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Some New Results From Applying Thermodynamics to Wetting Phenomena

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Abstract

This contribution focuses on some non-classical aspects of capillary phenomena, mostly omitted in classical approaches, in particular the non-isothermal aspects. A systematic thermodynamic approach is proposed that allows a rigorous formulation of the governing equations in non-isothermal situations, by introducing the surface effects in the energy and entropy balances. The energetic quantities (work and heat) are calculated in a number of examples, such as adiabatic and isothermal wetting/dewetting of a porous medium, nanofluids heating, emulsion split, and new equilibrium criteria are derived were appropriate.

Keywords: wetting phenomena, surface tension, thermodynamics, capillarity, energy and entropy balance

1. Introduction

The paper proposes a general thermodynamic analysis concerning the systems in which the wetting phenomena play a major role, a situation encountered when dealing with *capillary systems*. A capillary system may be defined as one composed of different phases (liquid(s), solid(s) and a vapour) having large specific contact surfaces between the phases (Melrose 1965, Eroshenko 1997, Laouir et al. 2003, Denoyel et al. 2004). A corresponding thermodynamic description requires taking into account surface effects in the mathematical models, in other words surface energies and surface entropies must be included in the energy balance and in the entropy balance respectively. This will also permit deriving the equilibrium criteria applicable to capillary systems. In the present paper, some representative situations are examined along these lines. On the one hand some known classical results are derived but also given in more general forms, on the other hand new problems are treated with the possibility to calculate heat and work involved.

2. Surface Energy and Entropy

Figure 1 shows a system consisting of a solid, a liquid and a vapour in equilibrium. The liquid and the solid are dissimilar from the chemical point of view while the vapour is the same compound as the liquid. The internal energy and entropy associated to the liquid-vapour (*lv*), solid-liquid (*sl*) and solid-vapour (*sv*) interfaces are given by (Defay and Prigogine 1951, Harkins and Jura 1944, Melrose 1965)

$$u_{**} = -T\frac{\partial \sigma_{**}}{\partial T} + \sigma_{**} \;,\quad s_{**} = -\frac{\partial \sigma_{**}}{\partial T} \tag{1}$$

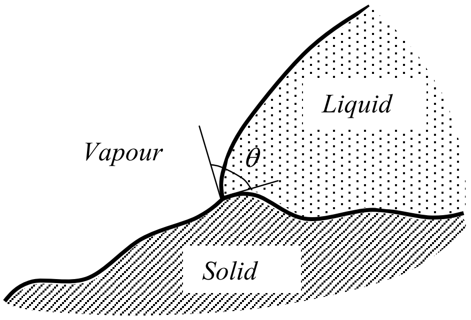

Figure 1. A three phase system in equilibrium.

the subscript (**) designates the surface type (*lv*), (*sl*) or (*sv*), and σ_{**} denotes the corresponding surface tension. In certain situations two immiscible liquids

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(or more) may be in presence with specified interfacial tensions σ_{ll}. It is well known that surface tensions are temperature dependent, but the pressure effect on these quantities seems to be practically ignored in the literature. Except for σ_{lv}, experimental data concerning temperature dependence of surface tensions are scarce. Using Young's equation $\sigma_{sl}=\sigma_{sv}-\sigma_{lv}\cos\theta$, u_{sl} and s_{sl} may be expressed in the following forms:

$$u_{sl}=T\frac{\partial(\sigma_{lv}\cos\theta)}{\partial T}-\sigma_{lv}\cos\theta+u_{sv} \qquad (2)$$

$$s_{sl}=\frac{\partial(\sigma_{lv}\cos\theta)}{\partial T}+s_{sv} \qquad (3)$$

The contact angle θ of the specified solid-liquid couple is a thermodynamic property which is a priori, as surface tensions, temperature and pressure dependent.

3. Energy and Entropy Balances

Thermodynamic properties associated to the system shown in *figure 1* involve those of the solid, the liquid, the vapour and those related to the contact interfaces discussed above. So the overall internal energy U_g for the system is (assuming of course some boundaries which need not be defined here):

$$U_g=m_s u_s+m_l u_l+m_v u_v+u_{sl}A_{sl}+u_{sv}A_{sv}+u_{lv}A_{lv} \qquad (4)$$

u_s ,u_l, u_v are the specific internal energies of the three phases and u_{sl}, u_{sv} , u_{lv} the internal energies related to the surfaces given by Equation (1). Similarly, the overall entropy S_g is:

$$S_g=m_s s_s+m_l s_l+m_v s_v+s_{sl}A_{sl}+s_{sv}A_{sv}+s_{lv}A_{lv} \qquad (5)$$

if immiscible liquids are in presence, Eqs. (4) and (5) should be extended accordingly to include liquid-liquid interactions. The general form of energy balance equation is:

$$\frac{d(U_g+E_c+E_p)}{dt}=\dot{Q}+\dot{W}+\sum\dot{m}(h_g+e_c+e_p) \qquad (6)$$

