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Influence of capillarity on chemical stability and of electric field on surface tension near the critical point

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In the present paper, we show that the stability of a chemical reaction occurring in a capillary layer depends on surface properties. A chemical reaction unstable in a bulk phase may be stabilized in a surface layer and, vice versa, a stable reaction in a bulk phase may be unstable when occurring at an interface. The second part of this paper shows how an applied electric field may be responsible for a shift of the critical point through the effect on surface tension.

Keywords: surface tension; stability; electric field; critical point

1. Introduction

For the physicist and the chemist, one of the primary interests in thermodynamics lies in its ability to establish a criterion of the stability of a given chemical or physical transformation under specified conditions. The first law of thermodynamics describes the conservation of energy while the second law expresses the evolution of all irreversible processes. The formulation of these two universal principles is, however, unable to forecast a stability transition for equilibrium or far from equilibrium states. The stability analysis gives the conditions for the regression or the amplification of the fluctuations of any physical and chemical variable.

It is well known that spontaneous microscopic fluctuations always occur in all systems. When these fluctuations are damped in time, and do not grow to change the macroscopic state, the system is stable. When dealing with stability problems, three types of situation have to be considered: the equilibrium states; the linear region near equilibrium; and the non-equilibrium situations beyond the linear region. At equilibrium, far from a phase transition, and near equilibrium, fluctuations play a minor role. They give 'corrections' to macroscopic results. In the region of phase transition, equilibrium instabilities give rise to the formation of equilibrium structures that are maintained in reversible processes, or for processes that slightly remove the system from equilibrium. To study the equilibrium stability, the concept of thermodynamic potentials was first used, such as the Helmholtz free energy F, or other potentials (Gibbs 1928), according to the boundary conditions. Later, a concept of stability which was not dependent on the boundary conditions was introduced (De Donder 1942). The method adopted by Prigogine & Defay (1967) is based upon the direct evaluation of the entropy production in the course of a perturbation and so permits a discussion of stability with respect to any kind of perturbation.

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In his famous 'Traité d'Energétique', Duhem (1911, ch. XVI) used the basic idea of Gibbs to obtain thermal and mechanical conditions for the stability of equilibrium states. They derived explicitly the curvature of the specific mass entropy $\delta^2 s$ ($\delta^2 s \leqslant 0$ for stable states) in a quadratic form containing fluctuations of temperature and density. Later, Glansdorff & Prigogine (1970) extended their theory to diffusion or chemical stability and Sanfeld & Steinchen (1971) to charged layers. Far from equilibrium the situation is totally different. In that case, fluctuations play a major role by changing the spatio-temporal symmetry of the system. However, contrary to equilibrium transitions, new types of transitions can give rise to a new order characterized by a macroscopic spatial scale. Such states, called by Glansdorff–Prigogine 'dissipative structures', are able to exhibit a permanent temporal activity, regular or chaotic with a macroscopic time scale. Considering that external or internal perturbations (amplification of fluctuations) can destabilize the state of a system, two cases are generally discussed: the steady states and the mobile boundaries. In the former case, the stability criterion (sufficient condition) is given by the product of the fluxes and generalized force fluctuations. In the latter case, a more general formulation based on the trajectories of the processes is needed. The basic idea was introduced and developed by Lyapunov (Cesari 1963; Minorsky 1962; Lin 1967) who introduced a quantity related to the initial perturbation at a given time and which was defined to be positive or negative. If the time derivative of this quantity ($(\partial/\partial t)\delta^2 s$) has the reverse sign of the same quantity, the stability condition for non-equilibrium states is satisfied. If we assume that the state of local equilibrium is stable, the fundamental hypothesis of local equilibrium $\delta^2 s$ can be used as a Lyapunov function. The choice of $\delta^2 s$, instead of any other quadratic function, finds its justification in its physical significance in terms of fluctuations in the Einstein theory (Landau & Lifshitz 1958). In the first part of our study we shall apply the Lyapunov concept of stability to a surface chemical reaction in order to display the role of the surface tension. In addition to the thermodynamic stability approach many authors have devoted more attention to hydrodynamical treatments (Chandrasekar 1961; Lin 1967; Drazin & Reid 1981). One of the major points is the role played by the surface tension on the stability of fluid surfaces and more specifically of external fields acting at gas–liquid or liquid–liquid interfaces (Sørensen 1979).

