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functional model

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Line Adsorption in a Mean-Field Density-Functional Model

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Abstract

Recent ideas about the analog for a three-phase contact line of the Gibbs adsorption equation for interfaces are illustrated in a mean-field density-functional model. With $d\tau$ the infinitesimal change in the line tension τ that accompanies the infinitesimal changes $d\mu_i$ in the thermodynamic field variables μ_i and with Λ_i the line adsorptions, the sum $d\tau + \sum \Lambda_i d\mu_i$, unlike its surface analog, is not 0. An equivalent of this sum in the model system is evaluated numerically and analytically. A general line adsorption equation, which the model results illustrate, is derived.

1 Introduction

Three phases may meet at a line in which all three are in simultaneous contact with one another. Associated with this line is a line tension τ , which is the excess grand-canonical free energy per unit length of the contact line, and line adsorptions Λ_i , which are the linear excesses of the several components, per unit length [1]. It had long been thought that if the thermodynamic state of the three-phase equilibrium is displaced infinitesimally by infinitesimal changes $d\mu_i$ in the thermodynamic field variables (such as the chemical potentials and temperature) μ_i , the resulting infinitesimal change $d\tau$ in the line tension would be $-\Sigma\Lambda_i d\mu_i$. This would then have been the analog of the Gibbs adsorption equation for interfaces, which relates the infinitesimal change $d\sigma$ in the interfacial tension σ to the surface adsorptions (surface excesses per unit area) Γ_i by

$$d\sigma = - \sum_i \Gamma_i d\mu_i . \quad (1.1)$$

The individual Γ_i in (1.1) are defined with respect to, and in general depend on, the arbitrary location of a Gibbs dividing surface, but the sum $-\Sigma\Gamma_i d\mu_i$, and so also $d\sigma$, are invariant to that choice. It was then surprising when it was discovered that not only do the individual line adsorptions Λ_i depend on the arbitrary choice of location of the line, as expected, but the sum $-\Sigma\Lambda_i d\mu_i$ does, too [2]. It cannot, therefore, be $d\tau$, which is known by independent arguments to be invariant.

Figure 1 is a view along the contact line, which is perpendicular to the plane of the figure and passes through an arbitrarily chosen point in the plane. The equilibrium phases α, β , and γ fill the dihedral angles between the $\alpha\beta, \beta\gamma$, and $\alpha\gamma$ interfaces. These interfaces meet at the contact line. The surfaces (seen as lines in the figure) that meet at the contact line are taken to be the Gibbs dividing surfaces of the several interfaces, and thus share with the contact line the arbitrariness in its location. The $\mathbf{e}_{\alpha\beta}, \mathbf{e}_{\beta\gamma}$, and $\mathbf{e}_{\alpha\gamma}$ are unit vectors in the directions of the respective interfaces. With $\sigma_{\alpha\beta}$, etc., the three interfacial tensions, the condition of mechanical stability is

$$\sigma_{\alpha\beta}\mathbf{e}_{\alpha\beta} + \sigma_{\beta\gamma}\mathbf{e}_{\beta\gamma} + \sigma_{\alpha\gamma}\mathbf{e}_{\alpha\gamma} = 0 . \quad (1.2)$$

There is no arbitrariness in any of the terms in (1.2).

It was shown in ref. [2] that, as expected, the line adsorptions $\Lambda_i(\mathbf{r})$ depend on the arbitrary location \mathbf{r} of the point in the plane of Fig. 1 through which the contact line is chosen to pass, and that (unexpectedly) so does $\Sigma\Lambda_i(\mathbf{r})d\mu_i$, but that

$$- \sum_i \Lambda_i(\mathbf{r})d\mu_i - (\mathbf{e}_{\alpha\beta} d\sigma_{\alpha\beta} + \mathbf{e}_{\beta\gamma} d\sigma_{\beta\gamma} + \mathbf{e}_{\alpha\gamma} d\sigma_{\alpha\gamma}) \cdot (\mathbf{r} - \mathbf{r}_0) , \quad (1.3)$$

where \mathbf{r}_0 is an arbitrary origin from which \mathbf{r} is measured, does not: for any fixed \mathbf{r}_0 , the expression (1.3) is independent of \mathbf{r} .

Because of (1.2), the invariant (1.3) is equally well

$$- \sum_i \Lambda_i(\mathbf{r})d\mu_i + (\sigma_{\alpha\beta} d\mathbf{e}_{\alpha\beta} + \sigma_{\beta\gamma} d\mathbf{e}_{\beta\gamma} + \sigma_{\alpha\gamma} d\mathbf{e}_{\alpha\gamma}) \cdot (\mathbf{r} - \mathbf{r}_0) . \quad (1.4)$$

This form of the expression is important in interpreting in physical terms the origin of the non-invariance of $\Sigma\Lambda_i d\mu_i$. We may also note here for later reference (Section 3) that while (1.3) and (1.4) are invariant to \mathbf{r} for any fixed \mathbf{r}_0 , the value of these expressions for any fixed \mathbf{r} obviously depends on the choice of origin, \mathbf{r}_0 , from which \mathbf{r} is measured.

In a density-functional theory of line tension there is a free-energy-density functional Ψ , a functional of the densities $\rho_i(\mathbf{r})$ that are the thermodynamic conjugates of the field variables μ_i . (When μ_i is the temperature, ρ_i is the entropy density). This Ψ is the density of the excess grand-canonical free energy due to the inhomogeneities in the system. Most of this inhomogeneity free energy comes from the interfaces, but when this is subtracted, what remains is that due to the contact line. In Fig. 2 is shown a Neumann triangle, the sides of which are perpendicular to the interfaces and of lengths proportional to the respective interfacial tensions. The contact line is taken to pass through an arbitrary point in the triangle at the distances $R_{\alpha\beta}$, $R_{\beta\gamma}$, and $R_{\alpha\gamma}$ from the triangle's sides. This, then, defines the locations of the Gibbs dividing surfaces that meet at the contact line. The line tension τ is then obtained from

$$\tau = \lim_{R_{\alpha\beta} \rightarrow \infty, \text{ etc.}} \left[\min_{\rho_i(\mathbf{r})} \int_A \Psi da - (\sigma_{\alpha\beta} R_{\alpha\beta} + \sigma_{\beta\gamma} R_{\beta\gamma} + \sigma_{\alpha\gamma} R_{\alpha\gamma}) \right] \quad (1.5)$$

where the integration is through the area A of the triangle with da an element of area, where the integral is minimized with respect to the densities $\rho_i(\mathbf{r})$ of which Ψ is a functional, and where, with the contact line fixed at its arbitrarily chosen position, one takes the thermodynamic limit in which the $R_{\alpha\beta}$, etc., all become infinite proportionally to one another: $R_{\alpha\beta} = \ell_{\alpha\beta} R$, etc., with $R \rightarrow \infty$ while $\ell_{\alpha\beta}, \ell_{\beta\gamma}, \ell_{\alpha\gamma}$ are fixed.