U_g, E_c and E_p are respectively the overall internal energy, kinetic energy and potential energy of the system, $\dot{Q}$ the rate of heat transfer, $\dot{W}$ the mechanical power transfer, h_g, e_c and e_p are respectively the specific overall enthalpy, kinetic and potential energies related to the flow stream $\dot{m}$. The overall enthalpy h_g is to be defined in relation to the energies transferred with matter across the system boundary. The entropy balance equation is:

$$\frac{d(S_g)}{dt}=\frac{\dot{Q}}{T}+\sum\dot{m}s_g+\dot{\varepsilon} \qquad (7)$$

where S_g is the overall entropy of the system, s_g is the specific overall entropy of the corresponding flow stream and $\dot{\varepsilon}$ the entropy production rate which is zero for reversible processes. Eqs. (6) and (7) are so general that they allow the study of a wide range of problems involving surface phenomena. In the following sections some typical problems are considered to illustrate the application of these equations and to show the quantitative and qualitative results that may be expected.

4. Equilibrium

Capillary systems show states (Bosworth 1950, Chitour 2004) that may be perceived and described as thermodynamic equilibrium states, such that no flow nor transfer occurs and nothing changes with time. However, the usual equilibrium criteria do not all apply. Temperature must indeed be uniform for absence of heat flows, and chemical potentials for absence of diffusional mass flow but on the other hand it should be stressed that pressure is generally non-uniform, because of pressure gradients across interfaces. The general equilibrium criteria may be derived by considering an infinitesimal change of state in the vicinity of the equilibrium point of a closed and non-moving system:

$$dU_g+dE_p=\delta Q+\delta W \quad \text{and} \quad dS_g=\frac{\delta Q}{T}+\delta\varepsilon \qquad (8)$$

In many cases the work δW is zero (capillary rise, sessile drop…), in others it corresponds to the work of change in volume $-PdV$ (bubble in a liquid, equilibrium of non-wetting liquid in a porous solid…); the work is defined in relation to the pressure acting at the system boundary. At the equilibrium state, since no flow or transfers occur, the entropy production is zero, that is $\delta\varepsilon=0$. Thus ,

$$dU_g+PdV+dE_p-TdS_g=0 \qquad (9)$$

the equation defines in a general form the equilibrium state and gives the minimum of the differentiated quantity. For an equilibrium achieved at constant T and V, $dF_g+dE_p=0$ and F_g+E_p is minimum ($F_g=U_g-TS_g$ is the overall Helmholtz free energy of the system). If the equilibrium concerns an isolated system, $dS_g=0$, S_g is maximum and U_g+E_p constant in this case.

4.1 Capillary pressure

As a first example, let us show how to establish a general expression for (isothermal) capillary pressure in a system such as that shown in *figure 2* composed of a solid, a liquid at a pressure P and the vapour trapped in the capillary at a pressure P_v.

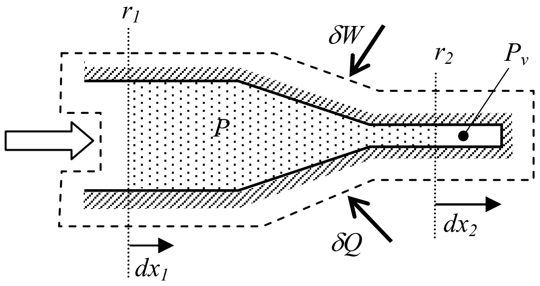

Figure 2. Equilibrium of a liquid in a capillary.

We are interested in determining the pressure difference involved in maintaining such an equilibrium, known as capillary pressure. To an infinitesimal displacement dx_1 corresponds a displacement dx_2 in the capillary, a heat δQ and a work $\delta W = -PdV$; for this system $dE_p = 0$ therefore:

$$dU_g + PdV - TdS_g = 0 \tag{10}$$

For the liquid and the vapour, one may write separately $du_l - Tds_l = -Pdv_l$ and $du_v - Tds_v = -P_v dv_v$. The solid is assumed incompressible, so that $du_s - Tds_s = 0$, and its mass is constant, $dm_s = 0$. The properties of the solid-vapour interface are assumed constant, $du_{sv} = 0$ and $ds_{sv} = 0$. The liquid and the vapour across meniscus 2 are in equilibrium, thus $h_l - Ts_l = h_v - Ts_v$ so $(u_v - u_l) - T(s_v - s_l) = Pv_l - P_v v_v$. In addition $dA_{sl} = -dA_{sv}$, $dm_l = -dm_v$ and $dV = dV_l + dV_v$. Using these relations in conjunction with Eqs. 4 and 5 for U and S and substituting u_{sl} and s_{sl} by their expressions from Eqs. 2 and 3 into Equation (10), one gets:

$$(P - P_v)d(V - V_l) - d(A_{sl}\sigma_{lv}\cos\theta) = 0 \tag{11}$$

Relation (11) is a general differential equation taking into account various aspects like the presence of condensable vapour, compressibility of the liquid, pressure effects on surface tension σ_{lv} and contact angle θ. High pressure might change the wetting properties of a solid-liquid system; unfortunately there is practically no information that may be exploited about the dependence of σ_{lv} and θ on pressure. Keeping in mind that it is a restriction, we therefore assume in the subsequent sections that $\sigma_{lv}\cos\theta$ does not vary with pressure. Using $dV = -\pi r_1^2 dx_1$, $dV_l = \pi(r_2^2 dx_2 - r_1^2 dx_1)$ and $dA_{sl} = 2\pi(r_2 dx_2 - r_1 dx_1)$, Equation (11) reduces to:

$$P - P_v = -2\sigma_{lv}\cos\theta\left(\frac{1}{r_2} - \frac{r_1}{r_2^2}\frac{dx_1}{dx_2}\right) \tag{12}$$

To make this expression more explicit, and to recover known results, one must introduce additional assumptions. For example, if the liquid is assumed incompressible and if the vapour density remains practically constant one could write $dV_l / v_l = -dV_v / v_v$ and $dx_1 / dx_2 = \left(1 - v_l / v_v\right) r_2^2 / r_1^2$, thus:

$$P - P_v = -2\sigma_{lv}\cos\theta\left(\frac{1}{r_2} - \frac{1}{r_1}\left(1 - v_l / v_v\right)\right) \tag{13}$$

In general v_l / v_v is small and relation (13) then reduces to the classical Washburn-Laplace equation $P - P_v = -2\sigma_{lv}\cos\theta(1/r_2 - 1/r_1)$.

4.2 Adiabatic capillary rise

In this second example, we introduce non-isothermal effects into the classical problem of capillary rise. The height to which the meniscus of a liquid rises in a vertical capillary is given by Jurin's law. We are interested in determining the equilibrium height if the rising process is performed adiabatically instead of isothermally (Laouir and Tondeur 2004). The thermodynamic system comprises the tube and the liquid above the reference level as shown in *figure 3*. The system is incompressible and there is no work transferred to or from the system (we neglect the work involved to lift the gas above the liquid). We assume that there is no heat transfer between the system so defined and its environment. Hence the system is isolated, $d(U_g + E_p) = 0$ and $d(S_g) = 0$, while $dA_{sl} = -dA_{sv}$. The energy and entropy balances are written:

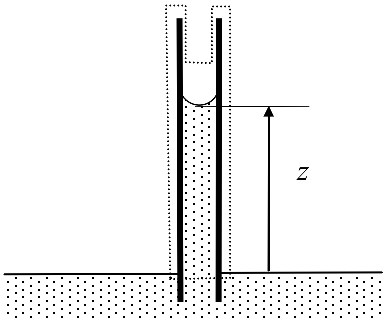

Figure 3. Capillary rise.

$$\begin{aligned} &m_s du_s + m_l du_l + (u_{sl} - u_{sv})dA_{sl} + \\ &\quad + A_{sl}du_{sl} + A_{sv}du_{sv} + gzdm_l = 0 \end{aligned} \tag{14}$$

$$\begin{aligned} &m_s ds_s + m_l ds_l + (s_{sl} - s_{sv})dA_{sl} + \\ &\quad + A_{sl}ds_{sl} + A_{sv}ds_{sv} = 0 \end{aligned} \tag{15}$$

Heat capacities of the solid and the liquid are c_s and c_l so that $du_s = c_s dT,\ du_l = c_l dT$, $ds_s = c_s dT / T$ and $ds_l = c_l dT / T$. Eliminating $m_s c_s dT + m_l c_l dT$ between the two previous equations and noting that $du_{sv} - Tds_{sv} = 0$ in accordance with relations (1) we get $-\sigma_{lv}\cos\theta dA_{sl} + gzdm_l = 0$. If r is the capillary radius and ρ_l the liquid density, $dm_l = \pi r^2 \rho_l dz$ and

$dA_{sl} = 2\pi r dz$. Combining these relations with Equation (14) results in a relation of the same form as Jurin's law, but involving an unknown variable, namely the equilibrium temperature:

$$z = \frac{2\sigma_{lv}(T)\cos\theta(T)}{\rho_l g r} \qquad (16)$$

This equilibrium temperature may be calculated by substituting relation (16) back into the energy balance equation, the initial state being defined as $z=0$, $A_{sl}=0$, $T=T_0$. One then obtains,

TABLE I. HEIGHTS RATIO $z(T)/z(T_0)$ AND EQUILIBRIUM TEMPERATURE T (IN BRACKETS) FOR CAPILLARY RISE IN THE SYSTEM DECANE/ SILICONED GLASS, $T_0 = 20°C$.