In § 3 we describe the influence of an applied electric field on the surface near the critical point (Gouin & Sanfeld 1997). As the surface tension is zero at the critical point, the interface vanishes. Therefore the influence of an applied external field in that region could be of importance to maintain a discontinuity (or semi) domain between the two bulk phases. To this purpose we use a generalized chemical potential (de Groot & Mazur 1962, p. 396; Sanfeld 1968) combined with a statistical mean field theory (Rowlinson & Widom 1982).

2. Non-equilibrium stability of a plane surface

As previously shown by Steinchen & Sanfeld (1981) for capillary systems, the local time derivative of a Lyapunov function including the curvature of entropy and a convective term contains boundary flux terms, Laplace, Marangoni and surface Benard effects and fluctuations of flux-forces. We shall restrict here our analysis to pure chemical reactions in a monolayer at constant and uniform temperature with no accumulation of matter at the sublayer. We shall then compare the monolayer phase to the volume phase. Both systems are considered at rest and for appropriate Newmann or Dirichlet boundary conditions. Restricted to small perturbations around a non-equilibrium process, a sufficient condition for the local stability of pure chemical reactions in a bulk phase (Glansdorff & Prigogine 1970) is given by

$$\frac{1}{2}\frac{\partial}{\partial t}\delta^2 s = T^{-1}\sum_{\rho}\delta\mathcal{A}_\rho\delta v_\rho \geqslant 0, \tag{2.1}$$

where $\mathcal{A}_\rho$ and v_ρ are the chemical affinity and rate of reaction ρ, respectively.

For reactions in a monolayer (superscript 'c') the stability criterion reads (Steinchen & Sanfeld 1981)

$$\frac{1}{2}\frac{\partial}{\partial t}\delta^2 s = T^{-1}\sum_{\rho}\delta\mathcal{A}^{\mathrm{c}}_\rho\delta v^{\mathrm{c}}_\rho \geqslant 0. \tag{2.2}$$

In order to calculate the chemical contribution $\delta\mathcal{A}^{\mathrm{c}}_\rho\delta v^{\mathrm{c}}_\rho$ in equation (2.2), let us now consider a totally irreversible surface chemical reaction ρ characterized by the general kinetic law

$$v^{\mathrm{c}}_\rho = \boldsymbol{k}^{\mathrm{c}}_\rho(\gamma^{\mathrm{c}}_\gamma)^{m_\gamma}(\gamma^{\mathrm{c}}_\beta)^{m_\beta}\cdots, \tag{2.3}$$

where $\boldsymbol{k}^{\mathrm{c}}_\rho$ is the kinetic constant; $\gamma^{\mathrm{c}}_\gamma$, $\gamma^{\mathrm{c}}_\beta$ are the surface activities (in terms of surface concentrations) of γ; m_γ, m_β are the partial orders. Strictly speaking, $\boldsymbol{k}^{\mathrm{c}}_\rho$ is a pseudo-constant. Indeed, $\boldsymbol{k}^{\mathrm{c}}_\rho$ is directly related to the surface activation energy which depends on the state of the monolayer lattice, i.e. the capillary parameters. By neglecting the fluctuations of $\boldsymbol{k}^{\mathrm{c}}_\rho$, as a first approximation, we get, for only one fluctuating component β,

$$\delta v^{\mathrm{c}}_\rho = \boldsymbol{k}^{\mathrm{c}}_\rho(\gamma^{\mathrm{c}}_\gamma)^{m_\gamma}\cdots m_\beta(\gamma^{\mathrm{c}}_\beta)^{m_\beta^{-1}}\delta\gamma^{\mathrm{c}}_\beta. \tag{2.4}$$