In a general mean-field density-functional theory [2, 3] the functional Ψ is of the form

$$\Psi = e[\rho_1(\mathbf{r}), \rho_2(\mathbf{r}), \dots] - \sum_i \mu_i \rho_i(\mathbf{r}) + p(\mu_1, \mu_2, \dots) + K \quad (1.6)$$

where $e(\rho_1, \rho_2, \dots)$ is the mean-field-theory energy density, a function of the ρ_i alone, independent of the μ_i ; where $p(\mu_1, \mu_2, \dots)$ is the mean-field-theory pressure, a function of the μ_i alone, independent of the ρ_i ; and where K is a non-local functional of the ρ_i , independent of the μ_i . It then follows that [2, 3]

$$- \sum_i \Lambda_i d\mu_i = d\tau' \quad (1.7)$$

where $d\tau'$ is that part of the infinitesimal change in the right-hand side of (1.5) that comes from all sources *other than* the change in the shape of the Neumann triangle itself; i.e., $d\tau'$ is what $d\tau$ would have been had there been no contributions to it from the infinitesimal changes in the contact angles, as measured by the $d\mathbf{e}_{\alpha\beta}$, etc. in (1.4), that also result from the infinitesimal changes $d\mu_i$. The latter contributions to $d\tau$, missing from $d\tau'$ and therefore from $-\Sigma\Lambda_i d\mu_i$, also depend on the arbitrary location of the contact line because the energetic cost of any given contact-angle distortion depends on the physical environment of the contact line at which that distortion occurs [2]. This contribution to $d\tau$, in its dependence on the location of the contact line, exactly cancels that in $-\Sigma\Lambda_i d\mu_i$ and leaves $d\tau$ invariant [2]. That is the essential physical content of (1.4).

The purpose of the present study is to demonstrate in a model mean-field density-functional theory that $d\tau \neq d\tau'$, and thus to illustrate the (formerly surprising) fact that $d\tau \neq -\Sigma\Lambda_i d\mu_i$; and

to note explicitly that, while $d\tau'$ depends on the arbitrary location \mathbf{r} of the contact line, $d\tau$ does not, and that

$$d\tau' - (\mathbf{e}_{\alpha\beta}d\sigma_{\alpha\beta} + \mathbf{e}_{\beta\gamma}d\sigma_{\beta\gamma} + \mathbf{e}_{\alpha\gamma}d\sigma_{\alpha\gamma}) \cdot (\mathbf{r} - \mathbf{r}_0) \quad (1.8)$$

also does not. [Cf.(1.3)]. This observation will lead in Section 3 to the recognition and derivation of a general adsorption equation for the contact line, which the model results illustrate.

The matter of the inequality $d\tau \neq d\tau'$ was also addressed earlier [3] with an example in which the Ψ in (1.6) was of the form

$$\Psi = F[\rho_1(\mathbf{r}), \rho_2(\mathbf{r}); b] + K, \quad (1.9)$$

with $F(\rho_1, \rho_2; b)$ a function of two densities ρ_1, ρ_2 and only one independently variable thermodynamic field b , and with K a non-local functional of $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ that is independent of b . With such a Ψ , the derivative $d\tau'/db$, which is the part of $d\tau/db$ that comes from differentiating the right-hand side of (1.5) with respect to b while ignoring the dependence on b of the shape of the Neumann triangle over which Ψ is integrated, is then

$$\frac{d\tau'}{db} = \lim_{R_{\alpha\beta} \rightarrow \infty, \text{ etc.}} \left[\int_A \frac{\partial F}{\partial b} da - \left(\frac{d\sigma_{\alpha\beta}}{db} R_{\alpha\beta} + \frac{d\sigma_{\beta\gamma}}{db} R_{\beta\gamma} + \frac{d\sigma_{\alpha\gamma}}{db} R_{\alpha\gamma} \right) \right]. \quad (1.10)$$

The $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ in $\partial F/\partial b$ are those that minimize $\int \Psi da$ in (1.5). As in the derivation of (1.7) [3], in differentiating the right-hand side of (1.5) with respect to b one need not consider the implicit b -dependence in the minimizing $\rho_i(\mathbf{r})$ themselves because the variational integral is stationary with respect to them. Only the explicit b -dependence in Ψ need be taken into account. (This is analogous to the Hellmann-Feynman theorem of molecular quantum mechanics.)

The particular F and K for the present numerical study, as for the earlier one [3], are

$$F(\rho_1, \rho_2; b) = 2(3\rho_2^2 + b^2\rho_1^2)^2 + 4b^2(3\rho_2^2 - b^2\rho_1^2) + 2b^4 - 32b\rho_2^3 \quad (1.11)$$

and

$$K = \frac{1}{2} (|\nabla\rho_1|^2 + |\nabla\rho_2|^2). \quad (1.12)$$

In the bulk phases, $\rho_1^\alpha = -1$, $\rho_2^\alpha = 0$; $\rho_1^\beta = 0$, $\rho_2^\beta = b$; $\rho_1^\gamma = 1$, $\rho_2^\gamma = 0$. At these densities $F = 0$, while $F > 0$ for all other ρ_1, ρ_2 .

