

## Generalized Kelvin equation and the water content of a cloud

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The thermodynamics of a system of droplets immersed in a saturated vapor (an emulsion without surfactant) is studied here. The relevant variables used to describe this phenomenon are the temperature, pressure, surface tension, and molar number of each phase; that is, the Gibbs free energy  $G(p(r), T, \sigma, n_i^g, \dots, n_c^g; n_1^l, \dots, n_c^l; n_1^\sigma, \dots, n_c^\sigma)$  of the system. From the variation of  $G$  around the equilibrium, two equations of state were obtained simultaneously, one for a curved and another for a plane interface. The obtained equation for the curved surface is compared with the Kelvin equation and with molecular dynamic data. The equation predicts the liquid-water content of a cloud.

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### I. INTRODUCTION

A study of equations of pure liquids, relating vapor pressure to temperature on the vapor+liquid equilibrium system has recently been done [1]. For droplets consisting of a mixture of several components in the presence of vapor the Kelvin equation predicts, in many situations [2,3], the equilibrium vapor pressure. Also this equation is of fundamental importance to an understanding of processes such as the evaporation-condensation (homogeneous nucleation theory) growth of crystals, capillary condensation, formation of clouds, embryonic formation of droplets [4,5], etc. The derivation of this equation is usually done without taking into account the molar number of each phase. With a droplet grows, a certain amount of gas is transformed into liquid. To describe this fact an appropriate choice of the specific variables to characterize the thermodynamic state is of crucial importance. It will be shown below that for a system of droplets with several components in equilibrium with the vapor, the pertinent function to be considered is the Gibbs free energy, which depends on the temperature, pressure, interfacial tension, and molar number of each component of the gas, the liquid, and the interfacial phase. From the variation of this function around the equilibrium state, two vapor pressure equations are found, one for a curved surface and another for a plane surface. By comparing the former equation with the Kelvin equation it turns out that the number of gas and liquid particles are equal. For droplets having a small-radius, embryonic state of formation, the gas-liquid particle relation is 3 to 1. The same result, on average, is found by using data from a molecular dynamic experiment [6]. However, by knowing the size of droplets in a cloud, the equation predicts its liquid-water content.

### II. DROPS IN EQUILIBRIUM WITH A SATURATED VAPOR

Let us consider, in the case of a mixture of several fluids, a system of liquid droplets immersed in a saturated

vapor phase. A thermodynamic description is done by using the Gibbs free energy  $G$  of the system. This function depends on the temperature  $T$ , the pressure  $p$ , the interfacial tension  $\sigma$ , and  $n_i^g, \dots, n_c^g; n_1^l, \dots, n_c^l; n_1^\sigma, \dots, n_c^\sigma$ , the molar number of the gas, the liquid, and the interface, respectively. The variation of this quantity [2] is given by

$$dG = -SdT + V^g dp^g + V^l dp^l - Ad\sigma + \sum_{i=1,2} [\mu_i^g dn_i^g + \mu_i^l dn_i^l + \mu_i^\sigma dn_i^\sigma], \quad (1)$$

where  $n_i^\alpha$  and  $\mu_i^\alpha$  are the molar number and the chemical potential of component  $i$  and phase  $\alpha$  (the gas, liquid, and interface, respectively).  $A$  is the interfacial area, and  $\mu_i^g, \mu_i^l$  and  $\mu_i^\sigma$  are the chemical potential of the component  $i$  in the gas the liquid, and the interface, respectively. At equilibrium this variation is null,  $dG=0$ . With the condition of physicochemical equilibrium,

$$\mu_i^l = \mu_i^g = \mu_i^\sigma, \quad (2)$$

and considering a constant temperature of the system, Eq. (1) reduces to

$$V^g dp^g + V^l dp^l - Ad\sigma + \sum_{i=1,2} [\mu_i^g (dn_i^g + dn_i^l + dn_i^\sigma)] = 0. \quad (3)$$

The pressure in the gas phase is nearly constant. By using the Laplace equation  $p^l - p^g = 2\sigma/r$  after the integration of Eq. (3), we obtain

$$\sum_{i=1,2} [\mu_i^g (n_i^g + n_i^l + n_i^\sigma)] = \frac{4}{3} \sigma A. \quad (4)$$

The chemical potential of each component in the gas  $\mu_i^g$  is [7]

$$\mu_i^g = \mu_i^\dagger(T) + RT \ln x_i p, \quad (5)$$

where  $\mu_i^\dagger(T)$  is the chemical potential of the gas at unit pressure and depends only on the temperature  $T$ , the partial pressure of the component  $i$  in the gas phase  $p_i = x_i p$

