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ORIGINAL CONTRIBUTION

Capillary theory of free fluid surfaces

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Abstract The traditional formulation of capillary theory does not explicitly contain the general dimension equation that is valid also for its own scalar variables. Its introduction enables the experimentally determinable physical properties to be interpreted. These properties individually characterize the bulk phases generating the layers that enter into the capillary interaction. Not only empirically known approximate relationships, such as the van der Waals and Walden equations, the Watson's formula, and the Cailletet–Mathias rule, can be derived through them, but also new findings can be made. By extending the formulation with a new type of parameters, the relationships of temperature, density-dependence, etc. may be directly generated. The individual concept, which differs from the traditional theory in only one extra power law, is compatible with other capillarity methods based on material structure and outperforms the heuristic power of the traditional theory in terms of operability.

Keywords Dimensional analysis · Law of similarity · Surface tension · Fluid/fluid interfaces

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Introduction

Classical capillarity theory [1–3] has been outstandingly successful. Its formulation involves the general (material-independent) interactions, in a more or less exact form: the Gibbs and Young equations, respectively, incorporate most adsorption and wetting effects. However, even the cardinal variables of the theory (such as solid surface tensions) cannot be determined within the traditional framework. In principle, the empirical rules for the free surface of fluids formed with their own vapor (e.g., temperature or density dependence) can be derived only with great difficulty.

The relationships for free surfaces are usually described by power functions containing critical state determinants, which can also be used to interpret a number of non-capillary effects [4]. However, such functions are seldom employed in the basic formulation, in spite of the correlation between the correspondence principle and the surface tension [5].

The theory can be extended only by introducing new variables (and their correlations). The general basic equation in the dimensional analysis [6–10] is a monomial power function. A capillary theory based on the traditional formulation can thus be constructed that is logically complete and also contains the empirical correlations. The formalism providing a scale-independent state description (parametric representation) is based on the resolution of collective variables such as the surface tension that are simultaneously dependent on the variables of adjoining bulk phases. At the same time, however, its separable quantities are multiplicative, in contrast to the dispersion, polar, and other components [11], which are additive [12].

This article focuses on additions to the formulation of the traditional theory and the determination of empirical relationships of free surface quantities, and on the applicability of the correspondence principle.

Basic theory

The existing relationships of capillarity and the general dimension equation form a coherent (algebraically compatible) system that can be unified. The state of the system is characterized by tensor order global canonical intensities of existing (thermal, strain, chemical material, electromagnetic, etc.) interactions and their scalar components $\{..., y_i,...\}$. At equilibrium, each of the latter quantities is separately equal in all phases. Furthermore, their relationships determine the values of the physical quantities related to the "locality" (e.g., intrinsic intensities). The so-called general dimension equation involves scalar variables; the variable set of the traditional formulation is constructed from the same type of physical quantities (scalar or reducible to scalar components): consequently, the former is ipso facto valid for the latter. Accordingly, the requirements of the general dimension equation are automatically fulfilled on the scalar surface tension $\gamma_{\varphi\psi}$, as they are implicitly present in the formulation. Thus, the character of the formulation interpreted by the unification is determined.

The surface tension is the Helmholtz energy of the free fluid surface, which, as a characteristic function, is a cardinal variable of capillarity. A descriptive theory can be based on it as, according to thermostatics, all analogous boundary layer quantities can be deduced from it.

The common affixes of the individual basic variables $\{\ldots, {}_{\phi}x_i, \ldots\}$ is the so-called material parameter

$$I_{\phi}(\ldots, {}_{\phi}x_i, \ldots) = \prod_i |{}_{\phi}x_i|^{\nu_i} \tag{1}$$

that determines the bulk phase potential for each phase ϕ based on the general dimension equation. ν_i is a universal invariable characterizing the ith interaction type. The product of the parameters of the adjoining phases

$$K_{\varphi\psi}(\ldots, {}_{\varphi}x_i; {}_{\psi}x_i, \ldots) = I_{\varphi} I_{\psi} \tag{2}$$

which may adopt only positive scalar values, determines the part of $K_{\varphi\psi}$ of the layer that is collective.

Equations 1 and 2 express the relationships between the various system domains (e.g., boundary layers separating fluid phases from bulk phases φ and ψ due to the transitive character of the equilibrium). Consequently, the collective layer quantities may be separated to the independent and individual state parameters of the bulk domains. These equations can be generalized to other boundary quantities derived from the γ_{LV}, and τ_{LV}^{eff} variables [12].

The basic quantities of the formulation and the material parameters may be interpreted in several ways by virtue of the product character of the power laws. The magnitude of the collective layer quantities is strictly fixed in accordance with the relationships of the traditional formulation. This holds also if the relationships contain the basic quantities $\{\ldots, \overline{{}_{\phi}x_i}, \ldots\}$ produced by the similarity transformation ${}_{\phi}x_i \rightarrow k_{i\phi}x_i \equiv \overline{{}_{\phi}x_i}$, instead of the material parameters $\{\ldots, {}_{\phi}x_i, \ldots\}$, in the case where the relationship

$$\chi_{\phi} = \prod_i |{}_{\phi}x_i|^{\nu_i} \equiv |k_{j\phi}x_j|^{\nu_j} \prod_i{}^{(j)} |k_{i\phi}x_i|^{\nu_i}$$

$$= \prod_i |k_i|^{\nu_i} \prod_i |{}_{\phi}x_i|^{\nu_i}$$

also holds, meaning that the compatibility condition $\prod_i |k_i|^{\nu_i} = |k_j|^{\nu_j} \prod_i{}^{(j)} |k_i|^{\nu_i} \equiv 1$ is satisfied by the dimensionless similarity parameters $\{...,k_i, k_j,...\}$. The validity of the latter is preserved if the similarity parameters are all arbitrary, with the exception of only one factor k_j. The basic variables may therefore also adopt various values.

The compatibility condition may be generalized. The value of the collective quantity $K_{\varphi\psi}$, from Eq. 2, is also invariant under the exchange of the material parameters $\overline{\chi_{\phi}} = k_{\phi}\chi_{\phi}$ and their similarity transforms, provided that $k_{\varphi} = (1/k_{\psi})$. The interactions are a priori equivalently characterized in the relationships, instead of basic factors, by their compatible similarity-transformed derivatives in any given choice.

The relationships in traditional capillarity theory that are defined to interpret collective quantities can be expressed in parametric representation, where the phases of the system are characterized exclusively by material parameters [12].

The numerical value of the material parameter is also accessible without the basic interaction quantities. However, the relationships characterizing the various physical and chemical–material interactions can be determined only if the formulas of the basic quantities are known.

