

# A Vapor Pressure Equation for an Organic Aerosol at Ultra-Low Pressure

Víctor A. Kuz

*Instituto de Física de Líquidos y Sistemas Biológicos, C.C. 565, (1900) La Plata, Argentina*

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A vapor pressure equation for an aerosol is presented here. The latent heat of evaporation (Clausius–Clapeyron contribution), the curvature, and the disjoining pressure effects are considered as the main contributions to the equation. Curvature (Kelvin effect) is shown to be irrelevant. Orientation of the amphiphilic molecules at the surface of the aerosol droplets generates an extra pressure. This pressure, represented here by the structural component of the disjoining pressure, contributes to the Clausius–Clapeyron equation with a nonlinear term proportional to  $\ln T$ . The prediction is in agreement with a recent experimental result.

## Introduction

A recent correlation in aerosols shows,<sup>1</sup> contrary to the accepted opinion,<sup>2</sup> a deviation from the Clausius–Clapeyron equation. This deviation only occurs in aerosols having droplets with amphiphilic structure. Inner and outer pressure of droplets are different  $p^l \neq p^g$  and is generally accepted that the origin of this difference is due to the effect of curvature (Laplace pressure). Curvature of droplets affects the pressure of a gas (Kelvin effect) and influences slightly the vaporization of droplets and bubbles.<sup>3</sup>

The effect upon pressure produced by the collective interaction between a solid and a liquid is well-known. When a solid surface like mica is in contact with water, a mutual interaction at the solid–liquid interface induces an orientational order of the water molecules close to the solid surface.<sup>4</sup> The pressure changes exponentially within the range of water interlayer thickness ( $10 \text{ nm} < h < 2 \text{ nm}$ ). This pressure, called the structural component of the disjoining pressure, is very important at very short distances. This phenomenon of orientation produced at the mica–water interface is similar to that at the surface of an amphiphilic droplet in contact with  $\text{N}_2$  gas. The amphiphilic molecules are oriented with their tails pointing to the gas phase. The collective interaction of the amphiphilic heads induces an extra pressure, different from Laplace pressure. This pressure acts in a very thin interlayer thickness and contributes with a nonlinear term. As will be seen below, this term is important in explaining the deviation experimentally found of the Clausius–Clapeyron equation.

## A Vapor-Pressure Equation

Let us consider a single-component organic droplets suspended in a gas. The relation between the vapor pressure and the temperature of this aerosol structure may be found by using the condition of equilibrium

$$\mu_g(p_g, T) = \mu_l(p_l, T) \quad (1)$$

where  $\mu_g$  and  $\mu_l$  are the chemical potential per unit mole of the gas and liquid phase, respectively. Here it must be kept in mind that the pressure  $p$  is a function of the temperature  $T$ . It must be remarked that  $p_g = p_l$  only when the surface of separation

between the two phases is plane. For a small variation around the equilibrium, eq 1 is

$$\left(\frac{\partial \mu_g}{\partial T}\right)_{p_g} + \left(\frac{\partial \mu_g}{\partial p_g}\right)_T \frac{dp_g}{dT} = \left(\frac{\partial \mu_l}{\partial T}\right)_{p_l} + \left(\frac{\partial \mu_l}{\partial p_l}\right)_T \frac{dp_l}{dT} \quad (2)$$

and remembering that  $(\partial \mu / \partial T)_p = -s$ , the molar entropy and  $(\partial \mu / \partial p)_T = v$  the molar volume, eq 2 for a droplet is

$$-(s^g - s^l) + v^g \frac{dp_g}{dT} = v^l \frac{dp_l}{dT} \quad (3)$$

The inner pressure of the droplet is different from that of the gas. They are related via the Laplace equation

$$p^l - p^g = 2\sigma/r \quad (4)$$

where  $\sigma$  is the surface tension and  $r$  the droplet radius.

