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Prediction of the liquid–vapor equilibrium pressure using the quasi-Gaussian entropy theory

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We derived a method to evaluate the liquid–vapor equilibrium pressure, with high accuracy over a large range of temperature, using the quasi-Gaussian entropy theory. The final expression that we obtain for the equilibrium pressure as a function of the temperature can be considered as a very accurate approximate solution of the Clausius–Clapeyron equation. The method was applied to water, methanol and mercury, and was compared to two usual approximations of the Clausius–Clapeyron equation. © 1996 American Institute of Physics. [S0021-9606(96)52140-9]

I. INTRODUCTION

The best known approximation to calculate the liquid–vapor equilibrium pressure is an approximated solution of the Clausius–Clapeyron equation:¹

$$p^*(T) \cong p^*(T_0) \exp \left\{ - \frac{\Delta H_m(T_0)}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) \right\}, \quad (1)$$

where it is assumed that the vapor is ideal and the vaporization enthalpy ΔH_m is independent of the temperature, the constant enthalpy approximation (CEA). However the latter assumption usually breaks down within a temperature range of ~ 50 – 100 K. When we use the first temperature derivative of ΔH_m along the saturation line, i.e., $C_\sigma = d\Delta H_m/dT$, we obtain²

$$p^*(T) \cong p^*(T_0) \left(\frac{T}{T_0} \right)^{C_\sigma/R} \times \exp \left\{ - \frac{\Delta H_m(T_0) - C_\sigma \left(\frac{1}{T} - \frac{1}{T_0} \right)}{R} \right\} \quad (2)$$

which is applicable over a larger temperature range than the previous equation. It should be noted that higher order expansions suffer from the difficulty to obtain reliable higher order derivatives along the saturation line and hence are generally not used.

In this paper we will derive an (approximated) expression of the equilibrium pressure in terms of the reduced Helmholtz free energy. This reduced free energy A^r (i.e., with respect to an ideal gas at the same density and temperature) can be evaluated using the quasi-Gaussian entropy theory,^{3,4} a theory which provides reduced thermodynamic

properties as a function of temperature at fixed volume. The basic idea of this theory is to rewrite in the canonical ensemble the expressions of the reduced Helmholtz free energy and entropy in terms of the potential energy distribution function. For a macroscopic system this distribution must be uninormal and very close to a Gaussian (“quasi-Gaussian”). Using a suitable framework to generate different uninormal distributions, the reduced entropy can be expressed in terms of the reduced isochoric heat capacity and a limited set of its temperature derivatives. Hence this serves as a closure relation for the general thermodynamic equation $(\partial S^r / \partial T)_V = C_V^r / T$, where S^r and C_V^r are the reduced entropy and heat capacity, thus forming a completely defined differential equation, the “thermodynamic master equation” at constant volume. The solution of this equation depends on the kind of potential energy distribution function, which hence defines different “statistical states” of the system.

We showed^{3,4} that, apart from conditions close to the critical density, for both fluid water and methane some approximations based on a Gamma distribution (the *effective Gamma* and *confined Gamma* state) can be used successfully as solutions of the thermodynamic master equation. In this paper we will apply the effective Gamma state to evaluate the liquid–vapor equilibrium pressure of water, methanol and mercury and we will compare the results with experimental data and the predictions of Eqs. (1) and (2).

II. THEORY

A. General theory

For small molecules like water and methanol where the classical intramolecular potential energy is absent (for the latter considering its dihedral angle freely rotating) and where the energy gap of the vibrational energy is much