		Capillary radius r in nm ($10^{-9}\,m$)			
		2	5	50	100
Mass ratio $\xi_s = m_s/m_l$	0	0.925 (42.4)	0.972 (28.6)	0.997 (20.8)	0.999 (20.4)
	1	0.945 (36.4)	0.979 (26.3)	0.998 (20.6)	0.999 (20.3)
	5	0.974 (27.9)	0.990 (23.1)	0.999 (20.3)	1.000 (20.1)
	50	0.996 (21.1)	0.998 (20.5)	1.000 (20.0)	1.000 (20.0)

$$2\pi r z\left[T\frac{\partial(\sigma_{lv}\cos\theta)}{\partial T} - \sigma_{lv}\cos\theta + u_{sv}(T)\right] + \frac{1}{2}\pi r^2 \rho_l g z^2$$
$$(m_s c_{vs} + m_l c_{vl})T = 2\pi r z u_{sv}(T_0) + (m_s c_s + m_l c_l)T_0 \quad (17)$$

Eqs. (16) and (17) allow calculating iteratively the height z and the temperature T at the equilibrium state. TABLE I shows the results for different values of capillary radius r and mass ratio $\xi_s = m_s/m_l$. The tube is made of glass treated with silicone, $c_s = 750$ J.kg^{-1}.K^{-1} and the liquid is decane, $c_l = 2213$ J.kg^{-1}.K^{-1}, $\rho_l = 724$ kg.m^{-3} and $\sigma_{lv} = -0.092T + 50.8$ mJ.m^{-2}. The contact angle variation with temperature fits the relation $\theta = -0.146T + 57.0$ as estimated from Neumann's (1974) experimental data. For this solid-liquid sytem Neumann has also shown that $\sigma_{sv}(T)$ is linear, so in accordance with relations (1) u_{sv} is constant and $u_{sv}(T) - u_{sv}(T_0) = 0$ in Equation (17). In TABLE I, $z(T)/z(T_0)$ is the ratio of adiabatic and isothermal capillary rise heights with T_0= 20°C. The difference between the two cases appears significantly for $r < 50nm$ and $m_s/m_l < 50$. The extreme values are shown as indications of trends. The adiabatic capillary rise with the considered solid-liquid couple leads to an increase of the temperature and a reduction of the equilibrium height. Other systems, having in particular a different dependence of the contact angle on temperature, may display a different qualitative behaviour.

5. Reversible Wetting of Porous Media

Wetting a porous solid or a powder by a liquid is the process which leads to create a solid-liquid interface from an initial state presenting only a solid-vapour surface. This thermodynamic transformation will bring into play heat and work. From a purely experimental point of view two cases may be distinguished namely "wetting" ($\theta < 90°$) and the "non-wetting" ($\theta > 90°$) case (Ritter and Drake 1945, Eroshenko et al. 2002, Coiffard and Eroshenko 2005). *Figure 4* is a general representation of the wetting process, the heat and work may be received or transferred to the surroundings depending on the surface properties of the given solid-liquid couple. Other aspects may be taken into account in studying such a system, like the presence of vapour in pores and the compressibility of the liquid.

The question that arises is whether or not the wetting process is a reversible transformation. Reversibility means that the reverse process is possible and will involve the same amount of heat and work to bring the system back to the initial state. The most critical criterion of reversibility is then that the work produced is fully collected outside the system, this means also that the system is assumed free of friction and causes of hysteresis. It can be shown (Laouir et al. 2007) that the reversibility of the wetting phenomenon is conceptually achievable in properly designed devices.

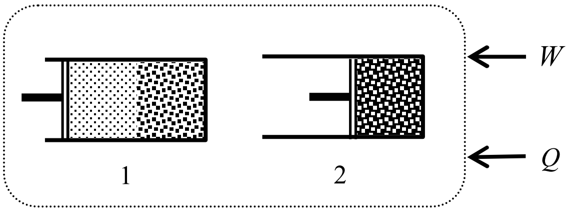

Figure 4. Wetting of a porous media.

