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Note: A simple correlation to locate the three phase coexistence line in methane-hydrate simulations

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Hydrates are formed when some gases (CH_4, CO_2, or similar) are mixed with water at temperatures of a few Celsius and pressures typically above a few MPa.[1] Several simulation studies on hydrates have appeared recently.[2–9] An interesting line appearing in the phase diagram of the water-methane binary mixture is the three phase coexistence line (on a p-T diagram). Along this line, three phases are in equilibrium: the solid methane-hydrate, a water rich liquid phase, and a methane rich gas phase. For nucleation studies on hydrate formation, the relevant temperature for a certain pressure is T_3 as it is only below this temperature that the hydrate can be obtained from the fluid phases (T_3 should not be confused with the mechanical stability limit of the hydrate). T_3 can be determined from free energy calculations.[10] In a recent work,[11] we have shown that it can also be obtained from direct coexistence simulations. Recently, we applied this technique to determine the three phases coexistence of the methane hydrate by using a Lennard-Jones (LJ) center to represent methane and using three water models TIP4P, TIP4P/2005, and TIP4P/Ice. It was found that for a given pressure, the model with the highest value of T_3 was the model with the highest value of the melting temperature T_m of ice I_h at normal pressure. The models considered in our previous work have a similar (TIP4P-like) charge distribution. Thus, it is not clear if the relation between T_3 and T_m found in our previous work is a general feature or a particular feature of TIP4P-like models. To address this issue in this note, we have studied two other models with a different charge distribution: SPC and SPC/E.[12] We performed long runs (of the order of the microsecond) for the set-up labeled as *B* in our previous work,[11] for two pressures, 100 and 400 bars. The rest of the conditions are similar to those described in our previous work (i.e., we used GROMACS, Ewald sums, a Nose-Hoover thermostat, and a Rahman Parrinello anisotropic barostat). Further details are provided in the supplementary material.[13] The results for T_3 are presented in Fig. 1. As it can be seen for the SPC and SPC/E models, the three phase coexistence line appears at much lower temperatures as compared to that of the TIP4P-like models in agreement with the results of Jensen *et al.*[14] and Ravipati and Punnathanam.[15] The slope of all the curves although not identical is quite similar (notice the logarithmic scale on the pressure). The results closest to experiment are obtained with the TIP4P/Ice model, followed by TIP4P/2005. In all the results presented in Fig. 1, methane was described by a single LJ site (with $\sigma = 3.73$ Å and $\epsilon/k = 147.5$ K),[11] and the LJ parameters of the crossed water-CH_4 interaction were obtained by applying the Lorentz-Berthelot (LB) combination rules.[11]

In Fig. 2, values of T_3 (as determined at 100 bars) are presented as a function of the melting point of ice I_h at normal pressure T_m. It is clear that there is a strong correlation between T_3 and T_m. That explains why the results of SPC and SPC/E in Fig. 1 deviates significantly from the experimental results (this is basically a consequence of the low melting temperature of ice I_h for these two models). Experimentally, the three phase coexistence of the methane-hydrate at low pressures begins at temperatures close to the melting temperature of ice I_h. As is illustrated here, the same is true for water-methane force fields. Since water models present important differences in the melting point, important differences are also expected in the three phase coexistence lines. To provide even further evidence of this correlation, we shall also consider a successful coarse grained model of water, denoted as mW,[16] proposed by Molinero and Moore. In this model, there are no H atoms, no charges, and tetrahedral ordering is obtained through a three body potential. Results for T_3 and T_m for the mW model have also been included in Fig. 2. The results of the mW model[5,16] fall in the correlation found in this work. An interesting issue is how T_3 changes when increasing the strength of the water-methane interaction while keeping constant water-water and CH_4-CH_4 interactions. Obviously, this change does not modify T_m. Results for two cases are presented in Fig. 2. For TIP4P/2005 increasing by 7% the value of ϵ of the water-methane LJ interaction with respect to the value predicted by the LB combination rule raises the value of T_3 by about 7 K. The solubility of methane in water increases by a factor of 1.5 with this change[17] and is now in agreement with the experimental value. In fact for many of the models along the straight line in Fig. 2, the solubility of methane in water is too low by a factor of two (i.e., the excess chemical of methane in water is too high by about 1−2 kJ/mol).[18] For the mW model, increasing the strength of the water-methane interaction by about 66% (i.e., changing ϵ from 0.18 kcal/mol to 0.30 kcal/mol while keeping constant the value $\sigma = 4$ Å) causes an increase of 44 K in T_3.[5] The modified model overestimates the solubility of methane in water by one order of magnitude.[5] The conclusion is that the correlation between T_3 and T_m presented in Fig. 2 holds for models with a reasonable description of the chemical potential and solubility of methane in water. Large positive deviations (i.e., of the