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larger than kT in the temperature range of interest [for water and methanol this is true at least up to 1000 K (Refs. 5 and 6)], we can express the reduced free energy A^r and entropy S^r (i.e., with respect to an ideal gas at the same temperature and density) as³

$$A^r = U^r + kT \ln \int e^{\beta \Delta \mathcal{U}} \rho(\Delta \mathcal{U}) d\Delta \mathcal{U}, \quad (3)$$

$$S^r = -k \ln \int e^{\beta \Delta \mathcal{U}} \rho(\Delta \mathcal{U}) d\Delta \mathcal{U}, \quad (4)$$

with

$$\Delta \mathcal{U} = \mathcal{U} - \langle \mathcal{U} \rangle = \mathcal{U} - U^r, \quad (5)$$

where \mathcal{U} is the potential energy difference between the system and the ideal gas, i.e., the classical intermolecular potential energy plus the possible shift in the vibrational zero point energy between the system and the ideal gas (for mercury only the intermolecular potential energy is involved in \mathcal{U} since no vibrational energy is present), $\beta = 1/kT$, and $\rho(\Delta \mathcal{U})$ is the probability distribution of the energy fluctuation $\Delta \mathcal{U}$. We showed³ that for macroscopic systems,⁷ using the central limit theorem,⁸ $\rho(\Delta \mathcal{U})$ must be close to a Gaussian (“quasi-Gaussian”). Therefore we can use a generalized Pearson system of uninormal distributions^{9–11} to evaluate A^r and S^r , finding that S^r can be expressed as a function of T , C_V^r and a limited number of its temperature derivatives.

It must be noted that the central limit theorem does not guarantee that the distribution of the potential energy has no (small) deviations from a uninormal function in the far tail. However, the integral in Eqs. 3 and 4 should not be affected if the corresponding integrand, which is in general also a uninormal curve, is negligible in the far-tail range, as is usually the case since $\rho(\Delta \mathcal{U})$ is very sharply peaked.^{12,13}

Using the general thermodynamic equation $(\partial S^r / \partial T)_V = C_V^r / T$ and defining the *intrinsic entropy function*^{3,4} $\alpha = S^r / C_V^r$, we finally obtain the *thermodynamic master equation*³

$$\frac{C_V^r}{T} = C_V^r \left(\frac{\partial \alpha}{\partial T} \right)_V + \alpha \left(\frac{\partial C_V^r}{\partial T} \right)_V. \quad (6)$$

This equation can be solved once the distribution $\rho(\Delta \mathcal{U})$ is known at one temperature, since the parameters defining $\rho(\Delta \mathcal{U})$ can be expressed in terms of T , C_V^r and a limited set of its temperature derivatives. Hence via Eq. (4) we can also express S^r and α in terms of these quantities, and so Eq. (6) is a completely defined differential equation yielding the temperature dependence of C_V^r and hence of S^r , U^r and A^r . Therefore every type of potential energy distribution function defines a different statistical state providing the complete reduced thermodynamics of the system. We showed^{3,4} that one of the first acceptable distributions of the generalized Pearson system is the Gamma distribution^{8,14}

$$\rho(\Delta \mathcal{U}) = \frac{b_1 (1/b_1^2)^{b_0/b_1^2}}{\Gamma(b_0/b_1^2)} (b_0 + b_1 \Delta \mathcal{U})^{b_0/b_1^2 - 1} \times \exp \left\{ -\frac{b_0 + b_1 \Delta \mathcal{U}}{b_1^2} \right\} \quad (7)$$

with b_0 and b_1 parameters which can be expressed in terms of T , C_V^r and $(\partial C_V^r / \partial T)_V$. This distribution can be used to obtain solutions of the thermodynamic master equation (effective Gamma state and confined Gamma state solutions) which reproduce accurately the thermodynamic properties of fluid systems at fixed density as a function of the temperature. In this paper we will use the effective Gamma state solution, valid for systems in a perturbed Gamma state condition, which can be considered as the “closest” Gamma state solution to the real statistical state of the system around the reference temperature T_0 (i.e., the Gamma state solution with the same entropy and heat capacity of the system at the reference temperature T_0). The general expression of the reduced Helmholtz free energy (at fixed density as function of the temperature) derived from the effective Gamma solution is:^{3,4}

$$A^r(T) = U^r(T_0) - \frac{T_0 C_V^r(T_0)}{\delta_0^*} - \frac{T C_V^r(T_0)}{(\delta_0^*)^2} \ln \left(\frac{T(1 - \delta_0^*)}{T(1 - \delta_0^*) + T_0 \delta_0^*} \right) \quad (8)$$

with U^r the reduced internal energy, T_0 an arbitrary reference temperature and δ_0^* a parameter defining the Gamma state, connected to the skewness of the corresponding Gamma distribution, which can be evaluated via the intrinsic entropy function at the reference temperature.^{3,4}

$$\alpha(T_0) = \frac{S^r(T_0)}{C_V^r(T_0)} = \frac{1}{\delta_0^*} + \frac{1}{(\delta_0^*)^2} \ln(1 - \delta_0^*). \quad (9)$$