Approximate formulas for the critical state and basic quantities

The state of the free fluid phase pairs is determined by the algebraic expressions of the interaction basic quantities in all points of the coexistence domain. The domain of existence of a one-component system that simultaneously contains liquid and vapor phases is represented in the state diagram by the vapor pressure curve. The density of the (equilibrium–) fluid phases in the intermediate domain changes antibatically with the temperature, according to observations (Cailletet–Mathias rule [13]). If the curve is extended, the system transforms in extreme states to a solid/vapor phase pair, or, above the critical temperature T_{crit}, to a single phase, the fluid state. Accordingly, in contrast to the triple point phase transition, in the critical state the densities necessarily equilibrate. The change of state is simultaneously characterized by the equilibration of the potential of the bulk phases, or rather of the boundary surface of the layer. In homogenous domains, however, there is no boundary layer. Only intrinsically zero collective capillary quantities can be assigned to homogenous areas of the system.

According to the transformation formula 2, the state quantities of coexistent phase pairs (e.g., the collective γ_{LV} and the individual χ_L and χ_V variables) span a hyperbolic paraboloid. Thus, if any one of them is zero, then (and only then) all the other quantities also necessarily vanish. Consequently, the material parameters of the coexistent phases, in agreement with Eq. 2, also contain at least one so-called pseudolocal basic quantity with identical $\mapsto_\phi x_i$ substitution value (calculated with the same algebraic formula). The pseudolocal basic quantities characterize the coexistent phases as a property of the system. Their value disappears at the critical state: the descriptive formulas of the various interactions can actually be determined on the basis of this feature.

The basic variable determining the temperature dependence is the function of the canonical temperature T, ${}_\phi x_T(T)$, that is equal in all points of the adjoining phases. This function, which is positive, single-valued, continuous, and strictly monotonic, can be separated dichotomically in the material parameter expression from the collective affixes of the other independent interactions

$${}^0\chi_\phi = \prod_i {}^{(T)}\left|{}_\phi x_i\right|^{\nu_i}$$

Both are replaceable by their similarity transforms satisfying the compatibility condition. Thus, an analytic function (i.e., transformable to a power series based on its algebraic structure) $k_{T\phi}x_T = |\tau(T)|$ usually corresponds to the dimension equation of the thermal basic quantity, the MacLaurin series of which is

$$\tau(T) \cong {}_0c_\phi + {}_1c_\phi T + {}_2c_\phi T^2 + \ldots + {}_nc_\phi T^n + \ldots + O(\ldots, T, \ldots)$$

(The elements of the infinite group $\left\{{}_0c_\phi, \ldots, {}_ic_\phi, \ldots\right\}$ are constants that discretely characterize the phase system $\phi \in \{\varphi;\ \psi\}$). The polynomial $\tau(T)$ can be satisfactorily substituted in a domain in which terms of order higher than T converge sufficiently fast to zero in a finite partial polynomial. The thermal virial equation

$$\tau^{(n)}(T) \cong {}_nc_\phi\left\{\frac{{}_0c_\phi}{{}_nc_\phi} + \frac{{}_1c_\phi}{{}_nc_\phi}T + \ldots + \frac{{}_{n-1}c_\phi}{{}_nc_\phi}T^{n-1} + T^n\right\} = {}_nc_\phi \sum_{k=0}^{n} \frac{{}_kc_\phi}{{}_nc_\phi} T^k \tag{3}$$

expresses the relationship in the nth order approximation $\left({}_nc_\phi \neq 0\right)$, which is also valid for the free surface. The condition $\chi_\phi(T_{\text{crit}}) = 0$ necessarily holds for the material parameter of the vanishing phases of the critical state. Thus, owing to the invariance of the temperature independent quantity ${}^0\chi_\phi$, $\tau^{(n)}(T_{\text{crit}}) \equiv 0$ is simultaneously true. The only existing value of T_{crit} is also the only root of the equation (with n-multiplicity). It follows that Eq. 3 is necessarily the nth order binomial expression of the quantities T and T_{crit}

$$\tau^{(n)}(T) = {}_nc_\phi (T - T_{\text{crit}})^n = {}_nc_\phi \left\{ \sum_{k=0}^{n} \left\{ \binom{n}{k} (-1)^k T_{\text{crit}}^{k-1} \right\} T^k \right\} \tag{4}$$

The exponent n may be fractional or negative. Comparison of Eqs. 3 and 4 yields ${}_nc_\phi = -\left({}_1c_\phi / n\, T_{\text{crit}}^{n-1}\right)$, where $\left({}_1c_\phi \neq 0\right)$. With the introduction of the reduced temperature $T_{\text{red}} = (T/T_{\text{crit}})$, the thermal basic quantity gives $\tau^{(n)}(T) \equiv \left|-{}_1c_\phi \frac{1}{n} T_{\text{crit}}(T_{\text{red}} - 1)^n\right|$.

The material parameter, because $T_{\text{red}} \leq 1$ in the liquid/vapor coexistence domain, is

$$\chi_\phi = {}^0\chi_\phi \{k\, |{-{}_1c}|^{\nu_T}\} \left(\frac{1}{n} T_{\text{crit}}(1 - T_{\text{red}})^n\right)^{\nu_T}.$$

The function $\tau^{(n)}$ (T) contains the factor ${}_1c_\phi$ in all possible approximations. The number k, which is a free variable, can be chosen to satisfy the compatibility condition $k = \left(1/\left|-{}_1c_\phi\right|^{\nu_T}\right)$. Thus $k_T = \left|-{}_1c_\phi\right|^{\nu_T}$, i.e., the quantity in braces is unity. However, according to the interpretation ${}^0\chi_\phi$ is the total value of the nonthermal increment, and consequently the expression for the thermal basic quantity in the nth order approximation is

$${}_\phi x_T(T) = \left(\frac{1}{n} T_{\text{crit}}(1 - T_{\text{red}})^n\right)$$

while that of the material parameter is

$$\chi_\phi = {}^0\chi_\phi \left\{\frac{1}{n} T_{\text{crit}}(1 - T_{\text{red}})^n\right\}^{\nu_T} \tag{5}$$

For gases, on the other hand, the parameters do not vanish even in critical state, and hence their formulas necessarily differ from the expressions in liquid/vapor systems.

The material parameters of the phases can be expressed in terms of various independent basic variables that have a different meaning but can be mapped into each other.

The virial equation, which has the same form as Eq. 3, can be established for all of the relevant basic quantities (e.g., pressure and density dependence). The analogous expressions, in which T is replaced by p or the density difference $\Delta\rho$, contain different constants $\left\{{}_0C_\phi, \ldots, {}_nC_\phi\right\}$.