Also, as earlier, we specialize to the case $b = \sqrt{3}$, where the three phases play symmetrical roles in the phase equilibrium and the contact angles are all 120° . The earlier study [3] compared $d\tau'/db$ with $d\tau/db$ at $b = \sqrt{3}$ for one choice of location of the contact line. Here we make that comparison with a range of choices, and at the same time verify the invariance of $d\tau/db$ and of

$$\frac{d\tau'}{db} - \left(\frac{d\sigma_{\alpha\beta}}{db} \mathbf{e}_{\alpha\beta} + \frac{d\sigma_{\beta\gamma}}{db} \mathbf{e}_{\beta\gamma} + \frac{d\sigma_{\alpha\gamma}}{db} \mathbf{e}_{\alpha\gamma} \right) \cdot (\mathbf{r} - \mathbf{r}_0). \quad (1.13)$$

In Section 2 we outline the numerical methods used and tabulate the numerical results; in Section 3 we analyze the results of the calculations and derive a properly invariant adsorption equation for the contact line, which the model results illustrate; and in Section 4 we provide a brief summary.

2 Numerical methods and results

Here we evaluate the line tension τ and the derivatives $d\tau/db$ and $d\tau'/db$. First we calculate the equilibrium density profiles $\rho_1(z)$ and $\rho_2(z)$ for each interface far from the contact line, and then obtain the surface tensions. This determines the contact angles and the boundary conditions for the equilibrium densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ of the system that include the three phases in contact. With the boundary conditions we calculate $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ over a rectangular area that includes the three phases in contact. We then evaluate τ from the Kerins-Boiteux integral [4]

$$\tau_{\text{KB}} = \int_A (\Psi - 2F[\rho_1, \rho_2]) da \quad (2.1)$$

and $d\tau'/db$ from (1.10), both with the equilibrium $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$. The $d\tau/db$ is accurately evaluated from τ at $b \pm \epsilon$.

For the interfaces far from the contact line, we obtain the $\rho_1(z)$ and $\rho_2(z)$ that minimize $\int_{-\infty}^{\infty} \Psi(z) dz$ by solving the one-dimensional Euler-Lagrange equations subject to the boundary conditions of bulk densities at the extremes. With the model functional Ψ the Euler-Lagrange equations may be solved analytically for the $\alpha\gamma$ interface and the surface tension is $\sigma_{\alpha\gamma} = 8b^2/3$ for any b ; in the fully symmetric case $b = \sqrt{3}$ the density profiles for the other two interfaces are also given analytically and the tensions associated with the three interfaces have the common value: $\sigma_{\alpha\beta} = \sigma_{\beta\gamma} = \sigma_{\alpha\gamma} = 8$ [5]. In cases of arbitrary b , the density profiles and tensions for the $\alpha\beta$ and $\beta\gamma$ interfaces are obtained numerically. In such numerical calculations, we discretize the Euler-Lagrange equations with a 5-point difference equation in z , and then solve the discretized equations iteratively with a successive overrelaxation (SOR) method [6]. The criterion for convergence is an rms difference of less than 1×10^{-15} between iterates. As a check, we also evaluate the density profiles and tensions numerically at $b = \sqrt{3}$, taking the range of z to be $[-3 : 3]$ and the grid spacing to be 0.003. Then the converged profiles completely overlap with the analytical profiles and the surface tensions evaluated from the numerical profiles are accurate to 8 digits.

The equilibrium densities $\rho_1(\mathbf{r})$ and $\rho_2(\mathbf{r})$ over the region that includes the three phases in contact are obtained by solving the two-dimensional Euler-Lagrange equations. The Euler-Lagrange equations are discretized with a 9-point stencil over a rectangular box. The size of the box is chosen such that the equilibrium densities near the boundaries of the box have their bulk-phase values in all three phases. When $b = \sqrt{3}$, we use a box of dimension 3×3 length units with a spacing $\Delta x (= \Delta y)$ of 0.003. We solve the discretized two-dimensional Euler-Lagrange equations iteratively with the SOR method. The criterion of convergence is taken to be an rms difference of less than 1×10^{-12} between iterates.

As noted earlier [3], the line tension τ is evaluated more accurately from the Kerins-Boiteux integral (2.1) than from the original variational formula (1.5). This is illustrated by plotting τ as a function of grid spacings Δx and extrapolating to $\Delta x = 0$. Figure 3 shows that when $b = \sqrt{3}$, τ_{KB} is essentially constant with $\Delta x \leq 0.003$ while τ from the variational formula varies with Δx and converges to τ_{KB} only when it is extrapolated to $\Delta x = 0$. The extrapolated values of τ and τ_{KB} are -0.577399 and -0.577349 , respectively. Note that $-1/\sqrt{3} = -0.577350269\dots$, which will be commented on in Section 3.

We evaluate $d\tau'/db$ from (1.10). Since the integrand $\partial F/\partial b$ is non-zero along the interfaces, like

the integrand Ψ in (1.5) and unlike the integrand $\Psi - 2F$ in (2.1), its numerical integral gives rise to noticeable numerical error depending on the grid spacing. Thus, to evaluate $d\tau'/db$ accurately, we need to extrapolate the numerical results of several grid spacings to $\Delta x = 0$, just as we needed to do when evaluating τ from the variational formula. In addition, the accuracy of the numerical evaluation is improved as follows: Express the terms $(d\sigma_{\alpha\beta}/db)R_{\alpha\beta} + \dots$, which are to be subtracted from the integral in (1.10), as the integrals over the same area over which $\partial F/\partial b$ is integrated; then subtract the sum of their integrands from $\partial F/\partial b$; and finally perform the numerical integration of the resulting integrand, which is non-zero only around the contact line, like the integrand $\Psi - 2F$ in (2.1). Even with this short-ranged integrand, extrapolation of the numerical results to zero grid spacing is necessary to achieve the desired precision.

The derivative $d\tau/db$ at given b is evaluated accurately from τ at $b \pm 0.001$; use of five points, τ at $b, b \pm 0.001, b \pm 0.002$, gives essentially the same results.