B. Application to the liquid–vapor equilibrium pressure

We can link the liquid–vapor equilibrium pressure and the reduced Helmholtz free energy in the following way.

We can express the chemical potential of the liquid in equilibrium with its vapor (considered as an ideal gas), equating the chemical potentials, as

$$\mu_l(\rho_N^*(T), T) = \mu_g^\ominus(T) + RT \ln \left(\frac{p^*(T)}{p^\ominus} \right), \quad (10)$$

where p^* and ρ_N^* are the equilibrium pressure and the equilibrium liquid density and p^\ominus and μ_g^\ominus are the pressure and the chemical potential of the ideal gas in the standard condition. On the other hand we can also express the chemical potential of the liquid as

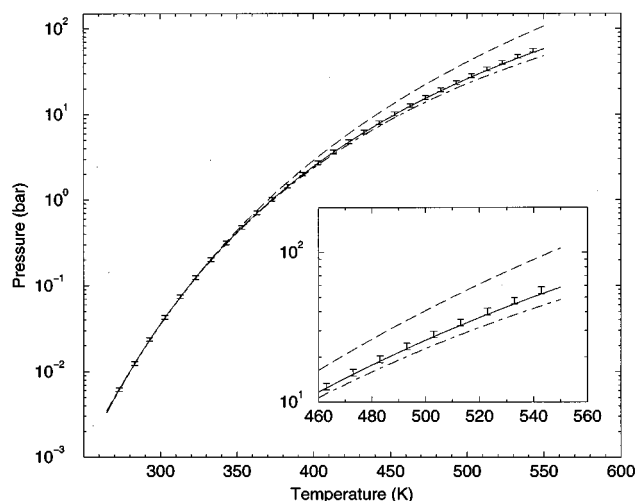


FIG. 1. Experimental results and predictions for water. Legend: experimental data are represented with error bars ($\pm 5\%$), effective Gamma approximation (—), CEA (---), and LEA (---).

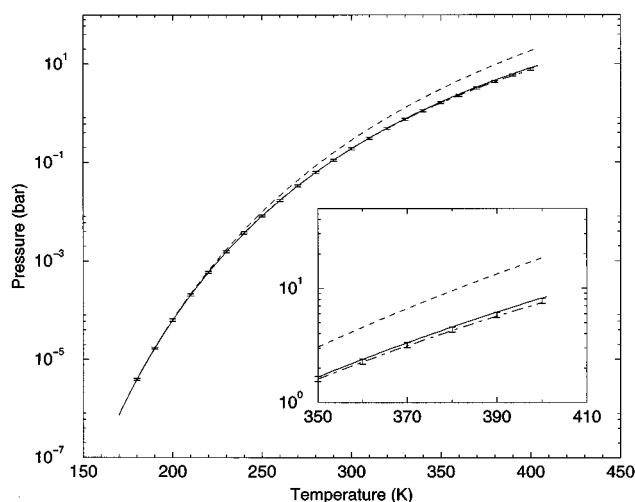


FIG. 2. Experimental results and predictions for methanol. Legend: experimental data are represented with error bars ($\pm 5\%$), effective Gamma approximation (—), CEA (---), and LEA (---).