5.1 Isothermal intrusion of a non-wetting liquid

Considering the system shown in *figure 4*, the liquid is introduced at constant temperature and reversibly ($\varepsilon = 0$). Initially the porous media contains vapour ($m_{v1} \neq 0$) and at the end of the process, the vapour is completely condensed ($m_{v2} = 0$). All thermodynamic properties will be expressed per *kg* of liquid at initial state m_{l1}. The mass ratio of the vapour and the specific wetted surface are defined as $\xi_v = m_{v1}/m_{l1}$ and $a_{sl} = A_{sv1}/m_{l1}$ respectively. First and second law balances expressed per *kg* of liquid are $\Delta u_g = Q+W$, $\Delta s_g = Q/T$; the solid is considered incompressible so $u_{s2}=u_{s1}$ and $s_{s2}=s_{s1}$; we have also $m_{l2}=m_{l1}+m_{v1}$ and $a_{sl2}=a_{sv1}$, so that finally:

$$u_{l2}-u_{l1}+\xi_v(u_{l2}-u_{v1})+a_{sl}(u_{sl2}-u_{sv1})=Q+W \qquad (18)$$

$$s_{l2}-s_{l1}+\xi_v(s_{l2}-s_{v1})+a_{sl}(s_{sl2}-s_{sv1})=\frac{Q}{T} \qquad (19)$$

During the intrusion, the properties of the solid-vapor interface remain practically constant, $u_{sv1}=u_{sv2}$ and $s_{sv1}=s_{sv2}$. Equation (19) shows that the heat Q transferred may be decomposed as follows

$$Q=\underbrace{T(s_{l2}-s_{l1})}_{Q_I}+\underbrace{T\xi_v(s_{l2}-s_{v1})}_{Q_{II}}+\underbrace{T\frac{\partial(\sigma\cos\theta)}{\partial T}a_{sl}}_{Q_{III}} \qquad (20)$$

were Q_I is the heat related to the compressibility of the liquid, Q_{II} the fraction related to vapour condensation and compression of the resulting liquid and Q_{III} is the reversible heat of wetting. Similarly the work transferred $W=\Delta u_g - Q$ may be expressed as a sum of three fractions: compression work W_I, work of condensation and compression of the resulting liquid W_{II} and work of wetting W_{III}.

TABLE II. HEAT AND WORK IN KJ/(KG OF LIQUID)
OF ISOTHERMAL INTRUSION OF WATER IN POROUS SILICONED GLASS.

T	σ_{lv} (mJ.m^{-2})	θ	Q_I	Q_{II}	Q_{III}	$\sum Q$	W_I	W_{II}	W_{III}	$\sum W$
20 °C	72.70	107.2°	-3.46	-0.04	-5.31	-8.81	0.51	0.00	32.25	32.76
50°C	67.90	108.7°	-8.02	-0.20	-2.00	-10.22	0.38	0.01	31.80	32.19

TABLE III. WORK IN KJ/(KG OF LIQUID) OF ISENTROPIC
INTRUSION OF DECANE IN POROUS SILICONED GLASS.

T_1	σ_{lv1} (mJ.m^{-2})	θ_1	T_2	σ_{lv2} (mJ.m^{-2})	θ_2	W (kJ/kg$_l$)
20 °C	23.83	14.2°	26.30 °C	23.25	13.3°	-47.34
50°C	21.07	9.8°	56.85 °C	20.44	8.8°	-42.34

TABLE II shows the results calculated for intrusion of water at 20°C and 50°C in porous siliconed glass, the solid having a porosity $\varphi=0.2$ cm^3.g^{-1} and a specific surface area $\Omega=300$ m^2.g^{-1}. The specific wetted area with a quantity of water ($\rho_l=1$ g.cm^{-3}) occupying the pore volume is $a_{sl}=\Omega/\varphi\rho_l=1500$ m^2.g^{-1} of water or $a_{sl}=1.5\ 10^6$ m^2.kg^{-1}of water. The pressure at the end of the process is supposed to be 450 bar. The wetting properties for this solid-liquid system are $\partial\sigma_{lv}/\partial T=-0.16$ mJ.m^{-2}.K^{-1} and $\partial\theta/\partial T=8.55\ 10^{-4}$ rad.K^{-1} (Neumann, 1974). The mass ratio ξ_v may be calculated from $\xi_v=\rho_{v1}/\rho_{l1}=v_{l1}/v_{v1}$ and supposing the vapour saturated at the temperature considered. The properties of saturated and compressed water are taken from thermodynamic tables.

The results show that the total work involved in performing the process is practically equal to that of the wetting phenomenon W_{III}; compressibility and vapour condensation play a negligible role from this point of view. The work done on the system is positive because the liquid is non-wetting, it must be forced to occupy the voids of the solid in order to accomplish the wetting process. On the contrary the heat rejected due to compressibility Q_I is not negligible, it becomes greater than the heat of wetting Q_{III} at T=50 °C.

Qualitatively, we notice that the heat of wetting is negative (the intrusion process is exothermal); this result belongs to the solid-liquid system considered; for other couples, the heat of wetting may be positive even with wetting liquids (e.g. the case of the couple water-cholesteryl acetate mentioned in Laouir et al. 2003). In the later cases heat of compression and heat of wetting are of opposite signs so the process may be endo- or exothermal depending on which of these heats is larger. The heat as well as the work related to vapour are quite negligible, which means that the presence of vapour may be ignored in this type of problem.