We evaluate $d\tau'/db$ at four locations of the contact line: $\mathbf{r}_0 = 0$, $\mathbf{r}_1 = -(1/2)\mathbf{e}_{\alpha\gamma}$, $\mathbf{r}_2 = -(1/2)\mathbf{e}_{\alpha\gamma} + (1/2)\mathbf{g}_{\alpha\gamma}$, $\mathbf{r}_3 = (1/2)\mathbf{g}_{\alpha\gamma}$, where all the vectors are measured from the symmetry point of the phase equilibrium as origin and $\mathbf{g}_{\alpha\gamma}$ is a unit vector that is perpendicular to $\mathbf{e}_{\alpha\gamma}$ and is rotated from it counterclockwise. Figure 4 shows the four locations of the contact line at which $d\tau'/db$ is evaluated and compared with $d\tau/db$. In the fully symmetric case $b = \sqrt{3}$, $d\tau/db = -0.333353$ and $d\tau'/db = -0.333344$ if the location of the contact line is chosen to be the symmetry point; the two are deemed to be identical. If this had been true for any location of the contact line, what was in earlier times thought to be the line adsorption equation would have been correct. But we find $d\tau'/db \neq d\tau/db$ at \mathbf{r}_1 and \mathbf{r}_2 , while $d\tau'/db = d\tau/db$ at \mathbf{r}_3 , as shown in Table I. It is also confirmed that the sum of $d\tau'/db$ and

$$\frac{d\tau''}{db} = - \left(\frac{d\sigma_{\alpha\beta}}{db} \mathbf{e}_{\alpha\beta} + \frac{d\sigma_{\beta\gamma}}{db} \mathbf{e}_{\beta\gamma} + \frac{d\sigma_{\alpha\gamma}}{db} \mathbf{e}_{\alpha\gamma} \right) \cdot \mathbf{r} \quad (2.2)$$

is independent of \mathbf{r} and is equal to $d\tau/db$.

Further calculations are done for a range of b . Over this range, $\rho_1(z)$ in the $\alpha\beta$ and $\beta\gamma$ interfaces far from the contact line is still almost exactly antisymmetric about the point z at which $\rho_1(z) = -1/2$ and $+1/2$, respectively, and, in the $\alpha\gamma$ interface, is still exactly antisymmetric about the z at which $\rho_1(z) = 0$. Those define ‘‘midlines’’ of the three interfaces, and where the midlines, extrapolated into the region of the contact line, intersect, they define a ‘‘symmetry point’’. To numerical accuracy, this symmetry point proves still to have many of the properties the exact symmetry point at $b = \sqrt{3}$ has. Points \mathbf{r}_0 and \mathbf{r}_1 are defined as before (Fig. 4). In Fig. 5 are plotted $d\tau/db$ and $d\tau'/db$ against b at \mathbf{r}_0 and \mathbf{r}_1 . The results for $d\tau'/db$ at the symmetry point coincide with those for $d\tau/db$; i.e., the identity $d\tau'/db = d\tau/db$ holds at the symmetry point not only in the fully symmetric case but, to numerical accuracy, in any of the cases of b in this range. The difference between $d\tau/db$ and $d\tau'/db$ at \mathbf{r}_1 is larger than the absolute value of $d\tau/db$ in this range of b . We note the large discrepancy is brought about when the arbitrary location of the contact line is displaced in a special direction from the symmetry point by an amount comparable to half the interfacial thickness. The difference decreases with decreasing b , which also means decreasing contact angle β [5]. This trend is consistent with the fact noted earlier [2] that $\Sigma\Lambda_i d\mu_i$ will become invariant with respect to the location of the contact line as $\beta \rightarrow 0$ (the wetting transition).

3 Analysis and discussion

In the preceding section, τ , $d\tau/db$, and $d\tau'/db$ were evaluated numerically for the fully symmetric case $b = \sqrt{3}$ for several different choices of location of the contact line. It was noted that the properly extrapolated values of τ and $d\tau/db$ are independent of the location of the contact line, that $d\tau'/db$ is not, and that

$$\frac{d\tau}{db} = \frac{d\tau'}{db} - \left(\frac{d\sigma_{\alpha\beta}}{db} \mathbf{e}_{\alpha\beta} + \frac{d\sigma_{\beta\gamma}}{db} \mathbf{e}_{\beta\gamma} + \frac{d\sigma_{\alpha\gamma}}{db} \mathbf{e}_{\alpha\gamma} \right) \cdot \mathbf{r}, \quad (3.1)$$

where \mathbf{r} is the location of the contact line measured from the symmetry point of the phase equilibrium as origin. The dependence on \mathbf{r} of the separate terms on the right-hand side of (3.1) thus cancels in the combination.

As a parenthetical remark we may note that the numerical values obtained for τ and $d\tau/db$ at $b = \sqrt{3}$ are very close to

$$\tau = -\frac{1}{\sqrt{3}}, \quad \frac{d\tau}{db} = -\frac{1}{3}. \quad (3.2)$$

Because of the ubiquitous appearance of 3 and $\sqrt{3}$ in this fully symmetrical three-phase equilibrium it is very likely that these are exact, but proving it remains a challenge to analytical theory. What has been established analytically [3] is that in this symmetric case,

$$\frac{d\sigma_{\alpha\beta}}{db} = \frac{d\sigma_{\beta\gamma}}{db} = \frac{22}{\sqrt{3}}, \quad \frac{d\sigma_{\alpha\gamma}}{db} = \frac{16}{\sqrt{3}}, \quad (3.3)$$

while the contact angles are all 120° , so that $\mathbf{e}_{\alpha\beta} + \mathbf{e}_{\beta\gamma} = -\mathbf{e}_{\alpha\gamma}$. [Equivalently, in this symmetric case $\sigma_{\alpha\beta} = \sigma_{\beta\gamma} = \sigma_{\alpha\gamma}$, so $\mathbf{e}_{\alpha\beta} + \mathbf{e}_{\beta\gamma} + \mathbf{e}_{\alpha\gamma} = 0$, by (1.2).] Therefore (3.1) is equally well

$$\frac{d\tau}{db} = \frac{d\tau'}{db} + 2\sqrt{3} \mathbf{e}_{\alpha\gamma} \cdot \mathbf{r}. \quad (3.4)$$

We saw from the numerical results in Section 2 that when \mathbf{r} had a non-vanishing component in the direction of $\mathbf{e}_{\alpha\gamma}$ then $d\tau/db \neq d\tau'/db$ and $d\tau'/db$ depended on \mathbf{r} , whereas when \mathbf{r} was chosen perpendicular to $\mathbf{e}_{\alpha\gamma}$ then, but only then, $d\tau/db = d\tau'/db$. These are clearly in accord with (3.4).