Thus, relationships completely analogous to the above can be defined for the basic variable of the deformation interaction, which is a function of the canonical pressure. The chemical–material interaction is characterized by the deviation of the bulk phase densities $\rho_{\phi} : \Delta\rho = \rho_L - \rho_V$. $\Delta\rho$ is a pseudolocal quantity of the free fluid boundary layer, as it is an indirect function of the temperature and pressure. The material parameter defined as a function of the density difference can be defined analogously to the temperature relationships as the product of the collective increment of the interaction quantities ${}^{0}\chi_{\phi}^{(\rho)}$, which are independent of the temperature, pressure, etc., that determine the density, and the factors $\left\{{}_{\phi}x_{\rho}(\Delta\rho)\right\}^{\nu_{\rho}}$. At the critical state $\Delta\rho$ disappears owing to the homogenization of the phase pair. For the zero root, according to the fundamental theorem of algebra,

$$ {}_{\phi}x_{\rho}(\Delta\rho) = {}_{n}C_{\phi}\left(\Delta\rho - \Delta\rho^{(\mathrm{crit})}\right)^{n} \equiv {}_{n}C_{\phi}(\Delta\rho)^{n} $$

Thus, using a compatible similarity transformation, the material parameter formula can be produced

$$ \chi_{\phi}(\Delta\rho) = \left({}^{0}\chi_{\phi}^{(\rho)}\right)\left({}_{\phi}x_{\rho}(\Delta\rho)\right)^{2\nu_{\rho}} = {}^{0}\chi_{\phi}^{(\rho)}\left((\Delta\rho)^{n}\right)^{\nu_{\rho}} \qquad (6) $$

In the critical state, the difference $\Delta^{(2)}\rho = \rho_L^2 - \rho_V^2$ also disappears. Thus the pseudolocal basic quantity and the material parameter can both be defined for the difference, even with different exponents. According to the Gibbs phase rule, which restricts simultaneous application of the derived approximation formulas, a two-phase heterogeneous system has (i−2) degrees of freedom, where i is the number of allowed interactions. The number of independent canonical intensive variables $\{\ldots,y_i,\ldots\}$ determining the change of state remains the same. In a one-component system, where i=3, only one independent state variable can be defined in its domain of existence. Consequently, its surface tension can only change simultaneously either with temperature T, or, exclusively, with pressure or phase densities depending on chemical potential etc. The basic quantities $\arg\left(\chi_{\phi}\right)$, however, by virtue of the power function of Eq. 1 and the Gibbs–Duhem equation, mutually determine each other's value unambiguously (e.g., the temperature, pressure, etc. determine the density conditions, and vice versa).

The basic quantities of the various interactions in the parametric description determine the expressions of the material parameters unambiguously.

Uniqueness of the state equations of the free fluid surface

The individual state variables indirectly determine the capillary quantities derived from surface tension.

From Eqs. 2 and 5, together with the quantity $\left\{{}^{0}\chi_{\varphi}{}^{0}\chi_{\psi}\right\} = {}^{0}\gamma_{\varphi\psi}$. formed from the temperature-independent basic quantities, the surface tension can de defined by the general relationship

$$ \gamma_{LV} = {}^{0}\gamma_{LV}\,{}_{\phi}x_T^{2\nu_T} = {}^{0}\gamma_{LV}\left\{\frac{1}{n}T_{\mathrm{crit}}\left(1 - T_{\mathrm{red}}\right)^{n}\right\}^{2\nu_T} $$

Using this expression, the thermal coefficient

$$ \begin{aligned} \left(\frac{\partial\gamma_{LV}}{\partial T}\right) &= \gamma_{LV}\left\{2\nu_T\left(\frac{\partial \ln {}_{\phi}x_T}{\partial T}\right)\right\} \\ &= -\gamma_{LV}\left\{2\nu_T n\frac{1}{(T_{\mathrm{crit}} - T)}\right\} \qquad (7) \end{aligned} $$

and the Gibbs–Helmholtz equation $u_{LV} = \gamma_{LV} - T(\partial\gamma_{LV}/\partial T)$ can be formulated. Hence, the expression for the internal energy u_{LV} (T) of the layer

$$ \begin{aligned} u_{LV} &= \gamma_{LV}\left[1 - 2\nu_T\left(\frac{\partial \ln {}_{\phi}x_T}{\partial \ln T}\right)\right] \\ &= \gamma_{LV}\left\{1 + 2\nu_T n\frac{T}{T_{\mathrm{crit}} - T}\right\} = \gamma_{LV}K_{LV} > \gamma_{LV} \qquad (8) \end{aligned} $$

is obtained from the surface tension in a single factor K_{LV}. According to Eq. 7 the exponent ν_T can be defined as

$$ \nu_T = \frac{1}{2}\left(\frac{\partial \ln \gamma_{LV}}{\partial \ln {}_{\phi}x_T}\right) = -\frac{1}{2}\frac{1}{\gamma_{LV}}\left(\frac{\partial\gamma_{LV}}{\partial T}\right)\left(T_{\mathrm{crit}} - T\right)\frac{1}{n} \qquad (9) $$

Its sign determines the sign of $\left(\partial\gamma_{\varphi\psi}\big/\partial T\right)$. The order of the virial approximation of the thermal basic variable can be determined unambiguously and exactly from experimental data. The substitution value of ${}_{\phi}x_T$, with fixed T, depends also on the order n of the approximation. The magnitude of the characteristic quantities is, however, not arbitrary, owing to the universality of ν_T. From Eqs. 5 and 6, the relationships

$$ \begin{aligned} \ln\chi_{\phi} &= \ln\left({}^{0}\chi_{\phi}\right) + \nu_T \ln\left({}_{\phi}x_T\right) \quad \text{and} \quad \ln\gamma_{LV}(T) \\ &= \ln {}^{0}\gamma_{LV} + 2\nu_T \ln {}_{\phi}x_T(T) \end{aligned} $$

can be formulated between χ_{ϕ} or γ_{LV} and the substitution value of the basic variable ${}_{\phi}x_T(T)$ containing the temperature in nth order. These determine straight lines with the same gradient for all liquid/vapor phase pairs. Figure 1 shows the calculated quantities from surface tension [14] measured over a relatively wide temperature range for selected fluids.

The linearity is already fulfilled in the so-called first-order approximation, with an average value of ν_T=0.5634, except for water, the deviation of which can also be reduced, e.g., in noninteger order (n=0.6) ν_T=0.7027.

The exponent of the fractal analogue power relationships defined for the individual formulation variable set determines the universality class of the effects. Its value is strictly fixed in the derived expressions.