Now we have to calculate the second factor $\delta\mathcal{A}^{\mathrm{c}}_\rho$ given by

$$\delta\mathcal{A}^{\mathrm{c}}_\rho = -\sum_{\gamma}\nu_{\rho\gamma}\delta\mu^{\mathrm{c}}_\gamma, \tag{2.5}$$

where the chemical potential in the monolayer μ^{c}_γ (Defay & Prigogine 1966, p. 166) reads

$$\mu^{\mathrm{c}}_\gamma = \mu^{\infty}_\gamma + RT\ln\gamma^{\mathrm{c}}_\gamma - RT\ln\mathit{\Gamma} - \sigma a_\gamma, \tag{2.6}$$

where μ^{∞}_γ is the standard chemical potential, $\mathit{\Gamma}$ the dimensionless total surface molar concentration ($\mathit{\Gamma} = \sum\mathit{\Gamma}_\gamma$). The activity coefficient f^{c}_γ is defined by

$$\gamma^{\mathrm{c}}_{\mathrm{c}} = f^{\mathrm{c}}_\gamma\mathit{\Gamma}_\gamma. \tag{2.7}$$

At constant T and p and for one fluctuating reactant β,

$$\delta\mathcal{A}^{\mathrm{c}}_\rho = RT\left\{-\nu_{\rho\beta}\frac{\delta\gamma^{\mathrm{c}}_\beta}{\gamma^{\mathrm{c}}_\beta} + \nu_{\rho\beta}\frac{\delta\mathit{\Gamma}_\beta}{\mathit{\Gamma}} + \delta\left(\sum_{\gamma}\nu_{\rho\gamma}a_\gamma\sigma/RT\right)\right\}. \tag{2.8}$$

As $\mathit{\Gamma} > \mathit{\Gamma}_\beta$,

$$\frac{\delta\mathit{\Gamma}_\beta}{\mathit{\Gamma}} \ll \frac{\delta\mathit{\Gamma}_\beta}{\mathit{\Gamma}_\beta},$$

so that equation (2.8) reduces to

$$\delta\mathcal{A}^{\mathrm{c}}_\rho = RT\left\{-\nu_{\rho\beta}\frac{\delta\gamma^{\mathrm{c}}_\beta}{\gamma^{\mathrm{c}}_\beta} + \delta\left(\sum_{\gamma}\nu_{\rho\gamma}a_\gamma\sigma/RT\right)\right\}. \tag{2.9}$$

Taking into account the fluctuations of the chemical rate (2.4), one has finally

$$\begin{aligned}\tfrac{1}{2}\partial_{\mathrm{t}}(\delta^2 s^{\mathrm{c}})_\rho &= T^{-1}\delta v_\rho^{\mathrm{c}}\delta\mathcal{A}_\rho^{\mathrm{c}}\\ &= R\boldsymbol{k}_\rho^{\mathrm{c}}(\gamma_\rho^{\mathrm{c}})^{m_\gamma}\cdots m_\beta(\gamma_\rho^{\mathrm{c}})^{m_\beta-1}\left\{-\nu_{\rho\beta}\frac{(\delta\gamma_\beta^{\mathrm{c}})^2}{\gamma_\beta^{\mathrm{c}}}+\delta\left(\sum_\gamma \nu_{\rho\gamma}a_\gamma\sigma/RT\right)\delta\gamma_\beta^{\mathrm{c}}\right\}.\end{aligned} \tag{2.10}$$