5.2 Adiabatic intrusion of a wetting liquid

The wetting process is adiabatic (Q=0) and reversible ($\varepsilon=0$), thus the overall entropy remains constant; therefore $\Delta s_g=0$ and $\Delta u_g=W$. The mass ratio of the solid is $\xi_s=m_s/m_{l1}$ and the vapour is neglected ($\xi_v=0$). As we consider a wetting behavior, the intrusion process takes place spontaneously, and the system can produce work. The pressure on the liquid-side is the lowest in accordance with Washburn-Laplace equation when $\theta<90°$. Thus compressibility effects are quite negligible in this case. The energy and entropy balance expressions are:

$$W = c_l(T_2 - T_1) + \xi_s c_s(T_2 - T_1) + \left[T\frac{\partial(\sigma\cos\theta)}{\partial T} - \sigma_{lv}\cos\theta \Big|_2 + (u_{sv2} - u_{sv1}) \right] a_{sl} \tag{21}$$

$$c_l \ln(T_2/T_1) + \xi_s c_s \ln(T_2/T_1) + \left[\frac{\partial(\sigma_{lv}\cos\theta)}{\partial T}\Big|_2 + (s_{sv2} - s_{sv1}) \right] a_{sl} = 0 \tag{22}$$

In general the relation $\sigma_{sv} = \sigma_{sv}(T)$ is needed in order to calculate the differences $(s_{sv2} - s_{sv1})$ and $(u_{sv2} - u_{sv1})$ and this is the case every time a non-isothermal process is considered. Fortunately, for certain solid-liquid couples like decane/siliconed glass considered in section 4.2, σ_{sv} is a linear function of *T*, so u_{sv} and s_{sv} are constant, and we have $u_{sv2} - u_{sv1} = 0$ and $s_{sv2} - s_{sv1} = 0$. TABLE III shows the results calculated for two values of initial temperature T_1, the solid having the same properties as given in the previous section. With decane, the specific wetted surface area is $a_{sl} = 2.07\ 10^6$ m^2.kg^{-1} of decane, the mass ratio is $\xi_s = 1/\varphi\rho_l = 6.90$ (for surface properties and heat capacity values see section 4.2). Temperature T_2 is calculated iteratively using Equation (22). The system can produce a significant amount of work and the process leads to an increase of the final temperature.

6. Heat Transfer to Nanofluids

Liquids containing suspended solid nanoparticles are termed nanofluids, and the presence of the particles enhances dramatically the transport properties of the mixture (Boualit and Zeraibi 2006, Trisaksri and Wongwises 2007). The thermodynamic properties of such a fluid may be calculated as follows. We shall assume that densities as well as interfacial tension are not affected by the small particle size. Then the specific volume of the suspension is $v_g = xv_s + (1-x)v_l$ where *x* is the particles mass fraction.

According to Equation (4), the internal energy is $U_g = m_s u_s + m_l u_l + u_{sl} A_{sl}$. The specific internal energy of the suspension is then $u_g = xu_s + (1-x)u_l + a_{sl}u_{sl}$, and similarly the specific entropy is $s_g = xs_s + (1-x)s_l + a_{sl}s_{sl}$, in which a_{sl} is the specific wetted surface $a_{sl} = A_{sl}/(m_s + m_l) = xA_{sl}/m_s$. If the particles are supposed spherical, thus with a surface $4\pi r^2$ and a mass $4/(3\pi r^3 v_s)$, a_{sl} may be expressed as $a_{sl} = 3xv_s/r$. Using Equation (1) for u_{sl} and s_{sl} we obtain:

$$u_g = xu_s + (1-x)u_l + 3xv_s\frac{1}{r}\left[-T\frac{\partial\sigma_{sl}}{\partial T} + \sigma_{sl} \right] = \widetilde{u} + u^\sigma \tag{23}$$

$$s_g = xs_s + (1-x)s_l + 3xv_s\frac{1}{r}\left[-\frac{\partial\sigma_{sl}}{\partial T} \right] = \widetilde{s} + s^\sigma \tag{24}$$

The expression for specific enthalpy is $h_g = u_g + Pv_g$ and the heat capacity is defined by $c_g = \partial u_g/\partial T$ thus,

$$c_g = xc_s + (1-x)c_l + 3xv_s\frac{1}{r}\left[-T\frac{\partial^2\sigma_{sl}}{\partial T^2} \right] = \widetilde{c} + c^\sigma \tag{25}$$