( $p = \sum_{i=1,2} x_i p_i$ ), with  $x_i$  the mole fraction  $x_i = n_i^g / \sum_i n_i^g$ . The substitution of Eq. (5) into (4) gives

$$\ln \frac{p}{p_\infty} = \frac{1}{(1 + N^g/N^l + N^\sigma/N^l)} \frac{4\sigma v}{rRT}, \quad (6)$$

where  $N^g/N^l = \sum_{i=1,2} (n_i^g/n_i^l)$ ,  $N^\sigma/N^l = \sum_{i=1,2} (n_i^\sigma/n_i^l)$ ,  $v = V/N^l$  with  $V = \frac{4}{3}\pi r^3$  (vapor pressure of a mixture for a plane surface). The quantity  $\ln p_\infty$  indicates the vapor pressure of a mixture for a plane surface and is given by

$$\ln p_\infty = -\frac{1}{nRT} \sum_{i=1,2} \mu_i^\dagger(T)(n_i^l + n_i^g + n_i^\sigma) - \frac{1}{n} \sum_{i=1,2} (n_i^l + n_i^g + n_i^\sigma) \ln x_i, \quad (7)$$

where  $n = \sum_{i=1,2} (n_i^l + n_i^g + n_i^\sigma)$ , and  $\mu_i^\dagger(T)$  is [1]

$$\mu_i^\dagger(T) = \left[ h(0) - C_p(0)T \ln T - \int_0^T \frac{r dT_1}{T_1} \int_0^{T_1} C(T_2) dT_2 - jRT \right]_i, \quad (8)$$

with  $h(0)$  the enthalpy of the respective component extrapolated to absolute zero,  $C_p(0)$  the contribution of the molar heat capacity at constant pressure,  $j$  a chemical constant, and  $C(T_2)$  the molar specific heat of vibration. Equation (6) predicts the vapor pressure of drops as a function of temperature  $T$ , vapor pressure of a mixture, plane surface pressure  $p_\infty$ , the interfacial tension  $\sigma$ , the specific volume of a drop  $v$ , the radius  $r$ , and  $n_i^g, \dots, n_i^g; n_i^l, \dots, n_i^l; n_i^\sigma, \dots, n_i^\sigma$ , the molar number of the gas, the liquid, and the interface, respectively. It will be shown below that this equation can be seen as a generalization of the Kelvin equation.

### III. EXPERIMENTS AND THE PRESENT EQUATION

Before testing Eq. (6) with the experiments, let us write the Kelvin equation for a saturated vapor,

$$\ln \frac{p}{p_\infty} \cong \frac{2\sigma v}{rRT}. \quad (9)$$

A quantitative experimental test of this equation has been

carried out by Thomä and La Mer and Gruen (see Defay and Prigogine [2]). These experiments provide the validity of the Kelvin equation for droplets down to  $10^{-5}$  cm in radius. For these droplets it is acceptable to consider that, away from the critical point, the molar number of the interface is unimportant with respect to the molar number of the liquid droplet; that is,

$$N^\sigma \ll N^l. \quad (10)$$

In such a situation Eq. (6) reduces to

$$\ln \frac{p}{p_\infty} = \frac{1}{(1 + N^g/N^l)} \frac{4\sigma v}{rRT}. \quad (11)$$

Equation (11) is the Kelvin equation if

$$N^g = N^l. \quad (12)$$

This orthobaric relation tells us that the liquid and vapor are equally distributed, when liquid droplets of  $10^{-5}$  cm in radius coexist with a saturated vapor.

In the case of the embryonic formation of droplets, Israelachvili showed that an almost linear relation between  $-\ln(p/p_\infty)$  and  $-1/r$  holds for condensing cyclohexane onto mica surfaces. In this case the vapor pressure equation is

$$\ln \frac{p}{p_\infty} \cong \frac{\sigma v}{rRT}. \quad (13)$$

The validity of this relation goes down to radii of  $r \cong 4$  nm. If in this case it is valid to assume that the molar number of the interface is of the same order of the liquid phase, then

$$N^\sigma \cong N^l. \quad (14)$$

By comparing Eqs. (13) and (6) and using Eq. (14), it results in

$$N^g = 2N^l \quad (15)$$

in the embryonic state of formation, the molar number of the gas phase is twice that of the liquid phase.

Finally let us test the Kelvin equations, Eq. (9), and the alternative equation proposed here, Eq. (11), with molecular dynamic data [6] for noninteracting drops. Here we use Eq. (11) instead of (6) because in the experiment, the equimolecular dividing radius is calculated by using the condition of null adsorption. The data are presented in Table I.