In Figure 6 the contact line is again perpendicular to the plane of the figure, where it passes through an arbitrarily chosen point P . This point is at \mathbf{r} , as measured from the symmetry point of the three-phase equilibrium. Then $d\tau/db$, which is independent of the location P , and $d\tau'/db$, which is not, are related by (3.4). The dashed line in the figure passes through the symmetry point and is orthogonal to $\mathbf{e}_{\alpha\gamma}$. The same point P , which is at \mathbf{r} measured from the symmetry point as origin, is at \mathbf{r}' when measured from an origin elsewhere on the dashed line, as indicated in the figure. Then (3.4) would continue to hold with \mathbf{r} replaced by any such \mathbf{r}' , because \mathbf{r} and \mathbf{r}' have the same component in the $\mathbf{e}_{\alpha\gamma}$ direction (see figure), so the same scalar product with $\mathbf{e}_{\alpha\gamma}$.

This property of the fully symmetrical model, if one recalls (1.7), may now be seen to be a special case of a general line adsorption equation, unrelated to any model symmetry, which we shall first anticipate and later derive. In Fig. 7, which is again for any plane perpendicular to the contact line, is indicated the direction $\sigma_{\alpha\beta} d\mathbf{e}_{\alpha\beta} + \sigma_{\beta\gamma} d\mathbf{e}_{\beta\gamma} + \sigma_{\alpha\gamma} d\mathbf{e}_{\alpha\gamma}$ that is determined by the infinitesimal changes $d\mu_i$ in the system's thermodynamic field variables. Our assertion is now that

there is in that plane a special line, shown dashed in the figure, perpendicular to $\sigma_{\alpha\beta} d\mathbf{e}_{\alpha\beta} + \dots$, with the property that

$$d\tau = - \sum_i \Lambda_i(\mathbf{r}) d\mu_i + (\sigma_{\alpha\beta} d\mathbf{e}_{\alpha\beta} + \sigma_{\beta\gamma} d\mathbf{e}_{\beta\gamma} + \sigma_{\alpha\gamma} d\mathbf{e}_{\alpha\gamma}) \cdot (\mathbf{r} - \mathbf{r}_0) \quad (3.5)$$

when the contact line is chosen to pass through an arbitrary point \mathbf{r} in the plane, with \mathbf{r}_0 any point on the special line. Thus, $\mathbf{r} - \mathbf{r}_0$ in (3.5) is the arbitrary location of the contact line as measured from an origin that is any point on the special line.

We remark first, from (1.4), that the right-hand side of (3.5) is invariant to the choice of \mathbf{r} for any \mathbf{r}_0 , whether on the special line or not. But, as noted in the Introduction, the invariant value in question depends, in general, on \mathbf{r}_0 . Thus, it is not for any \mathbf{r}_0 that the right-hand side of (3.5) could be the physically measurable $d\tau$. But (3.5) itself determines some \mathbf{r}_0 for which the invariant value is indeed $d\tau$, independently of \mathbf{r} . Once such an \mathbf{r}_0 is identified, any \mathbf{r}_0 on a line that passes through that one and is orthogonal to $\sigma_{\alpha\beta} d\mathbf{e}_{\alpha\beta} + \dots$ will have the same property. That is our special line. Its existence, and the form (3.5) for the line adsorption equation, which had already been conjectured [7], will be formally derived below.

From (3.5), choosing any such \mathbf{r}_0 for the location of the contact line yields

$$d\tau = - \sum_i \Lambda_i(\mathbf{r}_0) d\mu_i . \quad (3.6)$$

This is as close as it is possible to come to a relation analogous to the Gibbs adsorption equation (1.1).

In the fully symmetrical model we analyzed, the special line had of necessity, by symmetry, to pass through the symmetry point of the three-phase equilibrium. That it had to be orthogonal to $\mathbf{e}_{\alpha\gamma}$ was again a consequence of the model's symmetry: as the field variable b changes (in particular, but not only, when it changes from $\sqrt{3}$), the α and γ contact angles remain equal, as do $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$, so $d\sigma_{\alpha\beta}/db$ and $d\sigma_{\beta\gamma}/db$ remain equal and $\mathbf{e}_{\alpha\beta} + \mathbf{e}_{\beta\gamma}$ continues to lie in the direction of $\mathbf{e}_{\alpha\gamma}$. Thus, the only unique direction in the model, as b changes, is that of $\mathbf{e}_{\alpha\gamma}$ or the direction orthogonal to it. Therefore, from (3.1), the special line, which is the locus of choices of \mathbf{r} for which $d\tau/db = d\tau'/db$, had to be orthogonal to $\mathbf{e}_{\alpha\gamma}$.

The form (3.5) anticipated for the line adsorption equation is now derived by completing an argument begun earlier [2]. It was remarked above, in the Introduction, that what had been missing from $-\sum\Lambda_i d\mu_i$ as an expression for $d\tau$ were contributions to the energy from changes in the contact angles that would accompany the changes $d\mu_i$ in the thermodynamic state. These contributions were earlier [2] expressed as scalar combinations of the infinitesimal changes $d\alpha$, $d\beta$, and $d\gamma$ in the contact angles α , β , and γ (the dihedral angles between planes, named after the corresponding phases). (Such terms in the energy differential appear also in a general thermodynamic analysis by Boruvka and Neumann [8].) We see from (1.4) that it would be more convenient, although equivalent, now to take these terms as combinations of $d\mathbf{e}_{\alpha\beta}$, $d\mathbf{e}_{\beta\gamma}$, and $d\mathbf{e}_{\alpha\gamma}$. These then enter the fundamental energy differential as the additional reversible-work terms $L(\mathbf{f}_{\alpha\beta} \cdot d\mathbf{e}_{\alpha\beta} + \mathbf{f}_{\beta\gamma} \cdot d\mathbf{e}_{\beta\gamma} + \mathbf{f}_{\alpha\gamma} \cdot d\mathbf{e}_{\alpha\gamma})$, where L is the length of the contact line and the $\mathbf{f}_{\alpha\beta}$, etc. are phenomenological coefficients. These additional terms in the energy differential then appear in $d\tau$ in the same way the previously

introduced $d\alpha, d\beta, d\gamma$ had [2]; i.e., now, as

$$d\tau = - \sum_i \Lambda_i d\mu_i + (\mathbf{f}_{\alpha\beta} \cdot d\mathbf{e}_{\alpha\beta} + \mathbf{f}_{\beta\gamma} \cdot d\mathbf{e}_{\beta\gamma} + \mathbf{f}_{\alpha\gamma} \cdot d\mathbf{e}_{\alpha\gamma}) . \quad (3.7)$$