For the same mechanism in the bulk phase, we will have

$$\tfrac{1}{2}\partial_{\mathrm{t}}(\delta^2 s)_\rho = T^{-1}\delta v_\rho\delta\mathcal{A}_\rho = -\boldsymbol{k}(\gamma_\gamma)^{m_\gamma}\cdots m_\beta(\gamma_\beta)^{m_\beta-2}\{R\nu_{\rho\beta}(\delta\gamma_\beta)^2\}, \tag{2.11}$$

where the activity of component γ in the bulk phase is defined by $\gamma_\gamma = f_\gamma C_\gamma$. The autocatalytic (or non-autocatalytic) character of a bulk phase chemical reaction is characterized by the sign of $\nu_{\rho\beta}$. As shown by expression (2.10), there is an additional contribution in the monolayer due to the intrinsic contribution of the surface free energy to the chemical potential, i.e. $(a_\gamma\sigma)$. Suppose now a monolayer composed, either by reacting solutes of surfactant impurities and gaseous species on a liquid metal support, or by a non-reacting rare gaseous solvent containing reacting metal atoms and gaseous species on a metal support. In that case, we may write, for the sum on the chemical reacting components s in equation (2.10)

$$\sum_\gamma \nu_{\rho\gamma}a_\gamma\sigma = \sum_s \nu_{\rho s}a_s\sigma, \tag{2.12}$$

where the partial molar surface area of γ is defined by

$$a_\gamma = \left(\frac{\partial A}{\partial n_\gamma^{\mathrm{c}}}\right)_{T,p,n^{\mathrm{c}}_{\beta\neq\gamma},\sigma}. \tag{2.13}$$

The surface pressure, which is equal to the lowering of surface tension of pure solvent (σ_1), can be defined by the heuristic relation

$$\sigma_1 - \sigma = \sum_s \frac{\alpha_s n_s^{\mathrm{c}}}{A} = \sum_s \alpha_s\mathit{\Gamma}_s, \tag{2.14}$$

with α_s an empirical positive constant in the considered dilute domain of composition. The coefficient α_s depends on T and on the nature of the media. For one fluctuating solute β, we thus have

$$\delta\sigma = -\alpha_\beta\delta\mathit{\Gamma}_\beta. \tag{2.15}$$

By combining equations (2.13) and (2.14) we obtain

$$a_s = \frac{\alpha_s}{\sigma_1-\sigma} \tag{2.16}$$

and by using expressions (2.14) and (2.12), we have

$$\delta\left(\sum_s \nu_{\rho s}a_s\sigma\right) = \frac{\sigma_1}{(\sigma_1-\sigma)^2}\sum_s \alpha_s\nu_{\rho s}\delta\sigma. \tag{2.17}$$

Assuming a quasi-constant activity coefficient in the domain of the considered compositions, and taking into account equations (2.10), (2.17), and (2.15), we finally obtain the criterion for the chemical suface stability:

$$\tfrac{1}{2}\partial_{\mathrm{t}}(\delta^2 s^{\mathrm{c}})_\rho = -T^{-1}\boldsymbol{k}^{\mathrm{c}}_\rho(\gamma^{\mathrm{c}}_\gamma)^{m_\gamma}\cdots m_\beta(\gamma^{\mathrm{c}}_\beta)^{m_\beta-2} \times\left\{\nu_{\rho\beta}RT+\sum_s \alpha_s\nu_{\rho s}\alpha_\beta\varGamma_\beta\frac{\sigma_1}{(\sigma_1-\sigma)^2}\right\}(\delta\gamma^{\mathrm{c}}_\beta)^2 \geqslant 0, \tag{2.18}$$

whereas, in the bulk phase, equation (2.10) should be written as

$$\tfrac{1}{2}\partial_{\mathrm{t}}(\delta^2 s)_\rho = -T^{-1}\boldsymbol{k}_\rho\gamma_\gamma^{m_\gamma}\cdots m_\beta\gamma_\beta^{m_\beta-2}\{\nu_{\rho\beta}RT\}(\delta\gamma_\beta)^2 \geqslant 0. \tag{2.19}$$