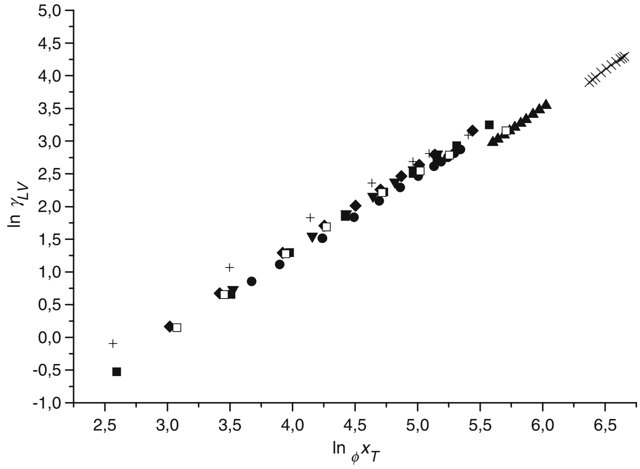

Fig. 1 $\ln\gamma_{LV}(T)$vs. $\ln{}_\phi x_T(T)$ functions of various liquids calculated from the temperature dependence of their surface tension. *Filled square*, carbon tetrachloride; *filled circle*, chlorobenzene; *times sign*, water; *upright triangle*, dimethyl aniline; *inverted triangle*, diethylether; *diamond*, ethyl acetate; *plus sign*, ethanol; *open square*, acetic acid. ν_T=0.5634

Empirical expressions for the free surface

Usually, all empirical expressions in capillarity can already be derived with the linear approximation assumption for the thermal basic quantity. Thus, from Eq. 6, with the linear approximation, the temperature dependence of the free surface tension is determined from

$$\gamma_{LV}(T) = \left({}^0\gamma_{LV} T_{\text{crit}}\right)\left(1 - T_{\text{red}}\right)^{2\nu_T}.$$

This contains variables with the same property in the same algebraic position as the van der Waals equation $\gamma_{LV} = A\left(1 - [T/T_{\text{crit}}]\right)^N$ (A is temperature-independent, N is constant [15]). The expressions are therefore equivalent. From Eq. 5, with the nth order thermal basic quantity approximation, the expression

$$\chi_\phi(T) = \chi_\phi(T_{\text{ref}})\left(\frac{1 - T_{\text{red}}}{1 - T_{\text{red}}^{\text{ref}}}\right)^{n\overline{\nu_T}} \tag{10}$$

is valid for the current (T) and reference (T_{ref}) temperatures. The material parameter can be thus determined on the basis of one single value with respect to the temperature $T_{\text{red}}^{\text{ref}}$, and the value of surface tension belonging to any temperature T can be determined using the transformation formula 2. Figure 2 shows the data from carbon tetrachloride at a reference temperature of 20 °C, determined by calculation (based on a surface tension of 25.68 mN/m) and measurement [14].

The collective characteristic quantities can also be determined from the formulas for surface tension. The expressions can also be used for normal freezing $T^{(\text{frig})}$ and boiling points $T^{(\text{ebu})}$

$$\frac{\gamma_{LV}\left(T^{(\text{ebu})}\right)}{\gamma_{LV}\left(T^{(\text{frig})}\right)} = \left(\frac{T_{\text{crit}} - T^{(\text{ebu})}}{T_{\text{crit}} - T^{(\text{frig})}}\right)^{2\nu_T} \equiv \left(\frac{1 - T_{\text{red}}^{(\text{ebu})}}{1 - T_{\text{red}}^{(\text{frig})}}\right)^{2\nu_T}.$$

Thus, the ratio of the surface tensions of systems having similar temperature quotients is the same, in agreement with the Lorenz–Herz equation [16]. The expression relating to the boiling point, derived identically from Eq. 7,

$$\frac{T^{(\text{ebu})}}{T_{\text{crit}}} = T_{\text{red}}^{(\text{ebu})} = 1 + 2\nu_T n \frac{1}{T_{\text{crit}}} \frac{\gamma_{LV}}{(\partial\gamma_{LV}/\partial T)} = Q,$$

is a statement of the empirical Guldberg rule [17]. The quotient Q, which is equal only for systems with the same reduced boiling point, is usually not fixed, but is a function of the chemical–material quality. The rule is only an approximation, although its analog can be applied for the normal melting point.

According to the empirical Trouton rule, the relationship $\left(\lambda^{(\text{ebu})}\big/T^{(\text{ebu})}\right) \approx 21$ is valid for the heat of evaporation $\lambda^{(\text{ebu})}$ (measured in [calories/mole]) at the normal boiling point [18]. The heat of evaporation $\Lambda^{(\text{ebu})}$ (measured in calories/gram) is given by $\lambda_\nu^{(\text{ebu})} = \Lambda^{(\text{ebu})}\rho_L^{(\text{ebu})}V_M^{(\text{ebu})}$, where $\rho_L^{(\text{ebu})}$ (g/cm^3) is the liquid density and $V_M^{(\text{ebu})}$ is the molar volume. Thus, because $2\nu_T \approx 1$, using the Guldberg rule the basic formula for the surface tension can be written in the following approximate form

$$\gamma_{LV}^{(\nu)} \approx \left\{{}^0\gamma_{LV}\left[\frac{V_M^{(\text{ebu})}}{21}\left(\frac{1}{T_{\text{red}}^{(\text{ebu})}} - 1\right)\right]\right\}\rho_L^{(\text{ebu})}\Lambda^{(\text{ebu})}$$

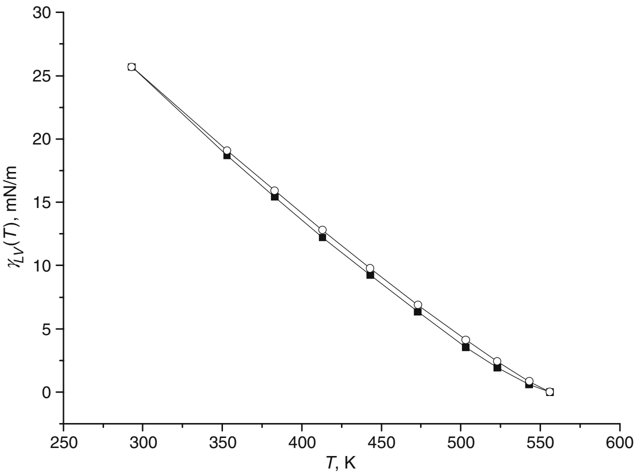

Fig. 2 Comparison of measured (*square*) [14] and calculated (*circle*) surface tension data for carbon tetrachloride

The Walden rule [19] $\gamma_{LV}(T_v) \approx k\Lambda^{(\mathrm{ebu})}\rho_L^{(\mathrm{ebu})}$ contains the same quantities and the empirical constant k. The mutually identical expressions are equivalent.