In the case of organic liquid droplets suspended in a  $\text{N}_2$  atmosphere, another contribution to the pressure must be taken into account. In this case the amphiphilic molecules are oriented at the droplet surface with their tails pointing to the gas phase. At very low pressure, small droplets, the aerosol looks like an inverse micellar solution. It must be pointed out that the ordered layers are limited only to a small thickness  $h$  around the droplet. Liquid droplets without an amphiphilic structure will not have this ordered layer. The order results from the interaction of the amphiphilic molecules and the solvent gas. The orientation at the droplet surface affects the pressure of the droplet. The extra pressure results from the collective interaction of the oriented amphiphilic heads. This kind of effect is also revealed in fluids confined between parallel interfaces or in fluids in contact with a solid surface. In all these cases the range of action of the collective forces between the solid surface and fluid is very small (of the order of few nanometers). This collective effect is usually represented by a component of the disjoining pressure called structural component. The theoretical evaluation of this pressure was done only for especial cases, but its effects are well described by the following empirical formula<sup>4</sup>

$$\Pi_s(h) = K \exp(-h/l) \quad (5)$$

where  $K$  and  $l$  are two parameters. This empirical formula holds

for  $h > l$ . By introducing eq 5 into the expression of the inner pressure of the droplet, eq 4 becomes

$$p^l = p^g + \frac{2\sigma}{r} + K \exp(-h/l) \quad (6)$$

It must be mentioned that an equation similar to eq 6 was used by Overbeek et al.<sup>5</sup> in connection with microemulsions. They write a generalized Laplace equation for taking into account the "bending energy" of the amphiphilic surfactant that concentrates at the water–oil interface, by considering a curvature-dependent surface tension  $\sigma(r)$ . In the present version the bending stress coefficient is  $K = \partial\sigma(r)/\partial f(r)$ , with  $f'(r) = Ke^{-r/l}$ .

Substitution of eq 6 into 3 gives

$$\frac{dp_g}{dT} = \frac{(s^g - s^l)}{(v^g - v^l)} + \frac{v^l}{(v^g - v^l)} \frac{d}{dT} \left( \frac{2\sigma}{r} + K \exp(-h/l) \right) \quad (7)$$

The difference  $(s^g - s^l)$  is the change in the molar entropy  $\Delta s$  and is equal to the molar enthalpy change  $\Delta h/T$ . This quantity is associated with a flux of heat between the system and the reservoir, then eq 7 is

$$\frac{dp_g}{dT} = \frac{\Delta h}{T(v^g - v^l)} + \frac{v^l}{(v^g - v^l)} \frac{d}{dT} \left( \frac{2\sigma}{r} + K \exp(-h/l) \right) \quad (8)$$

This equation gives the variation of pressure with temperature for an aerosol (inverse micelle droplets). In general the volume of the gas  $v^g \gg v^l$ , then eq 8 reduces to

$$\frac{d \ln p_g}{dT} = \frac{\Delta h}{RT^2} + \frac{v^l}{RT} \frac{d}{dT} \left( \frac{2\sigma}{r} + K \exp(-h/l) \right) \quad (9)$$

where  $v^g = RT/p_g$ . We assume that the surface tension  $\sigma$  as well as the parameter  $K$  decreases linearly with temperature; then eq 9 is

$$\frac{d \ln p_g}{dT} = \frac{\Delta h}{RT^2} - \frac{v^l}{RT} \left( \frac{2}{r} \alpha + \beta \exp(-h/l) \right) \quad (10)$$

where  $d\sigma/dT = -\alpha$  and  $dK/dT = -\beta$ . The integration of eq 9 leads to the following expression:

$$\ln p_g = A - \frac{\Delta h}{RT} - \frac{v^l}{R} \left( \frac{2}{r} \alpha + \beta \exp(-h/l) \right) \ln T \quad (11)$$

$A$  being a constant. It must be mentioned that eq 11 reduces to the standard vapor pressure equation (plane interface),<sup>6–8</sup> when  $r \rightarrow \infty$  and the liquid is at least a thick film. Equation 11 is similar to that empirically developed from experimental data analysis of single-component organic droplet.<sup>1</sup>

$$\ln p = a - \frac{b}{T} - c \ln T + dT^k \quad (12)$$

where  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $k$  are empirical constants deduced for a given system. The experiment, which gives this correlation, was carried out with single-component organic droplet suspended  $N_2$  gas or in vacuum. The temperature range of the experiment was between 20 and 55 °C. The authors present results for methanesulfonic acid (MSA), glycerol, oleic acid, and dioctyl phthalate. The vapor pressure data of this experiment were combined with high-temperature vapor pressure data available