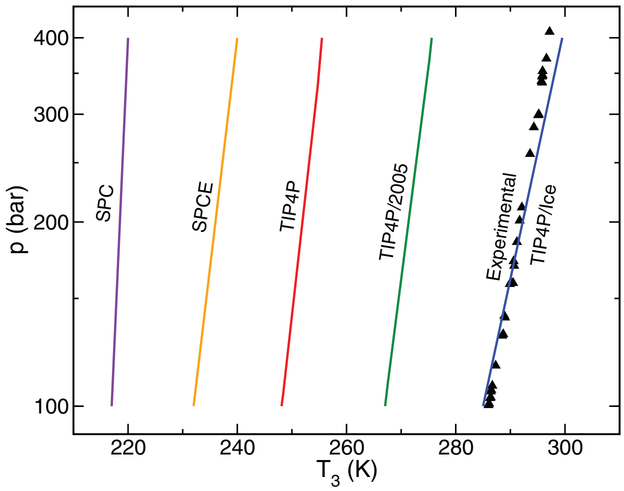

FIG. 1. Representation of the three-phase (water-hydrate-methane) coexistence temperature T_3 as a function of pressure for several potential models. Results for SPC and SPC/E as obtained in this work. Results for TIP4P/Ice, TIP4P/2005, and TIP4P models were taken from Ref. 11. Experimental results (triangles) were taken from Ref. 1.

order of 20 K or above) from the correlation presented in Fig. 2 probably suggest an incorrect estimate of the strength of the water-methane interaction leading to models with a too high solubility of methane in water.[19–21]

This work shows that as a rule of thumb, the three phase coexistence line of the methane hydrate at 100 bars for a water-methane force field is located approximately at about 15(7) K above the melting temperature of ice I_h of the considered water model. Since TIP4P/Ice reproduces nicely, the melting point of ice I_h that explains the proximity of T_3 to the experimental results and the same is true for the mW model. Models with a good T_m as TIP5P will also provide a good estimate of T_3 (provided that the strength of water-methane interaction is reasonable). For the majority of polarizable models of water, the T_m[22] is too low so that one should expect values of T_3 well below the experimental ones.

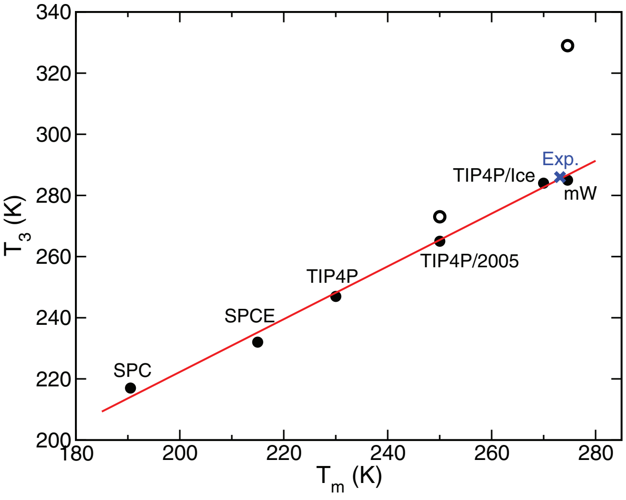

FIG. 2. Correlation (solid line) between the three phases (hydrate-water-methane) coexistence temperature at 100 bars T_3 and the melting point temperature of ice I_h at 1 bars T_m.[23] Filled circles are simulation results from this work and from our previous work.[11] For the mW model (filled circle), results were taken from Ref. 16 for T_m and from Ref. 5 for T_3. The slope and intercept of the correlation are 0.8484 and 52.79 K, respectively. The experimental value (cross) has been included in the plot. Open symbols: models where the methane-water interaction has been strengthened, 7% for TIP4P/2005 (Ref. 11) (open circle) and 66% for the mW model[5] (open circle on the right).