As can be easily seen, the sign of $\partial_{\mathrm{t}}(\delta^2 s^{\mathrm{c}})_\rho$ originates either in the capillary term or in the competition between two contributions:

(1) $\nu_{\rho\beta}$, related to the autonomous character of the chemical reaction ($\nu_{\rho\beta} < 0$ for non-autocatalytic reactions and $\nu_{\rho\beta} > 0$ for autocatalytic reactions);

(2) $\sum_s \alpha_s\nu_{\rho s}$ connected to the capillary ($\nu_{\rho\beta} \gtrless 0$). If $\sum_s \alpha_s\nu_{\rho s} > 0$, the state may become unstable, even for intrinsically stable surface chemical reactions.

A detailed analysis of the criteria (2.18) has been previously shown by Sanfeld *et al.* (1990). We shall restrict our analysis here to the simple but realistic case of a condensed or extended liquid monolayer containing (or not) the solvent.

The surface dilation defined by

$$\varDelta^{\mathrm{c}}_\rho = \sum_\gamma \nu_{\rho\gamma}a_\gamma \tag{2.20}$$

is almost constant. Suppose also that the activity coefficient f^{c}_γ is a constant quantity in the domain of the considered composition. Putting equations (2.15) into equation (2.9) one obtains finally

$$\tfrac{1}{2}\partial_{\mathrm{t}}(\delta^2 s^{\mathrm{c}})_\rho = -T^{-1}\boldsymbol{k}^{\mathrm{c}}_\rho(\gamma^{\mathrm{c}}_\gamma)^{m_\gamma}\cdots m_\beta(\gamma^{\mathrm{c}}_\beta)^{m_\beta-2}\{\nu_{\rho\beta}RT+(\alpha_\beta\varGamma_\beta\varDelta^{\mathrm{c}}_\rho)\}(\delta\gamma^{\mathrm{c}}_\beta)^2. \tag{2.21}$$

The first term in curly brackets is the same as the classical term relative to the volume chemical stability ($\nu_{\rho\beta}RT$ in the curly brackets of equation (2.19)). An additional intrinsic surface contribution $\alpha_\beta\varGamma_\beta\varDelta^{\mathrm{c}}_\rho$ can, however, induce new varieties of chemical instabilities. For example, if the reaction ρ is intrinsically stable ($\nu_{\rho\beta} < 0$), the criteria for surface chemical instabilities reads

$$\left.\begin{aligned}&\varDelta^{\mathrm{c}}_\rho > 0,\\ &\alpha_\beta\varGamma_\beta\varDelta^{\mathrm{c}}_\rho > RT|\nu_{\rho\beta}|,\end{aligned}\right\}\quad \text{instability}. \tag{2.22}$$

If the reaction is intrinsically unstable ($\nu_{\rho\beta} > 0$), the capillary term may stabilize the chemical state and the criteria reads

$$\left.\begin{aligned}&\varDelta^{\mathrm{c}}_\rho < 0,\\ &\alpha_\beta\varGamma_\beta|\varDelta^{\mathrm{c}}_\rho| > RT\nu_{\rho\beta},\end{aligned}\right\}\quad \text{stability}. \tag{2.23}$$

The role played by the surfactant parameters α_β on the chemical stability is equally important, as previously shown for convective regimes by Dalle Vedove (1982). As may be seen, due to the terms σa_γ, even non-autocatalytic surface reactions are able to provoke chemical instabilities. In a certain way, the presence of the surface free energy (σa_γ) in the expression of the chemical potential characterizes the existence of a potential barrier.