The state quantities of phase pairs (denoted $'$ and $''$) of different chemical–material quality are comparable, if the relation $\gamma'_{LV}(T') = \gamma''_{LV}(T'')$ is fulfilled by the free surface tensions at temperatures T' and T''. The derived general formula follows from Eq. 6,

$$\frac{(T'_{\mathrm{crit}} - T')^{n'}}{(T''_{\mathrm{crit}} - T'')^{n''}} = 2\nu_T \sqrt{\frac{{}^0\gamma''_{LV}}{{}^0\gamma'_{LV}}}\left(\frac{n'}{n''}\right)\frac{(T'_{\mathrm{crit}})^{n'-1}}{(T''_{\mathrm{crit}})^{n''-1}}.$$

Hence, with the approximation $n' = n'' = 1$, the temperature-invariant Carr–Wolczynski equation follows [20]:

$$\frac{T'_{\mathrm{crit}} - T'}{T''_{\mathrm{crit}} - T''} = \mathrm{const.}$$

The expression for the surface tension, from Eqs. 6 and 2, $\gamma_{LV} = C_\rho(\rho_L - \rho_V)^{2\nu_\rho}$, contains the densities of the coexisting phases (C_ρ is the density-independent product ${}^0\chi_L^{(\rho)}{}^0\chi_V^{(\rho)}$); the density exponent can be calculated from the logarithmic plot. Figure 3 shows the relationship of measured values for benzene and ethyl ether [21]. The exponent is practically equal to that of the McLeod formula [22].

The surface tension can be reliably approximated numerically by the Brock–Bird formula

$$\gamma_{LV} = \left\{(-0.281 + 0.133\alpha_{\mathrm{crit}})T_{\mathrm{crit}}^{1/3}p_{\mathrm{crit}}^{2/3}\right\}(1 - T_{\mathrm{red}})^{11/9}$$

where p_{crit} is the critical pressure [23] and α_{crit} the Riedel critical parameter [24]; the quantity in braces is the variable ${}^0\gamma_{LV}$, which depends on the chemical–material quality according to Eq. 6.

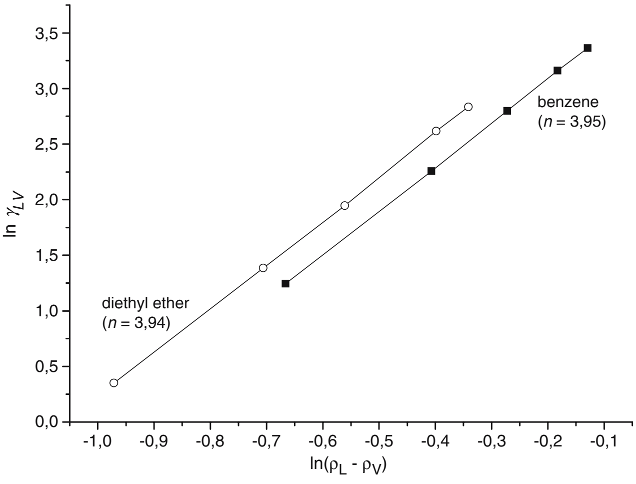

Fig. 3 Illustration of the $\gamma_{LV} = C_\rho(\rho_L - \rho_V)^{2\nu_\rho}$ relationship for benzene and ethyl ether. The ν_ρ density exponents derived from the slopes is practically equal to that of the McLeod formula

Empirical relations for free surfaces can be expressed in terms of the individual concept.

Surfaces of immiscible and partially miscible liquids

Expressions that are valid for the capillary quantities of free surfaces can be generalized to the boundary layer of two liquids.

The state of bulk phases of immiscible liquids $\{L'; L''\}$ does not change after the formation of the joint boundary layer if neither of the liquids occludes the other component from the mixed vapor phase. Thus, the parameters of the liquids are equal to those of free surfaces in the presence of closed boundary layers:

$$\chi'_L = {}^0\chi'_L\left\{\frac{1}{n'}T'_{\mathrm{crit}}\left(1 - T'_{\mathrm{red}}\right)^{n'}\right\}^{\nu_T},$$

$$\chi''_L = {}^0\chi''_L\left\{\frac{1}{n''}T''_{\mathrm{crit}}\left(1 - T''_{\mathrm{red}}\right)^{n''}\right\}^{\nu_T}.$$

However, the parameter $\widetilde{\chi}_V$ of the mixed vapor phase differs from χ'_V and χ''_V of pure vapors: The surface tensions of the layers of the liquids formed with the joint vapor are therefore different from those prevailing with their own vapor phases at the free surface. The temperature dependence of the interfacial tension in the common existence domain of the two liquids is determined by Eq. 2. By applying the appropriate approximate basic quantity in nth order, the experimentally verifiable linearized relationship is formed,

$$\ln\gamma_{L'L''}(T) = \ln{}^0\gamma_{L'L''} + \nu_T\ln\left[\frac{T'_{\mathrm{crit}}T''_{\mathrm{crit}}}{n'n''}\left(1 - T'_{\mathrm{red}}\right)^{n'}\left(1 - T''_{\mathrm{red}}\right)^{n''}\right]$$

The previously determined exponent can be obtained for water/carbon-tetrachloride system [14] with the approximation $n' = n'' = 0.6$ (Fig. 4).

The validity of the relationships is, in principle, extendable to partially miscible liquids.

Systems may in general display lower $T_{\mathrm{mix}}^{(\mathrm{inf})}$ and upper $T_{\mathrm{mix}}^{(\mathrm{sup})}$ separation temperatures (e.g., nicotine/water). A critical state belongs to both temperatures: The homogenous miscible phase separates into two different liquid phases (of fixed composition and in equilibrium with the same vapor mixed phase) at T values above the lower separation temperature and below the upper temperature. The virial equation of the system, consisting of separated liquid and equilibrated mixed vapor, has necessarily two

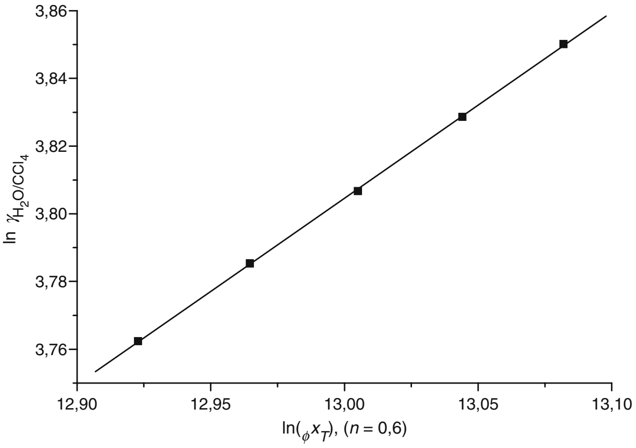

Fig. 4 The validity of the relationships is extendable to partially miscible liquids: calculated temperature dependence of the surface energy of water/carbon tetrachloride interface. The equation of the fitted line is: $y=-3.34+0.55x$

roots (with same multiplicity), according to the two states. In general, $\tau^{(n)}(T) = {}_n c_\phi \left(T_{\text{mix}}^{(\text{inf})} - T\right)^{n/2} \left(T_{\text{mix}}^{(\text{sup})} - T\right)^{n/2}$, where, with a compatible choice of similarity parameters, the material parameter is

$$\overline{\chi_\phi} = \overline{{}^0\chi_\phi} \left\{ \frac{1}{n} \sqrt{T_{\text{mix}}^{(\text{inf})} T_{\text{mix}}^{(\text{sup})}} \left(\left(1 - T_{\text{mix,red}}^{(\text{inf})}\right) \left(1 - T_{\text{mix,red}}^{(\text{sup})}\right) \right)^{n/2} \right\}^{\nu_T}. \tag{11}$$

Thus, both the interfacial tension and the surface tension formed by the free layers with the mixed vapor phase of the separated liquid disappears at both critical states, according to Eq. 2 (however, the surface tension of the system containing homogenous liquid and vapor formed in phase transition at the boundary curve of the existence range does not disappear because their constants in Eq. 5 are different). The above expression is valid for systems (e.g., triethyl amine/water or phenol/water) having one single (lower or upper) critical mixing temperature.