TABLE I. The reduced temperature  $T^* (= k_B T / \epsilon) = 0.9$ , the pressure  $p^* (= p \sigma^3 / \epsilon) = 0.0312$ ,  $\sigma$  is the length scale, and  $\epsilon$  is the energy scale.  $R_e^* (= R_e / \sigma)$  is the reduced equimolar radius.  $N$  denotes the number of particles. Equations (9) and (11) in reduced units are  $\Delta p^* / (T^* n^{*l})$  and  $\frac{8}{3} \pi \Delta p^* R_e^{*3} / (T^* N)$ .

$N$	$R_e^*$ (radii)	$n^{*l}$ (dens.)	$N^l$ (liq.)	$N^g$ (gas)	$N^g/N^l$	$\Delta p^*$	$\ln(p^{*g}/p_\infty^*)$	Eq. (9)	Eq. (11)
2299	5.63	0.677	562	1737	3.1	0.0384	0.208	0.094	0.041
5165	6.87	0.678	921	4244	4.6	0.0373	0.179	0.082	0.029
9322	7.17	0.683	1055	8267	7.8	0.0379	0.194	0.098	0.022
6131	8.73	0.677	1888	4243	2.3	0.0361	0.146	0.077	0.042
8642	9.08	0.678	2127	6515	3.1	0.0353	0.123	0.080	0.040
9295	10.15	0.676	2962	6333	2.1	0.0349	0.112	0.069	0.044
10 420	11.53	0.677	4388	6072	1.4	0.0341	0.089	0.064	0.053
12 138	13.03	0.374	6248	5890	1.0	0.0340	0.086	0.056	0.058

#### IV. COMMENTS

In the present derivation of the equations describing drops in equilibrium with a saturated vapor, it has been taken into account that the thermodynamic system not only depends on the variable  $p$ ,  $\sigma$ ,  $v$ ,  $r$ , and  $T$  but also on  $n_1^g, \dots, n_c^g; n_1^l, \dots, n_c^l; n_1^\sigma, \dots, n_c^\sigma$ ; the molar number of the gas, the liquid, and the interface, respectively. This last dependency makes a substantial difference with the classic derivations of the Kelvin equation [2,3]. In the latter equation only the molar number of the liquid phase was taken into account. The inclusion of the molar number of each phase as relevant variables of the system results in Eqs. (6) and (7). The last equation gives the vapor pressure of a mixture corresponding to a plane surface. This equation is similar to that found before by Wilson and reported by Rowlinson [8]. It also must be mentioned that in all the previous derivations of the Kelvin equation [2,3], the expression of the vapor pressure of a mixture for a plane surface [Eq. (7)] was not explicitly given because from the very beginning, the dependency on the variables  $n_1^g, \dots, n_c^g; n_1^l, \dots, n_c^l; n_1^\sigma, \dots, n_c^\sigma$  was removed.

In Table I molecular dynamics data are presented [6]. These data were used to evaluate Eqs. (11) and (9). The approximation done to the chemical potential by using Eq. (5) shows itself to be a poor approximation for the smallest droplets, where the gas phase is highly compressed. This approximation becomes acceptable at bigger radii, and in this situation both equations predict values of  $\ln(p^{*g}/p_\infty^*)$  of the same order. At  $R_c^*$  small,

Eq. (9) doubles the values of (11).

Let us get to the point and discuss the essential difference of both approaches. In the Kelvin approximation the gas phase is only considered, via the chemical potential, by the pressure  $p^g$  of the saturated vapor. The equation does not give information about the gas density or molar density of the gas phase as does Eq. (6). This last equation shows that the equilibrium is only possible if a certain amount of gas is present. This amount changes with the radius. For the smallest radius the relation between  $N^l/N^g$  is, on average, around 3 as is shown in the molecular dynamics experiment done by Nijmeijer *et al.* and also by the present model. At a bigger radius this relation is 1. Molecular dynamics data (see Table I, last row) and earlier experiments done by Thomä and La Mer and Gruen (see Defay and Prigogine [2]) tested Eqs. (11) and (9). Here the equilibrium is only possible if the number of liquid and the gas particles are present in the same proportion [Eq. (12)].

It is well known that the concentration of liquid water in a cloud is of considerable meteorological importance [9]. The droplet size radii distribution in a liquid-water cloud is of importance in determining the cloud liquid-water contents [10,11]. One approximation of this difficult problem can be provided by the present thermodynamic study. If a cloud contains droplets of such a size that the Kelvin equation is valid, it is clear that the number of gas and the liquid particles are the same, but in the case of the embryonic state of formation, this relation is 3 to 1, respectively.

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