**TABLE 1: Summary of the Coefficients for Two Characteristic Liquids**

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>k</i>
glycerol	92.5455	$1.44597 \times 10^4$	10.5648	$-9.49973 \times 10^{-18}$	6
MSA	22.81669	$9.03018 \times 10^3$	0	0	0

in the literature. We present in Table 1 the experimental values of the coefficients for glycerol and MSA.<sup>1</sup> The data shown in this table were obtained by least-squares fitting<sup>1</sup> and yield the following values of the coefficients,  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $k$  for glycerol and MSA.

It must be mentioned that in the experiment of Tang et al.,<sup>1</sup> only liquid droplets having molecules with amphiphilic structure (glycerol, oleic acid, DOP) have coefficient  $c$  different from zero. Coefficients  $c$  and  $d$  in MSA, which do not have this kind of molecular structure, are zero.

Coefficient  $b$  is proportional to the heat of vaporization  $\Delta h$ . Let us estimate coefficient  $c$  for glycerol using eq 11. According to this equation,  $c$  is given by

$$c = \frac{v^l}{R} \left( \frac{2}{r} \alpha + \beta \exp(-h/l) \right) \quad (13)$$

We see that  $c$  has two contributions, one we call capillary  $c_c$  and the other structural  $c_s$ . Glycerol: molar volume  $v^l = 73$  cm<sup>3</sup>/mol,  $\alpha = 0.063$  erg/(cm<sup>2</sup> K),  $r \approx 10^{-3}$  cm,  $R = 8.3 \times 10^7$  erg/(K mol). The capillary contribution to  $c$  is  $c_c \approx 1.108 \times 10^{-4}$ . There are no data available for  $\beta$  and we assume that  $h$  is twice the order parameter  $l$ ; this means that we have only two amphiphilic molecules oriented at the surface of the droplet. We also assume that  $K$  for oriented amphiphilic molecules of glycerol is of the order of a symmetrical aqueous interlayer,<sup>4</sup>  $K \approx 10^9$  erg/cm<sup>3</sup>, and the thermal gradient is around 10% of its value; then  $\beta \approx 10^8$  erg/(K cm<sup>3</sup>), and  $c_s \approx 12$ . The capillary contribution is several orders less than the structural contribution to coefficient  $c$  ( $c_c \ll c_s$ ).

In conclusion, the deviation from Clausius–Clapeyron equation in droplets at very low pressure is certainly not due to Laplace pressure.

## Discussion

The present work provides eq 11. It explicitly shows how droplets curvature and disjoining pressure, established via eq 6, reduce the equilibrium vapor pressure. Equation 11 is similar to that empirically developed in the determination of ultralow pressures from evaporation of submicron droplets by Tang et al.<sup>1</sup> (see eq 12). In the experiment, the unknown coefficients,  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $k$  were obtained by least-squares best-fitted values. The authors showed that this empirical vapor pressure correlation, which is similar to that derived here (eq 11), is superior to the commonly used Clapeyron equation applied by Ray et al.<sup>2</sup> because the former is applicable to a broad range of temperatures.

We have shown that the Kelvin contribution is irrelevant. Then, neither curvature nor variation of heat of vaporization (see Defay et al.)<sup>3</sup> changes substantially the linear relation between  $\ln p^g$  and  $1/T$ . Therefore, the effect of ordering produced at the droplets interface by the amphiphilic molecules in a gas such as  $N_2$  should be responsible of the diminution of the vapor pressure.

Finally, as was suggested by the reviewer, the present ideas could be applied to more complex systems like a microemulsion

to predict in some cases the vapor pressure curve for the coexistence of microemulsion—oil or microemulsion—water.

## References and Notes

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