In the equations above, $\widetilde{u}, \widetilde{s}$ and $\widetilde{c}$ are the average quantities of an "ideal" blend for which there are no surface effects; u^σ, s^σ and c^σ are the quantities related to the wetting phenomenon which may be regarded as *excess quantities*. If $\sigma_{sl} = \sigma_{sl}(T)$ is linear, u^σ and s^σ are constant and c^σ zero, so the fluid behaves like an ideal blend. Using Young's equation, and knowing that $\sigma_{lv}(T)$ is practically linear for pure substances ($\partial^2\sigma_{lv}/\partial T^2 \approx 0$), we get

$$u^\sigma = 3xv_s\frac{1}{r}\left(T\frac{\partial(\sigma_{lv}\cos\theta)}{\partial T} - \sigma_{lv}\cos\theta + u_{sv} \right) \tag{26}$$

$$s^\sigma = 3xv_s\frac{1}{r}\left(\frac{\partial(\sigma_{lv}\cos\theta)}{\partial T} + s_{sv} \right) \tag{27}$$

$$c^\sigma = 3xv_s\frac{1}{r}T\left(\sigma_{lv}\frac{\partial^2\cos\theta}{\partial T^2} - \frac{\partial^2\sigma_{sv}}{\partial T^2} + 2\frac{\partial\sigma_{lv}}{\partial T}\frac{\partial\cos\theta}{\partial T} \right) \tag{28}$$

TABLE IV shows the results for two hypothetical nanofluids containing siliconed glass nanoparticles, and where the base liquid is water or decane (see sections 4.2 and 5.1 for the corresponding properties). For both systems $\sigma_{sv}(T)$ is linear so u_{sv} and s_{sv} are constant (taken equal to zero). The particle size is $2r = 5$ nm, $\rho_s = 2500$ kg.m^{-3}; the concentration on a volume basis is taken as $x_{vol} = 10\%$ (this is a relatively high value for nanofluids) therefore with water $x = 21.7\%$, $a_{sl} = 1.04\,10^5$ m^2.kg^{-1} and with decane $x = 27.7\%$, $a_{sl} = 1.33\,10^5$ m^2.kg^{-1}.

Thermodynamic properties are calculated at 10°C and 40°C, and the results show that surface effects are quite weak. Internal energy variation Δu_g between the two temperatures is practically equal to $\Delta\widetilde{u}$ and $c_g \approx \widetilde{c}$. This means that to be heated the fluid will absorb practically the same amount of heat needed in absence of surface effects (macroscopic or “ideal” blend). This behaviour is due mainly to the weak sensitivity of surface properties to temperature variations. It should be noted that the heating process is performed while the wetted surface area is unchanged, in other words it is a “constant surface” transformation.

Although it may be tempting to conclude that nanofluids have the thermodynamic properties of ideal fluids, no general conclusion can be drawn about the importance of excess quantities from this unique example. Indeed, solid-liquid systems having highly non-linear variation of $\sigma_{sl}(T)$ will show more significant deviation from the ideal case.

TABLE IV. THERMODYNAMIC PROPERTIES OF SILICONED GLASS/WATER AND SILICONED GLASS/DECANE NANOFLUIDS.
IDEAL FLUID VALUES ARE GIVEN IN PARENTHESES.

	T °C	σ_{lv} $10^3\,J.m^{-2}$	θ deg	u_g $(\tilde{u})$ $kJ.kg^{-1}$	$s_g (\tilde{s})$ $kJ.kg^{-1}.K^{-1}$	c_g $(\tilde{c}=scte)$ $kJ.kg^{-1}.K^{-1}$	Δu_g $(\Delta\tilde{u})$	Δs_g $(\Delta\tilde{s})$
S-Glass/ Water	10	74.30	106.7°	975.71 (973.92)	19.418 (19.420)	3.448 (3.440)	103.45 (103.19)	0.347 (0.346)
	40	69.50	108.2°	1079.16 (1077.11)	19.766 (19.766)	3.450 (3.440)		
S-Glass/ Decane	10	24.75	15.66°	506.00 (511.86)	10.197 (10.206)	1.797 (1.807)	53.93 (54.24)	0.181 (0.182)
	40	21.99	11.28°	559.93 (566.10)	10.378 (10.388)	1.798 (1.807)		

7. Irreversible Emulsion Split

An emulsion is a mixture of immiscible liquids with one of the two liquids being finely dispersed as small droplets (discontinuous phase) in the second liquid which constitutes the continuous phase. In general (that is unless the emulsion is stabilized by surfactants, or we are dealing with a microemulsion having an extremely slow coalescence rate) droplets have a tendency to coalesce and at the end of this process the emulsion is separated into two continuous liquid phases as shown in *figure 5.*

