phases can be useful to test and improve potential models even for those researchers interested in the fluid phase. This point of view was advocated a long time ago by Whalley,⁷⁰ Morse and Rice⁷¹ (setting water as an example) and more recently by Monson.⁶⁸ Using melting properties and phase diagram calculations to develop and improve potential models is in our opinion a suggestion worth to consider in the future, especially once technical details about phase diagram calculations have been settled.

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