Let us now illustrate the two criteria (2.22) and (2.23) by a classical experiment:

(1) Suppose a non-autocatalytic surface reaction involving quasi-infinite reservoirs of metallic compounds (Me…) reacting with only one fluctuating gas (O_2 or $X_2 \equiv S_2, \ldots$). The proposed scheme is

$$\underset{O}{Me_2X} + \underset{X_2}{O_2} \rightarrow \underset{X}{2MeO} + \underset{O}{X}.$$

Equation (2.21) reads (neglecting the influence of activity coefficients)

$$\partial_t \delta^2 s^c = + \cdots \{RT - \alpha_{O_2} \varGamma_{O_2} \varDelta^c\}(\delta \varGamma_{O_2})^2 \gtrless 0.$$

For a volumic reaction, one would always obtain from (2.19) a stable chemical state:

$$\partial_t \delta^2 s = + \cdots RT(\delta C_{O_2})^2 > 0.$$

On the contrary, in the monolayer, the situation can be quite different. Indeed, if $\varDelta^c > 0$ and $\alpha_{O_2} \varGamma_{O_2} \varDelta^C > RT$, chemical states become unstable. For example such cases occur for realistic experimental values:

$$\begin{aligned} \alpha_{O_2} &= 5RT \text{ (condensed layer)}, \\ \varDelta^c &\cong 3 \times 10^9 \text{ cm}^2 \text{ mol}^{-1}, \\ \varGamma_{O_2} &\cong \omega^{-1} \cong 3 \times 10^{-10} \text{ mol cm}^{-2}. \end{aligned}$$

(2) Suppose now an autocatalytic surface reaction involving quasi-infinite reservoirs of metallic compounds (Me…) reacting with only one fluctuating gas (O or X). The proposed scheme is

$$2MeOX + \underset{X}{O} \rightarrow \underset{X}{2O} + \underset{X}{MeO} + \underset{O_2}{MeX_2}$$

Equation (2.21) reads (neglecting the influence of the activity coefficients)

$$\partial_t \delta^2 s^c = + \cdots \{-RT - \alpha_O \varGamma_O \varDelta^c\}(\delta \varGamma_O)^2 \gtrless 0.$$

For a volumic reaction, equation (2.19) gives

$$\partial_t \delta^2 s = + \cdots - RT(\delta C_O)^2 < 0.$$

The chemical state in the volume is thus always unstable, while in the monolayer a stable state might be expected if

$$\varDelta^c < 0 \quad \text{and} \quad \alpha_O \varGamma_O |\varDelta^c| > RT.$$

Such a situation is obtained for realistic experimental values:

$$\begin{aligned} \alpha_{O_2} &= 10RT, \\ \varDelta^c &\cong -3 \times 10^8 \text{ cm}^2 \text{ mol}^{-1}, \\ \varGamma_{O_2} &\cong 5 \times 10^{-10} \text{ mol cm}^{-2}. \end{aligned}$$

3. Shift of surface tension induced by an applied electric field

As shown in the previous sections, capillary properties play an important role on the stability of surface chemical reactions. In order to extend the same study to electro- and magnetosurface transformations (as, for example, on droplets in atmosphere) we have to study at first the influence of an external field on capillary properties. Several exhaustive contributions were published showing the condition for increasing or decreasing the surface tension far from the critical point (Rocard 1951; Defay & Sanfeld 1967; Liggieri *et al.* 1994).

More recently we extended the theory to a region near the critical point (Gouin & Sanfeld 1997). The question is more precisely to evaluate the importance of an imposed external electric field on the behaviour of a polar gas–liquid interface. Such an approach needs the use of the thermodynamic theory of polarized layers (Sanfeld 1968, p. 72). In the presence of an electric field $\boldsymbol{E}$ for polar materials,

$$\mu = \mu^* - \frac{1}{8\pi}\int_0^{\boldsymbol{E}^2}\left(\frac{\partial\varepsilon}{\partial\rho}\right)_{T\cdot\boldsymbol{E}} \mathrm{d}\boldsymbol{E}^2 \quad \text{(e.s.c.g.s.u.)}, \tag{3.1}$$

where μ^* is the classical chemical potential at zero field, ε is the dielectric constant and ρ is the density. The quantity in the integral of equation (3.1) is called the polarization term. For $\partial\varepsilon/\partial\rho$ independent of ε, equation (3.1) reduces to

$$\mu = \mu^* - \frac{E^2}{8\pi}\frac{\partial\varepsilon}{\partial\rho}. \tag{3.2}$$