As explained in the Introduction, the added terms in the energy would depend on the arbitrary location \mathbf{r} of the contact line about which the contact angles were changing. Here, that means that the phenomenological coefficients in (3.7) are functions $\mathbf{f}_{\alpha\beta}(\mathbf{r})$, etc., of that choice. We may identify the combination of them in (3.7) by choosing for a location of the contact line any \mathbf{r}_0 for which

$$\mathbf{f}_{\alpha\beta}(\mathbf{r}_0) \cdot d\mathbf{e}_{\alpha\beta} + \mathbf{f}_{\beta\gamma}(\mathbf{r}_0) \cdot d\mathbf{e}_{\beta\gamma} + \mathbf{f}_{\alpha\gamma}(\mathbf{r}_0) \cdot d\mathbf{e}_{\alpha\gamma} = 0 ; \quad (3.8)$$

i.e., for which (3.6) holds; while \mathbf{r} is any other location; so that, from (3.7) and the invariance of $d\tau$,

$$\sum_i \Lambda_i(\mathbf{r}) d\mu_i - \sum_i \Lambda_i(\mathbf{r}_0) d\mu_i = \mathbf{f}_{\alpha\beta}(\mathbf{r}) \cdot d\mathbf{e}_{\alpha\beta} + \mathbf{f}_{\beta\gamma}(\mathbf{r}) \cdot d\mathbf{e}_{\beta\gamma} + \mathbf{f}_{\alpha\gamma}(\mathbf{r}) \cdot d\mathbf{e}_{\alpha\gamma} . \quad (3.9)$$

But for *any* \mathbf{r} and \mathbf{r}_0 , from the known [2] invariance of (1.4),

$$\sum_i \Lambda_i(\mathbf{r}) d\mu_i - \sum_i \Lambda_i(\mathbf{r}_0) d\mu_i = (\sigma_{\alpha\beta} d\mathbf{e}_{\alpha\beta} + \sigma_{\beta\gamma} d\mathbf{e}_{\beta\gamma} + \sigma_{\alpha\gamma} d\mathbf{e}_{\alpha\gamma}) \cdot (\mathbf{r} - \mathbf{r}_0) . \quad (3.10)$$

We have therefore identified the right-hand side of (3.9) as that of (3.10), with \mathbf{r}_0 specifically a choice of location of the contact line for which (3.6) holds. With this identification, (3.7) is the anticipated adsorption equation (3.5). Once any \mathbf{r}_0 is identified, any other \mathbf{r}_0 lying on a line through that one and orthogonal to $\sigma_{\alpha\beta} d\mathbf{e}_{\alpha\beta} + \dots$ will do as well; that is the special line.

From (3.9) and (3.10) one might identify formally the individual coefficient $\mathbf{f}_{\alpha\beta}(\mathbf{r})$, etc., as $\mathbf{f}_{\alpha\beta}(\mathbf{r}) = \sigma_{\alpha\beta}(\mathbf{r} - \mathbf{r}_0)$, etc., but then they will themselves vary with the particular \mathbf{r}_0 that is chosen on the special line. Also, for any such \mathbf{r}_0 one would then have $\mathbf{f}_{\alpha\beta}(\mathbf{r}_0)$, etc., all vanishing separately, not only in the combination (3.8), which seems artificial. Thus, there may be no objective way of separating the individual terms in the sum $\mathbf{f}_{\alpha\beta}(\mathbf{r}) \cdot d\mathbf{e}_{\alpha\beta} + \dots$. In any case the three $\mathbf{f}(\mathbf{r})$ are not independent because the $d\mathbf{e}$ are not, being related by the identity (1.2).

It is remarked in Section 2 (see Fig. 5) that the numerical results are consistent with the requirement [2] that $-\sum \Lambda_i d\mu_i$ become invariant to the location of the contact line, and equal to $d\tau$, as a wetting transition is approached. In that limit the right-hand side of (3.9) vanishes, as does the coefficient of $\mathbf{r} - \mathbf{r}_0$ on the right-hand side of (3.10).

4 Summary

Adsorptions Λ_i at the line of mutual contact of three phases are the line analog of the surface adsorptions Γ_i in the Gibbs adsorption equation. Just as the Γ_i depend on the arbitrary location of the Gibbs dividing surface, so also do the Λ_i depend on the arbitrary location of the contact line. When the state of the phase equilibrium changes through infinitesimal changes $d\mu_i$ in the thermodynamic field variables there result infinitesimal changes $d\sigma$ in the several interfacial tensions σ and $d\tau$ in the line tension τ . Whereas in the Gibbs adsorption equation $d\sigma = -\sum \Gamma_i d\mu_i$ both sides

are invariant to the arbitrary choice of dividing surface, the analogous $-\Sigma\Lambda_i d\mu_i$ for the contact line still depends on the arbitrary choice of location of the line, and so cannot be $d\tau$, which is known to be invariant to that choice.

In Section 2, a mean-field density-functional model is analyzed numerically to illustrate these issues. In Section 3 it is seen that the equivalent of $-\Sigma\Lambda_i d\mu_i$ for that model is some $d\tau'$ that differs from $d\tau$ because in $d\tau'$ no account is taken of the changes in the contact angles that result from the changes $d\mu_i$ in the thermodynamic state. When terms proportional to the infinitesimal changes in the contact angles are incorporated in the fundamental energy differential the result is a properly invariant line adsorption equation. That is the equation (3.5) as derived in Section 3. Before being formally derived it is first anticipated based on the results of the model calculations and the previously known invariances of the expressions (1.3) and (1.4). This form of the adsorption equation had already been conjectured [7]. It is remarked in Section 2 (see Fig. 5) that the numerical results are consistent with the requirement [2] that $-\Sigma\Lambda_i d\mu_i$ become invariant and equal to $d\tau$, and the distinction between $d\tau$ and $d\tau'$ in the density-functional models disappear, as a wetting transition is approached.

The line adsorption equation, Eq.(3.5), entails the existence of a special line in any plane perpendicular to the contact line, with \mathbf{r}_0 any point on that line. Then with any choice \mathbf{r} for the location of the point in the plane through which the contact line passes, and with the $\Lambda_i(\mathbf{r})$ evaluated with that choice, the right-hand side of (3.5) is the same for all \mathbf{r} and is the invariant $d\tau$. Had \mathbf{r}_0 not been a point on the special line the right-hand side of (3.5) would still have been invariant to \mathbf{r} but would not have been equal to $d\tau$.