$$\begin{aligned}\mu_l(\rho_N^*(T), T) &= \mu^r(\rho_N^*(T), T) + \mu_g^\ominus(T) \\ &\quad + RT \ln \left(\frac{\rho_N^*(T) RT}{p^\ominus} \right) \\ &= A_m^r(\rho_N^*(T), T) - RT + \mu_g^\ominus(T) + RT \ln \left(\frac{\rho_N^*(T) RT}{p^\ominus} \right),\end{aligned}\quad (11)$$

where μ^r is the reduced chemical potential, A_m^r is the reduced molar Helmholtz free energy and where we used the fact that $p^* V_{m,l}^* \cong 0$ (here $V_{m,l}^*$ is the molar volume of the liquid). Combining Eqs. 10 and 11 we obtain

$$A_m^r(\rho_N^*(T), T) - RT = RT \ln \left(\frac{p^*(T)}{\rho_N^*(T) RT} \right). \quad (12)$$

From the definition of the Helmholtz free energy we also have

$$\begin{aligned}A_m^r(\rho_N^*(T), T) &= A_m^r(\rho_N^*(T_0), T) + \int_{\rho_N^*(T_0)}^{\rho_N^*(T)} p(\rho_N, T) \frac{d\rho_N}{\rho_N^2} \\ &\quad - RT \ln \left(\frac{\rho_N^*(T)}{\rho_N^*(T_0)} \right)\end{aligned}\quad (13)$$

and therefore from Eq. (12)

$$\begin{aligned}A_m^r(\rho_N^*(T_0), T) + \int_{\rho_N^*(T_0)}^{\rho_N^*(T)} p(\rho_N, T) \frac{d\rho_N}{\rho_N^2} - RT \\ = RT \ln \left(\frac{p^*(T)}{\rho_N^*(T_0) RT} \right)\end{aligned}\quad (14)$$

with T_0 any temperature in the range of interest and ρ_N and p the density and the pressure of the liquid. If for the liquid in equilibrium with its vapor, the density can be considered approximately constant in temperature (i.e., $d\rho_N^*/dT \cong 0$), from Eq. (14) it follows that

$$p^*(T) \cong \rho_N^*(T_0) RT \exp \left\{ \frac{A_m^r(\rho_N^*(T_0), T) - RT}{RT} \right\}, \quad (15)$$

where $A_m^r(\rho_N^*(T_0), T)$ can be evaluated from the effective Gamma state free energy [Eq. (8)], since it is the reduced Helmholtz free energy of a system at fixed density. It should be clear that Eq. (15) is valid only in a temperature range where the vapor can be considered an ideal gas and the liquid is approximately at constant density (or at least the integral in Eq. (14) is negligible).

III. RESULTS

For water we used as reference temperature $T_0 = 300$ K where the density of the saturated liquid is 55.3 mol/dm³. In this condition³ the molar reduced internal energy $U_m^r(T_0) = -41.43$ kJ/mol, the molar reduced heat capacity $c_V^r(T_0) = 0.0494$ kJ/mol K and $\delta_0^* = 0.772$. In Fig. 1 we compare the prediction of our approximation with experimental data,¹⁵ with the usual constant enthalpy approximation (CEA) and the linear enthalpy approximation (LEA) of the Clausius–Clapeyron equation, Eqs. (1) and (2). We used the same reference temperature T_0 where the molar vaporization enthalpy $\Delta H_m(T_0) = 43.9$ kJ/mol and $c_\sigma(T_0) = -0.0425$ kJ/mol K. Note the logarithmic vertical scale. From the figure it is evident that with our approach it is possible to reproduce the experimental data, within 5% of error, over 260 K. From the figure it is also clear that both the CEA and LEA predictions are valid (within 5% of error) for a more restricted temperature range, about 100 K and 160 K, respectively. At the highest temperature considered (550 K) the actual density of the saturated liquid is about 22% lower than the reference one. This implies that our method can be still valid for moderate variations of the liquid density if the integral in Eq. (14) can be neglected. In this case this integral yields a correction of only 0.3 kJ/mol at the highest temperature.