Formulas for free surfaces can be generalized to the boundary surfaces of liquids formed with other liquids based on the parametric representation.

Relationships of individual quantities

The measurement instructions of individual variables can usually be unambiguously given from the linearly approximated thermal basic quantity.

The algebraic expressions derived from Eq. 8 that define the surface tension and energy at the same temperature differ only in the value of parameter $K = \{1 + 2\nu_T n [T/(T_{\text{crit}} - T)]\} > 0$, which varies for phase pairs. Thus, the material parameters

$$u_\phi(T) = \sqrt{K}\chi_\phi(T) \tag{12}$$

can be defined for the internal energy, and the analogue of Eq. 2 $u_{LV}=u_L u_V$ relating to the tension parameters also holds. From Eq. 7, the specific entropy s_{LV} of the layer is

$$\begin{aligned} s_{LV}(T) &= -\left(\frac{\partial \gamma_{LV}}{\partial T}\right) \\ &= \left\{\chi_L \sqrt{\frac{2\,\nu_T\, n}{T_{\text{crit}} - T}}\right\} \left\{\chi_V \sqrt{\frac{2\,\nu_T\, n}{T_{\text{crit}} - T}}\right\} \\ &= s_L(T) s_V(T), \end{aligned} \tag{13}$$

i.e., the negative of the surface tension temperature coefficient (the temperature dependence of the temperature coefficient is hyperbolic, as ν_T and T_{crit} are fixed, and the exponent n of the thermal basic quantity is probably also constant in the existence range). From the equation the entropy parameters are also definable, so the validity of the formula 2 can be extended to the entropy.

The collective state quantities of the phase pairs are temperature-dependent, but the relation of the parameters $(u_L/u_V) = (s_L/s_V) = (\chi_L/\chi_V) \equiv ({}^0\chi_L/{}^0\chi_V)$ is temperature-independent and invariant.

The traditional formulation of the capillarity theory contains only in part the state quantities characterizing the thermal interactions of the free fluid phase boundary layers.

Properties ν_T, u_{LV} of the thermal interaction can be entirely determined from Eqs. 8 and 9. Table 1 contains values from measured data [14, 24–27].

The arithmetic average of the universal exponent ν_T is 0.5745 (in a linear approximation), which is in good agreement with that given above based on linearization. The value of the quantity $2\nu_T$ is also in good agreement with the experimentally determined value of the power exponent (n=1.17) of the van der Waals equation [28], and with the average (5/4)=1.25 calculated from data measured on a relatively large number of systems [29, 30]: The surface tension is only approximately linear function of the temperature. The material constants ${}^0\gamma_{\varphi\psi}$, ${}^0\chi_\phi$, u_ϕ, and s_ϕ, absent in the traditional theory, can be calculated from Eqs. 5, 6, 12, and 13 (Table 2).

The variables and formulas determining the temperature dependence of the free surface basic quantities of the individual representation can be determined within the frames of the apparatus.

Relation between the boundary layer and the bulk phase quantities

From the expressions containing the reduced temperature, relationships containing only bulk phase quantities can also be determined. The alternative formula for the surface

Table 1 Calculated material parameters of selected liquids (based on the data reported in [14], [21], [25–27])

Fluid	T (K)	T_{crit} (°C)	γ_{LV} (mN/m)	$-(\gamma_{LV})'_T$ (mN/m)	V_M (cm^3/mol)	u_{LV} (mN/m)	v_T
Argon	87.1	150.9	12.68	0.24	28.8	33.68	0.6053
Xenon	164.1	289.7	18.46	0.15	37.3	43.83	0.5259
Nitrogen	77.7	126.1	8.3	0.22	34.7	25.76	0.6643
Oxygen	90.4	154.8	13.1	0.256	14.0	36.25	0.6282
Fluorene	71.1	144.2	12.29	0.164	33.3	23.96	0.4870
Chlorine	201.1	417.2	33.65	0.189	47	71.66	0.6066
Carbon monoxide	81.1	411.9	9.6	0.2073	36.7	26.42	0.5754
Ammonia	244.1	405.6	41.8	0.38	24.7	134.58	0.7336
Water	293.1	647.2	76.64	0.147	18	119.73	0.3395
Hexane	293.1	508.0	18.4	0.102	130.5	48.30	0.5953
Heptane	293.1	571.4	21.6	0.095	162.3	49.45	0.6117
Octane	293.1	594.6	22.85	0.0934	178.8	50.23	0.6159
Decane	293.1	563.7	28.8	0.11	84.3	61.04	0.5165
Cyclohexane	293.1	554.2	25.24	0.118	180	59.83	0.6101
Benzene	293.1	563.6	28.8	0.11	84.3	61.04	0.6165
Toluene	293.1	594.0	28.52	0.118	106.3	63.11	0.6222
Chloroform	298.1	536.2	26.67	0.129	79.6	65.13	0.5755
Carbon tetrachloride	298.1	562.3	26.48	0.122	96.4	62.85	0.6083
Chlorobenzene	298.1	632.4	26.67	0.129	101.7	65.13	0.8082
Iodobenzene	293.1	721.2	39.27	0.112	111.3	72.10	0.6103
Methanol	293.1	513.2	22.5	0.077	40.2	45.07	0.3764
Ethanol	293.1	516.7	22.39	0.0832	58.3	46.78	0.4152
Propanol	293.1	536.9	23.71	0.0777	74.2	46.48	0.3993
Octanol	293.1	658.2	27.5	0.0795	158	50.80	0.5275
Acetic acid	293.1	595.0	27.59	0.0994	57.2	56.73	0.5436
Acetone	298.1	508.2	24.02	0.112	73.3	57.41	0.4895
Dioxane	293.1	587.2	33.45	0.139	85.2	74.19	0.6108
Methyl acetate	295.1	506.9	25.7	0.11	79.9	58.16	0.4530
Pyridine	293.1	620.2	37.21	0.13	80.5	75.32	0.5712
Butyl amine	293.1	524.2	24	0.1122	98.8	56.89	0.5399
Propionitrile	293.1	564.4	27.32	0.103	70.3	57.51	0.5112
Butyronitrile	293.1	582.3	27.44	0.103	86.8	57.63	0.5425