In summary, when modeling the methane-hydrate, if you are looking for a T_3 line in good agreement with experiment (while still providing reasonable estimates of the solubility of methane in water), you need first a water model that describes accurately the melting temperature of ice I_h. In addition, to that, if the strength of the water-methane interaction is reasonable you should obtain a value of T_3 at 100 bars, at about 15(7) K above the melting temperature of ice I_h for the considered water model.

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[1] E. D. Sloan and C. A. Koh, *Clathrate Hydrates of Natural Gases*, 3rd ed. (CRC, 2007).
[2] C. Moon, P. C. Taylor, and P. M. Rodger, J. Am. Chem. Soc. **125**, 4706 (2003).
[3] J. Vatamanu and P. G. Kusalik, J. Phys. Chem. B **110**, 15896 (2006).
[4] M. R. Walsh, C. A. Koh, E. D. Sloan, A. K. Sum, and D. T. Wu, Science **326**, 1095 (2009).
[5] L. C. Jacobson and V. Molinero, J. Phys. Chem. B **114**, 7302 (2010).
[6] M. R. Walsh, G. T. Beckham, C. A. Koh, E. D. Sloan, D. T. Wu, and A. K. Sum, J. Phys. Chem. C **115**, 21241 (2011).
[7] S. Alavi and J. A. Ripmeester, J. Chem. Phys. **137**, 054712 (2012).
[8] S. Sarupria and P. B. Debenedetti, J. Phys. Chem. Lett. **3**, 2942 (2012).
[9] G. S. Smirnov and V. V. Stegailov, J. Chem. Phys. **136**, 044523 (2012).
[10] S. J. Wierzchowski and P. A. Monson, J. Phys. Chem. B **111**, 7274 (2007).
[11] M. M. Conde and C. Vega, J. Chem. Phys. **133**, 064507 (2010).
[12] H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, J. Phys. Chem. **91**, 6269 (1987).
[13] See supplementary material at http://dx.doi.org/10.1063/1.4790647 for further details about the evaluation of T_3 for SPC and SPC/E models.
[14] L. Jensen, K. Thomsen, N. von Solms, S. Wierzchowski, M. R. Walsh, C. A. Koh, E. D. Sloan, D. T. Wu, and A. K. Sum, J. Phys. Chem. B **114**, 5775 (2010).
[15] S. Ravipati and S. N. Punnathanam, Ind. Eng. Chem. Res. **51**, 9419 (2012).
[16] V. Molinero and E. B. Moore, J. Phys. Chem. B **113**, 4008 (2009).
[17] H. Docherty, A. Galindo, C. Vega, and E. Sanz, J. Chem. Phys. **125**, 074510 (2006).
[18] D. Paschek, J. Chem. Phys. **120**, 6674 (2004).
[19] Y. T. Tung, L. J. Chen, Y. P. Chen, and S. T. Lin, J. Phys. Chem. B **114**, 10804 (2010).
[20] E. A. Mastny, C. A. Miller, and J. J. de Pablo, J. Chem. Phys. **129**, 034701 (2008).
[21] E. M. Myshakin, H. Jiang, R. Warzinski, and K. D. Jordan, J. Phys. Chem. A **113**, 1913 (2009).
[22] P. T. Kiss, P. Bertsik, and A. Baranyai, J. Chem. Phys. **137**, 194102 (2012).
[23] C. Vega, J. L. F. Abascal, M. M. Conde, and J. L. Aragones, Faraday Discuss. **141**, 251 (2009).