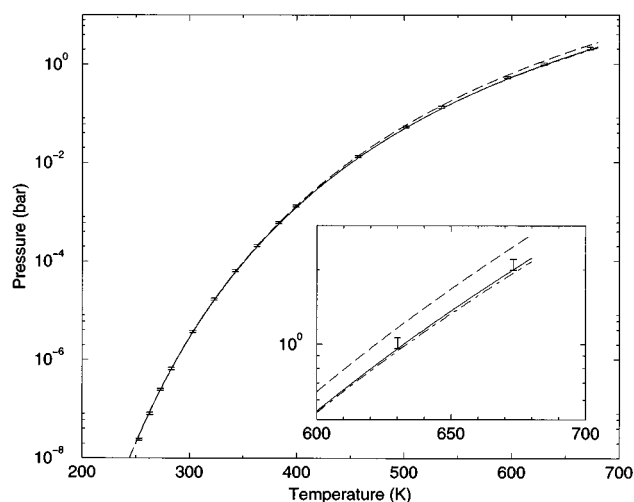


FIG. 3. Experimental results and predictions for mercury. Legend: experimental data are represented with error bars ($\pm 5\%$), effective Gamma approximation (—), CEA (---), and LEA (----).

In Fig. 2 we show the results for methanol. In this case we have used as reference temperature $T_0 = 180$ K with a saturated liquid density of 28.1 mol/dm^3 . In this condition³ $U_m^r(T_0) = -40.3 \text{ kJ/mol}$, $c_V^r(T_0) = 0.040 \text{ kJ/mol K}$ and $\delta_0^* = 0.926$. Also for methanol we compared our prediction with experimental data¹⁶ and with the CEA and LEA (using $\Delta H_m(T_0) = 41.8 \text{ kJ/mol}$ and $c_\sigma(T_0) = -0.030 \text{ kJ/mol K}$). In this case our method is able to reproduce the experimental data, within 5% of error, over 220 K. Also for methanol the CEA prediction is valid for a shorter temperature range (about 60 K), but the LEA approach has a comparable accuracy. It is interesting to note that at the highest temperature considered (400 K) the density of the saturated liquid has a deviation from the reference one comparable to the water case (about 25%) and the corresponding correction term is at most 0.6 kJ/mol.

Finally in Fig. 3 we show the results obtained for mercury. We used $T_0 = 273$ K where¹⁷ $\rho_N^*(T_0) = 67.77 \text{ mol/dm}^3$, $U_m^r(T_0) = -59.34 \text{ kJ/mol}$, $c_V^r(T_0) = 0.0155 \text{ kJ/mol K}$ and $\delta_0^* = 0.960$. For this metal our prediction reproduces (within 5% of error) the experimental data¹⁸ in almost the whole temperature interval where data are available (from 235 K to 670 K). Only for the initial 20 K a moderately higher error is present (this could be due to inaccuracies of the measurement of the pressure at such low values). At 670 K, the highest temperature, the deviation of the liquid density from $\rho_N^*(T_0)$ is only $\sim 6\%$ and our prediction is still almost within 5% of error. For mercury both the CEA and LEA (with $\Delta H_m(T_0) = 61.6 \text{ kJ/mol}$ and $c_\sigma(T_0) = -0.0661 \text{ kJ/mol K}$ (Ref. 19)) are comparable to our method up to 670 K, although the CEA is accurate within 5% of error for a more restricted temperature range, about 260 K.

IV. CONCLUSIONS

In this paper we showed that it is possible to use the quasi-Gaussian entropy theory to predict, over a large range

of temperature, the liquid–vapor equilibrium pressure with high accuracy. The approximation used is limited to conditions where the vapor can be considered an ideal gas, the corrections in the Helmholtz free energy due to the change in the liquid density are negligible and the effective Gamma state provides an accurate description of the thermodynamics at fixed density. The method was applied to water, methanol and mercury providing an excellent prediction of the equilibrium pressure over a temperature range larger than the range where the CEA has the same accuracy. For methanol and mercury the LEA is as accurate as our method over a comparable temperature range, while for water it is worse. It is moreover worth mentioning that a simple Gaussian distribution (defining the Gaussian state³) is in general unable to reproduce the fluid thermodynamics at fixed density and hence cannot be used in this application. Our method seems to be a more accurate approximation solution of the Clausius–Clapeyron equation than the CEA and LEA, requiring one more input quantity at the reference temperature than the latter. Besides ΔU_m^r , c_V^r and ρ_N we need also S_m^r (or equivalently p^*).

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