The special line was identified for the model functional studied in Section 2 and is shown as the vertical dashed line in Fig. 6, perpendicular to the direction $\mathbf{e}_{\alpha\gamma}$ and passing through the symmetry point of the fully symmetric model phase equilibrium. The density-functional model was thus important both for illustrating and for providing clues to the construction of a properly invariant line adsorption equation.

Acknowledgments

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Table 1: Comparison of $d\tau'/db$ with $d\tau/db$ at four locations of the contact line in the fully symmetric case ($b = \sqrt{3}$).

\mathbf{r}	$d\tau/db$	$d\tau'/db$	$d\tau''/db$	$d\tau'/db + d\tau''/db$
\mathbf{r}_0	-0.333353	-0.333344	0	-0.333344
\mathbf{r}_1	-0.333353	1.398707	-1.732051	-0.333344
\mathbf{r}_2	-0.333353	1.398707	-1.732051	-0.333344
\mathbf{r}_3	-0.333353	-0.333344	0	-0.333344

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Figure Captions

Fig. 1. The three-phase contact line is perpendicular to the figure plane, where it appears as a point; its arbitrary location is the intersection of the three dividing surfaces, which appear as lines in the figure. The phases α, β , and γ occupy the dihedral angles between planes. The $\mathbf{e}_{\alpha\beta}$, etc., are unit vectors in the directions of the interfaces.

Fig. 2. The sides of the Neumann triangle, shown dashed in the figure, are perpendicular to the interfaces. The contact line is at the distances $R_{\alpha\beta}$, $R_{\beta\gamma}$, and $R_{\alpha\gamma}$ from the triangle's sides.

Fig. 3. The line tension in the fully symmetric case $b = \sqrt{3}$ against the grid spacing Δx . Filled and open circles are the results obtained from the variational formula and the Kerins-Boiteux integral, respectively.

Fig. 4. Four locations of the contact line. The point P_0 is the symmetry point; P_1 , P_2 , and P_3 are given by the vectors $\mathbf{r}_1 = -(1/2)\mathbf{e}_{\alpha\gamma}$, $\mathbf{r}_2 = -(1/2)\mathbf{e}_{\alpha\gamma} + (1/2)\mathbf{g}_{\alpha\gamma}$, and $\mathbf{r}_3 = (1/2)\mathbf{g}_{\alpha\gamma}$, measured from P_0 .

Fig. 5. $d\tau/db$ and $d\tau'/db$ at P_0 and P_1 , two locations of the contact line in Fig. 4. Filled circles: $d\tau/db$; crosses: $d\tau'/db$ at P_0 ; and open circles: $d\tau'/db$ at P_1 .

Fig. 6. The contact line is perpendicular to the plane of the figure, where it passes through an arbitrarily chosen point P . This point is at \mathbf{r} , measured from the symmetry point of the fully symmetric phase equilibrium ($b = \sqrt{3}$). The same point P is at \mathbf{r}' , as measured from an arbitrary origin on the dashed line, which is orthogonal to $\mathbf{e}_{\alpha\gamma}$ and passes through the symmetry point of the phase equilibrium.

Fig. 7. The solid line is a vector in the direction $\sigma_{\alpha\beta}d\mathbf{e}_{\alpha\beta} + \sigma_{\beta\gamma}d\mathbf{e}_{\beta\gamma} + \sigma_{\alpha\gamma}d\mathbf{e}_{\alpha\gamma}$, in any plane perpendicular to the contact line. The dashed line is a special line in that plane and is orthogonal to that vector.