The extended initial conditions read

$$\frac{1}{\rho_{\mathrm{c}}}\left(\frac{\partial\mu}{\partial\rho}\right)^{\mathrm{c}} = \left(\frac{\partial^2\mu}{\partial\rho^2}\right)^{\mathrm{c}} = 0, \tag{3.3}$$

or

$$\frac{1}{\rho_{\mathrm{c}}}\left(\frac{\partial p}{\partial\rho}\right)^{\mathrm{c}} = \left(\frac{\partial^2 p}{\partial\rho^2}\right)^{\mathrm{c}} = 0. \tag{3.4}$$

By a limited expansion around the critical conditions we get

$$\frac{\partial p}{\partial\rho}(\rho_{\mathrm{c}\boldsymbol{E}}, T_{\mathrm{c}\boldsymbol{E}}) = \rho_{\mathrm{c}}\left(\frac{\partial^2\mu^*}{\partial\rho\partial T}\right)^{\mathrm{c}}(T_{\mathrm{c}\boldsymbol{E}} - T_{\mathrm{c}}). \tag{3.5}$$

The shift of the critical temperature is then deduced by

$$(T_{\mathrm{c}\boldsymbol{E}} - T_{\mathrm{c}}) = \frac{E^2}{8\pi}\rho_{\mathrm{c}}\left(\frac{\partial^2\varepsilon}{\partial\rho^2}\right)^{\mathrm{c}} \Big/ \left(\frac{\partial^2 p}{\partial\rho\partial T}\right)^{\mathrm{c}}. \tag{3.6}$$

Now in the absence of an applied electric field, σ can be expressed in terms of the spatial derivatives of ρ (Defay & Sanfeld 1974; Rowlinson & Widom 1984):

$$\sigma = \int_{\rho_{\mathrm{g}}}^{\rho_{\mathrm{l}}} [2c\psi(\rho, T)]^{1/2}\,\mathrm{d}\rho, \tag{3.7}$$

where ψ is the volume free-energy density. The density profile for the plane isothermal interface reads

$$C\frac{\mathrm{d}^2\rho}{\mathrm{d}z^2} = \mu^*(\rho, T) - \mu_0^*, \tag{3.8}$$

where μ_0^* is a constant.

In the critical region Rowlinson & Widom have shown the relation

$$\mu^* = \mu_0^* - A_0(T_{\mathrm{c}} - T)(\rho_{\mathrm{c}} - \rho) + B_0(\rho_{\mathrm{c}} - \rho)^3, \tag{3.9}$$

Table 1. *Surface tension of nitromethane near the critical point in the presence of an applied electric field*

	3×10^4 V cm^{-1}	10^5 V cm^{-1}	2×10^5 V cm^{-1}
van der Waals equation of state,	$\sigma_{\boldsymbol{E}} = 0.02$ dyn cm^{-1}	0.7 dyn cm^{-1}	5.5 dyn cm^{-1}
CCOR polar equation,	$\sigma_{\boldsymbol{E}} = 0.04$ dyn cm^{-1}	1.6 dyn cm^{-1}	12.6 dyn cm^{-1}

where

$$A_0 = \left(\frac{\partial^2 \mu^*}{\partial\rho\partial T}\right)^{\mathrm{c}} \quad \text{and} \quad B_0 = \frac{1}{6}\left(\frac{\partial^3 \mu^*}{\partial\rho^3}\right)^{\mathrm{c}}. \tag{3.10}$$

In an electric field μ^* must be replaced by μ. Considering then that the polarization term is a small quantity, which is a reasonable assumption, we then get the expression of σ in the presence of $\boldsymbol{E}$:

$$\sigma_{\boldsymbol{E}} = \frac{\sqrt{c}}{3B}[2A(T_{\mathrm{c}\boldsymbol{E}} - T)]^{3/2}, \tag{3.11}$$

where c is a constant associated to the mean field theory ($c \approx 0.5$ erg g^{-2} cm^5).