Table 2 Calculated material constants absent in the traditional capillary theory for selected fluids

Fluid	${}^0\chi_L$ (mN/m)$^{1/2}$	${}^0\chi_V$ (mN/m)$^{1/2}$	${}^0\gamma_{LV}$ (mN/m)	u_L (mN/m)	u_V (mN/m)	s_L	s_L
Water	0.9764	1.3783	0.9446	8.9513	12.6361	0.3136	0.4427
Chloroform	0.2690	0.1675	0.0490	9.8109	6.1087	0.4366	0.2718
Carbon tetrachloride	0.2274	0.1431	0.0299	10.4237	6.5582	0.4592	0.2889
Hexane	0.2924	0.1113	0.0307	11.5870	4.4115	0.5324	0.2027
Heptane	0.2600	0.1045	0.0269	11.0674	4.4505	0.4956	0.1993
Octane	0.2258	0.0981	0.0220	10.6932	4.6754	0.4686	0.2036
Benzene	0.3822	0.2281	0.0884	10.0423	5.9944	0.4262	0.2511
Toluene	0.1930	0.1249	0.0234	10.0085	6.4774	0.4327	0.2800
Cyclohexane	0.2389	0.1163	0.0284	10.9682	5.3383	0.4870	0.2370
Octanol	0.2959	0.1811	0.0544	9.0424	5.5368	0.3576	0.2190
Acetic acid	0.2781	0.1989	0.0555	6.3598	0.9967	0.3721	0.2662
Acetone	0.5073	0.2444	0.1278	10.7515	5.1798	0.4748	0.2287
Methyl acetate	0.6462	0.3106	0.2007	11.0008	5.2874	0.4783	0.2299
Chlorobenzene	0.0605	0.0456	0.0022	10.3669	7.8209	0.4613	0.3480
Bromobenzene	0.1764	0.1500	0.0256	9.2094	7.8317	0.3753	0.3192

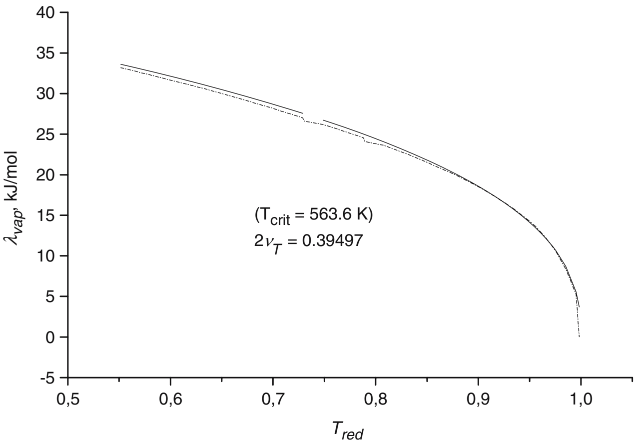

Fig. 5 Illustration of Eq. 14 for benzene. *Dotted line*, measured data; *solid line*, calculated data

tension contains both the difference of the temperature-dependent potentials of the adjoining phases and the effective layer thickness. Using Eqs. 2 and 5, this gives

$$^{0}\gamma_{LV}\left\{\frac{1}{n}T_{\text{crit}}(1-T_{\text{red}})^{n}\right\}^{2\nu_T}=\frac{1}{2}\left|u_L^0-u_V^0\right|\tau_{LV}^{\text{eff}}$$

The same potential difference can be used to express the heat of evaporation per unit volume of a component of relative molecule weight M and density ρ_L upon being transferred from the liquid to vapor phase with density ρ_v and $\lambda_{\text{vap}}=\left(\left|u_L^0-u_V^0\right|M/\rho_L\right)$. Thus, the surface tension of the a phase pair is

$$\gamma_{LV}=\left(\frac{1}{2}\frac{\rho_L}{M}\tau_{LV}^{\text{eff}}\right)\lambda_{\text{vap}}.$$

In this expression both the effective layer thickness and the liquid density are temperature-dependent. On increasing the temperature, the latter usually decreases, while the layer thickness increases. We may suppose that the two effects annul each other, and $\left(\rho_L\tau_{LV}^{\text{eff}}\right)\approx$ const. The surface tension and the evaporation heat are thus proportional. Therefore,

$$\begin{aligned}\lambda_{int}(T)&=\left\{2\frac{^{0}\gamma_{LV}M}{\rho_L\tau_{LV}^{\text{eff}}}\left[\frac{1}{n}T_{\text{crit}}\right]^{2\nu_T}\right\}(1-T_{\text{red}})^{2\nu_T n}\\&=C(1-T_{\text{red}})^{2\nu_T n}\end{aligned}\tag{14}$$

as C is fixed for each component. The exponent, apart from the universal ν_T, contains the order n of the thermal approximation and its value can be determined from measured quantities using a logarithmic representation, as illustrated in Fig. 5 for benzene [31].

From the graph, n=0.3449 (from Table 1, T_{crit}=563.6 K for benzene). Relationship 14 yields the Watson formula

$$\lambda_{\text{vap}}(T)=\lambda_{\text{vap}}^{\text{ref}}\left(\frac{1-T_{\text{red}}}{1-T_{\text{red}}^{\text{ref}}}\right)^{2\nu_T n}\tag{15}$$

on choosing an arbitrary reference system. This enables the heat of evaporation to be calculated [32]. Applying Kirchhoff's law to Eq. 15, the molar heat capacity C_ϕ of the phase pair can be written as

$$C_L(T)-C_V(T)=\left(\frac{\partial\lambda_{\text{vap}}(T)}{\partial T}\right)=2\nu_T n\frac{\lambda_{\text{vap}}(T)}{T_{\text{crit}}-T}$$

In the transition $T\rightarrow T_{\text{crit}}$, the difference of the specific heats disappears, in accord with the homogenization of liquid and vapor phases. On applying Eq. 14 to the normal boiling point (setting n=1 and $2\nu_T\approx1$) Trouton's rule $\left(\lambda_{\text{vap}}^{(\text{ebu})}/T^{(\text{ebu})}\right)\sim\left[\left(1/T^{(\text{ebu})}\right)-1\right]$ is obtained [18].