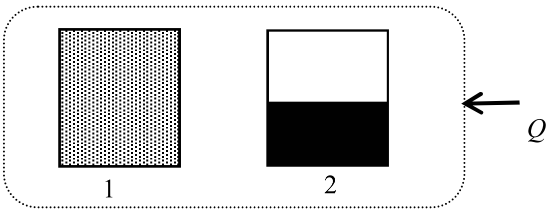

Figure 5. Emulsion decantation

As a thermodynamic transformation, the process starts from a state presenting a large specific liquid-liquid interface a_{ll} . Assuming spherical droplets, $a_{ll}=3xv_l/r$ where x is the concentration of the liquid forming the droplets and v_l its specific volume. At the end of the process the liquid-liquid interface is practically zero. It is obvious that no work is transferred during the transformation, only heat may cross the system boundary. In fact this is an irreversible transformation because the work previously absorbed in order to produce the emulsion, at least equal to $\sigma_{ll}a_{ll}$, is in no way restored to the surroundings during the inversion of the process. Considering an isothermal process, $\Delta u_g=Q$ and $\Delta s_g=Q/T+\varepsilon$; in addition we have $\Delta a_{ll}=-a_{ll}$. The expressions for heat and entropy production are:

$$Q=-\left(\sigma_{ll}-T\frac{\partial\sigma_{ll}}{\partial T}\right)a_{ll}\ ,\quad \varepsilon=\frac{\sigma_{ll}a_{ll}}{T} \qquad (29)$$

Let us consider an emulsion of benzene in water at 20°C having a concentration x= 0.40 with droplets size $2r=20$nm. Surface properties are (Meyers and Harkins 1935) $\sigma_{ll}=34.20\,\mathrm{mJ.m^{-2}}$; $\partial\sigma_{ll}/\partial T\approx-0.35$ $\mathrm{mJ.m^{-2}.K^{-1}}$ and $\rho_l=879\,\mathrm{kg.m^{-3}}$, so $a_{ll}=1.37\,10^5\,\mathrm{m^2.kg^{-1}}$. An assumption similar to that done with nanofluids is made here, namely that interfacial tension and density of benzene are not modified due to the small size of droplets. The heat evolved is $Q=-18.74$ $\mathrm{kJ.kg^{-1}}$ that is the coalescence process is exothermic, the entropy produced is $\varepsilon=0.016$ $\mathrm{kJ.Kg^{-1}.K^{-1}}$.

8. Conclusion

A contribution to the application of thermodynamics fundamentals to systems involving capillarity was presented. The energy and entropy balance equations extended to surface effects allow in principle the study of a wide variety of problems and the exploring of the behaviour of capillary systems. The scarcity of data on wetting properties, particularly those related to temperature dependences of contact angle, solid-vapour and solid-liquid interfacial tensions, may restrict the practical use of the equations, but a number of different qualitative situations may be identified. On the other hand, the problem of lack of data may be reversed and the relations exploited in such a manner as to determine unknown surface properties using appropriate experimental procedures.

Equilibrium criteria were derived for different situations. Equilibrium of liquids in capillaries was studied and a general expression for capillary pressure was derived, of which the classical Washburn-Laplace equation appears as a special case obtained by introducing some assumptions (mainly, that the wetting properties are not changed at elevated pressure and that the liquid is incompressible). The case of adiabatic capillary rise was considered, and it was shown that Jurin's law is still valid, but involves the equilibrium temperature as a parameter to be determined using the energy balance equation.

The different problems considered were readily treated using the general relations, the important aspect being the possibility to quantify heat and work involved for a given process. In other words, one can deal with the energetics of the wetting phenomenon and explore possible applications as energy systems based on surface effects. From this point of view, heat and work values will be more significant if the sensitivity to temperature of surface tensions is high and the variations non-linear. In addition, the application of the second law permits to examine the reversibility of this type of processes and to calculate the entropy produced in irreversible cases.

Nomenclature

A	surface area	m^2
a	specific surface area	$m^2.kg^{-1}$
c	heat capacity	$J.kg^{-1}.K^{-1}$
E_c, E_p	kinetic, potential energy	J
e_c, e_p	specific kinetic, potential energy	$J.kg^{-1}$
g	gravity acceleration	$m.s^{-2}$
h	specific enthalpy	$J.kg^{-1}$
m	mass	kg
P	pressure	Pa
$Q, \dot{Q}$	heat, heat transfer rate	$J, J.s^{-1}$
r	pore, particule radius	m
S	entropy	$J.K^{-1}$
s	entropy per kg or m^2	$J.kg^{-1}.K^{-1}, J.m^{-2}.K^{-1}$
T	temperature	K
t	time	s
U	internal energy	J
u	internal energy per kg or m^2	$J.kg^{-1}, J.m^{-2}$
V	volume	m^3
v	specific volume	$m^3.kg^{-1}$
$W, \dot{W}$	work, power	J, W
x	concentration	-
$\varepsilon, \dot{\varepsilon}$	entropy production	$J.K^{-1}, W.K^{-1}$
ρ	density $kg.m^{-3}$	
σ	surface tension	$J.m^{-2}$
θ	contact angle	rad
ξ	mass ratio	-

Subscripts

g	overall thermodynamic property
l	liquid
s	solid
v	vapour
**	surface separating two phases (*lv*, *sl*, *sv or ll*)

Superscripts

σ	surface phenomena contribution
~	average value

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