Taking now T equal to T_{c} at zero field, we finally obtain

$$\sigma_{\boldsymbol{E}} = \frac{2\sqrt{c}}{(\partial^3\mu^*/\partial\rho^3)^{\mathrm{c}}}\left[\boldsymbol{E}^2 \frac{(\partial^2\varepsilon/\partial\rho^2)^{\mathrm{c}}}{8\pi}\right]^{3/2}. \tag{3.12}$$

4. Results

In order to evaluate the shift of σ due to the field at a temperature corresponding to the critical value in the absence of the field, we use the Debye relation (Debye 1929, p. 36) and an equation of state.

The Debye relation reads

$$\frac{\varepsilon - 1}{\varepsilon + 2} = 4\pi\frac{N_{\mathrm{Av}}\rho}{3M}\left(\alpha + \frac{\boldsymbol{m}^2}{3kT}\right), \tag{4.1}$$

where M is the molar mass, α is the polarizability and $\boldsymbol{m}$ is the permanent dipolar moment. The results summarized in table 1 for nitromethane submitted to different electric fields show important discrepancies.

Several molecules were also studied using different equations of state (van der Waals, CCOR, Bender VO) and different relations giving $\varepsilon = \varepsilon(\rho)$. As predicted by equations (3.12) and (4.1), large values of the permanent dipolar moment increase the shift of σ. In all cases a constant applied field stabilizes the gas–liquid interface. More recently, electric field effects were investigated in non-ionic fluids near the critical point (Onuki 1995). This author derives an upward shift of the critical temperature proportional to the square of the field and also an induced dipolar interaction among the critical fluctuations.

5. Conclusions

The main purpose of this investigation was to first predict the influence of capillarity on chemical stability and, secondly, the effect of an applied electric field on surface tension near the critical point. It is clearly shown by using thermodynamic criteria that a stable (unstable) reaction in a volume phase can be destabilized (stabilized) when it occurs in a monolayer spread on a liquid surface. In the second part, we evaluate the shift of surface tension due to an applied electric field by using an extended expression for the chemical potential in the frame of mean field theory. Simple equations of state combined with the Debye relation for the dielectric constant show that the field tends to stabilize the gas–liquid interface. The larger the dipole moment the larger the shift of the surface tension. Significant values of the shift are obtained for nitromethane.

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Discussion

A. Passerone (*ICFAM-CNR, Genoa, Italy*). Is Professor Sanfeld's theoretical approach applicable to liquid–liquid interfaces, and in particular, to systems near the clouding point?

A. Sanfeld. When dealing with two immiscible liquids the situation is rather more complicated. Indeed, even far from the critical point the two fluids interpenetrate each other in a thin layer of a about a few molecular diameters. The density of each component changes regularly between the value in both bulk phases with a profile in accordance with the one of a liquid–vapour interface. Each density vanishes asymptotically in the complementary phase. For such an interfacial layer, density gradients are important.

Phase transitions induced by electric fields in near-critical polymer solutions have been recently studied by Wirtz & Fuller (1993). They show that the mixing of two-phase solutions induced by electric fields is a universal feature shared by a wide class of systems, including upper and lower critical point polymer solutions and mixtures of low-molecular-weight molecules in a solvent. The shift of the critical temperature is quadratic in the electric-field strength.

S. K. Wilson (*Department of Mathematics, University of Strathclyde, UK*). Professor Hondros raises the important question about the control of Marangoni flows. Considerable effort has already been devoted to the influence of various additional physical effects on the onset of Marangoni convection in a quiescent layer of fluid. For example, the effects of uniform rotation of the layer (Kaddame & Lebon 1994) and a uniform field (Wilson 1993) are now reasonably well understood.

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