On combining Eqs. 5 and 6, it follows that

$$\begin{aligned}\rho_L-\rho_V&=\left\{\nu_\rho N\sqrt{\frac{^{0}\chi_\phi}{0\chi_\phi^{(\rho)}}}\left(\frac{1}{n}T_{\text{crit}}\right)^{\frac{1}{N}\frac{\nu_T}{\nu_\rho}}\right\}(1-T_{\text{red}})^{\frac{n}{N}\frac{\nu_T}{\nu_\rho}}\\&=k(1-T_{\text{red}})^{\kappa}\end{aligned}\tag{16}$$

These calculated bulk phase quantities can be experimentally tested. Figure 6 illustrates the logarithmic function $\Delta\rho(T_{\text{red}})$ for the systems shown in Fig. 3. The exponent κ is identical for both liquids.

Like the Watson formula, the difference of the densities can be determined at all T from Eq. 16 using

$$\rho_L-\rho_V=(\rho_L-\rho_V)^{\text{ref}}\left(\frac{1-T_{\text{red}}}{1-T_{\text{red}}^{\text{ref}}}\right)^{\kappa}$$

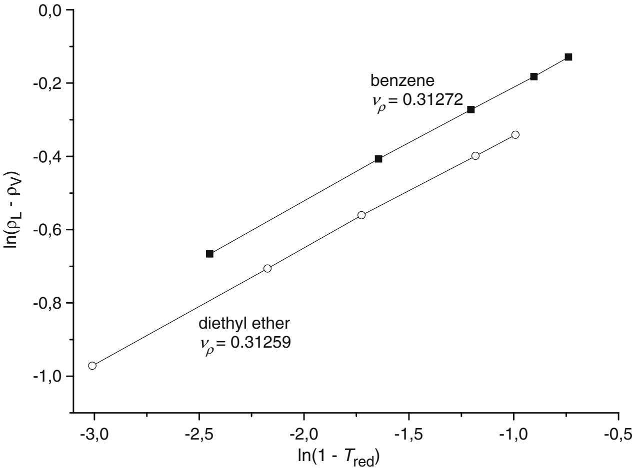

Fig. 6 Calculated bulk densities for the systems shown in Fig. 3

The complete analogue of Eq. 16 for the quadratic densities $\left(\rho_L^2 - \rho_V^2\right)$ of the coexistent phases can be written using the material parameter $\widetilde{\chi}_\phi\left(\Delta^{(2)}\rho\right) = {}^0\widetilde{\chi}_\phi\left(\rho_L^2 - \rho_V^2\right)^{\widetilde{\nu_\rho}\widetilde{N}}$.

From Eqs. 2 and 5, we can deduce the following equation

$$\rho_L^2 - \rho_V^2 = \widetilde{\nu}_\rho \widetilde{N} \sqrt{\frac{{}^0\gamma_{LV}}{{}^0\widetilde{\gamma}_{LV}} \left\{\frac{1}{n} T_{\text{crit}}\right\}^{\nu_T}} (1 - T_{\text{red}})^{\frac{\nu_T\, n}{\widetilde{\nu_\rho}\, \widetilde{N}}}$$

$$= k_{(2)} (1 - T_{\text{red}})^{\widetilde{\kappa}}$$

where $k_{(2)}$ and $\widetilde{\kappa}$ are the collective values of the phase constants. As $\left(\rho_L^2 - \rho_V^2\right) = (\rho_L + \rho_V)(\rho_L - \rho_V)$, from Eq. 16 it follows that

$$\rho_L + \rho_V = \frac{k_{(2)}}{k} \frac{(1 - T_{\text{red}})^{\widetilde{\kappa}}}{(1 - T_{\text{red}})^{\kappa}} = k_{(12)} (1 - T_{\text{red}})^{\widetilde{\kappa} - \kappa} \tag{17}$$

As the temperature factor is a binomial expression, the power series

$$(1 - T_{\text{red}})^{\widetilde{\kappa} - \kappa} = 1 - (\widetilde{\kappa} - \kappa) T_{\text{red}} + \frac{1}{2!} (\widetilde{\kappa} - \kappa)(\widetilde{\kappa} - \kappa - 1) T_{\text{red}}^2 - \ldots \tag{18}$$

can be approximated by its finite partial sum. To first order this yields

$$\rho_L + \rho_V = k_{(12)} \{1 - (\widetilde{\kappa} - \kappa)\ T_{\text{red}}\} \tag{19}$$

Expression 17 does not vanish for $T_{\text{red}} = 0$ or $T_{\text{red}} = 1$ because among the densities at least one has positive value. Hence, the condition $\widetilde{\kappa} < \kappa$ is necessarily fulfilled for the exponents. By extrapolation of Eq. 19 to 0 K or to the critical state, the coefficients are

$$k_{(12)} = \rho_L^0 \text{ and } (\widetilde{\kappa} - \kappa) = \left(\frac{2\rho_L^{\text{crit}}}{\rho_L^0} - 1\right)$$

if the vapor density disappears or becomes negligible compared to that of the liquid, ρ_L^0, at T=0 (ρ_L^{crit} is the density in the critical state). Thus, albeit by a different method from that of Eyring [33], Eq. 19 yields the Cailletet–Mathias rule [13]

$$\frac{1}{2}(\rho_L(T) + \rho_V(T)) = \frac{1}{2}\rho_L^0 + \left[\left(\rho_L^{\text{crit}} - \frac{1}{2}\rho_L^0\right) \frac{1}{T_{\text{crit}}}\right] T$$

$$= a + b\ T$$

The second-order approximation of Eq. 18 also yields Young's relationship [34], which hitherto has not been physically interpreted. From the four parameter relationships

$$\rho_L(T) = \frac{1}{2}\left\{k_{(12)}(1 - T_{\text{red}})^{\widetilde{\kappa} - \kappa} + k(1 - T_{\text{red}})^{\kappa}\right\}\ \rho_V(T)$$

$$= \frac{1}{2}\left\{k_{(12)}(1 - T_{\text{red}})^{\widetilde{\kappa} - \kappa} - k(1 - T_{\text{red}})^{\kappa}\right\}$$

that are generated by the sum and difference of Eqs. 16 and 17, the densities of the coexistent phases can be determined both in principle and experimentally. From the relationships of capillary quantities, the interactions of noncapillary physical quantities can also be determined. In this state the values of variables characterizing the various domains of the system are consistent.

Summary

Using the individual representation of the formalism of capillary theory and also considering the power law relationships, the laws determining the state of free fluid surfaces can be defined. The method is based on the general dimension equation implicitly contained in the formalism. The quantities of the extended formulation are relevant to the evaluation of measurements. Not only empirically known approximate relationships, such as the van der Waals and Walden equations, Watson's formula, the Cailletet–Mathias rule, etc. can be derived through them, but also new findings can be made. For instance, with respect to the correspondence principle, it becomes possible to calculate the critical temperatures of physical quantities that are hard to measure. The extended formalism outperforms the heuristic power of the traditional theory in terms of operability.

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