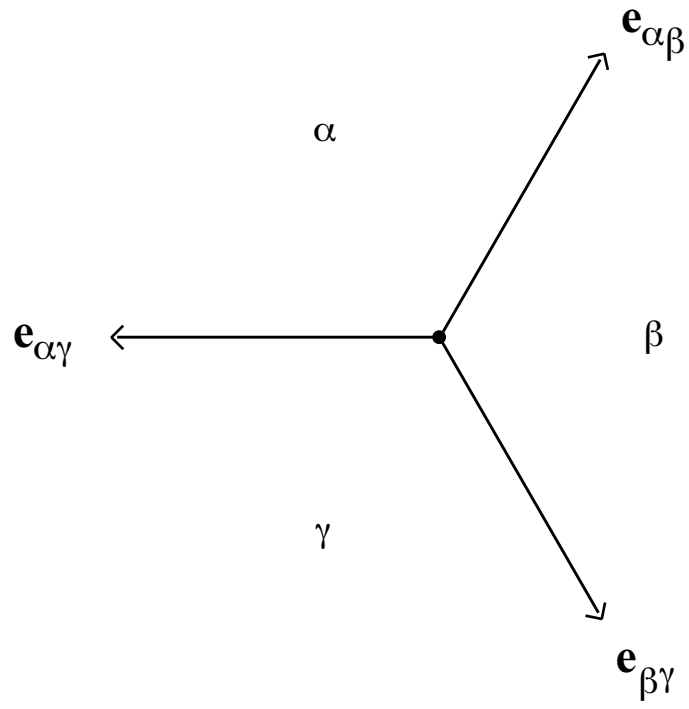


Fig. 1

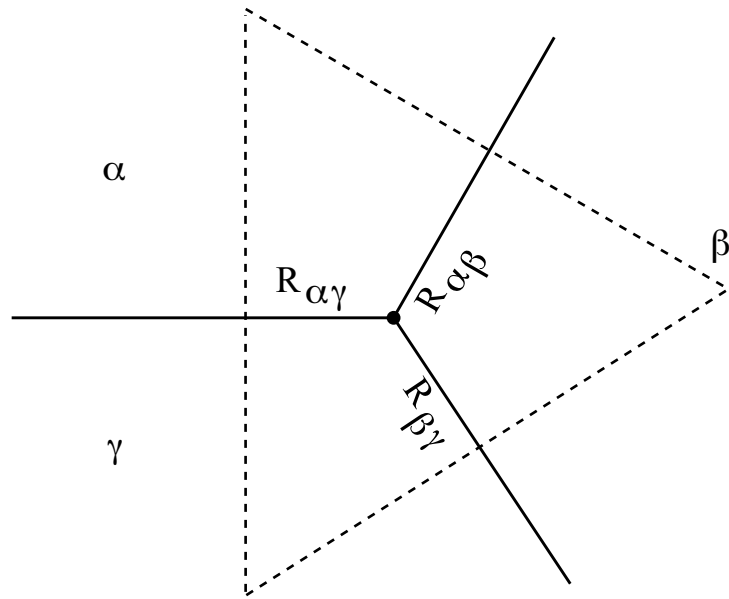


Fig. 2

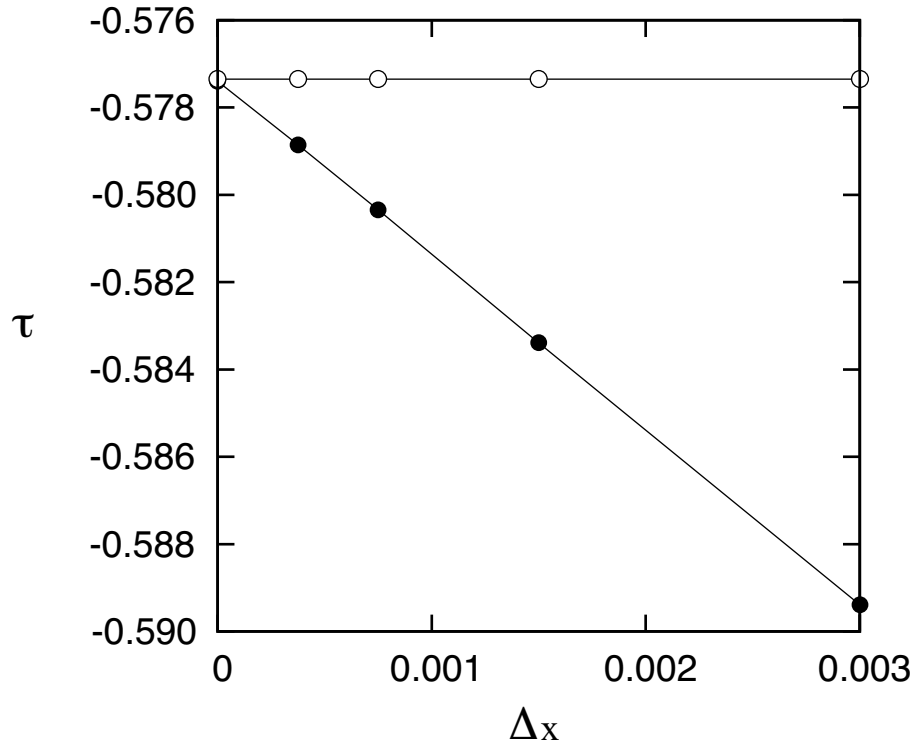


Fig. 3

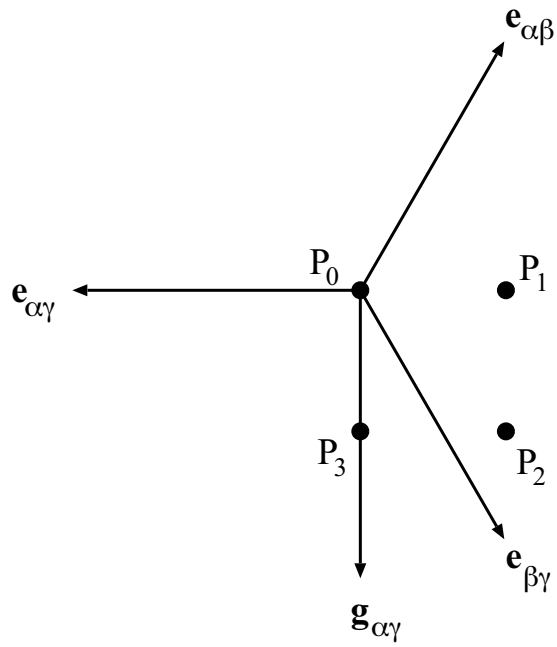


Fig. 4

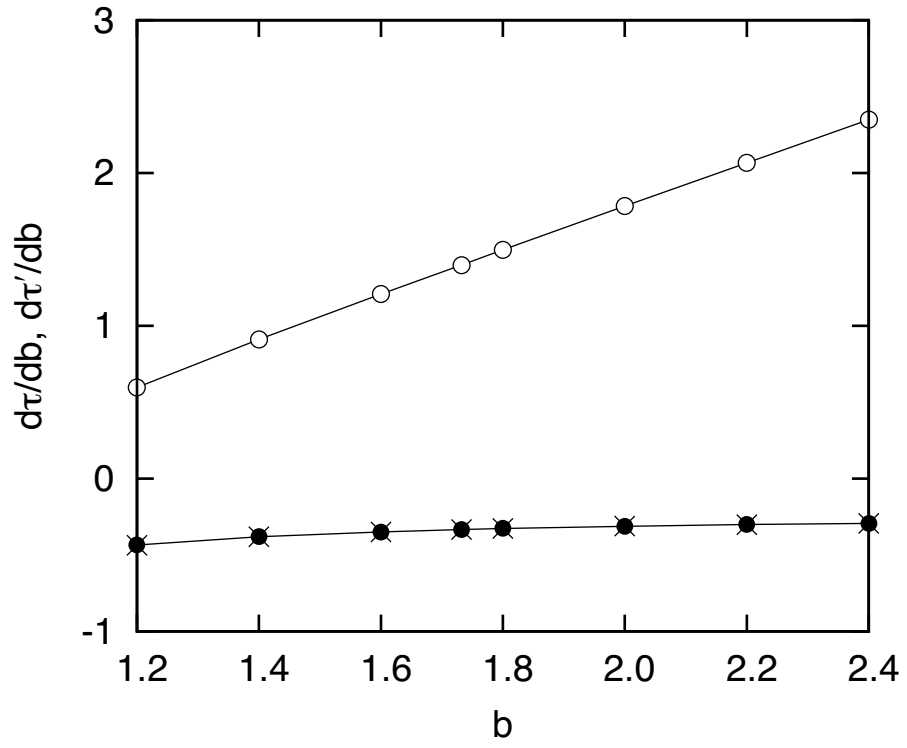


Fig. 5

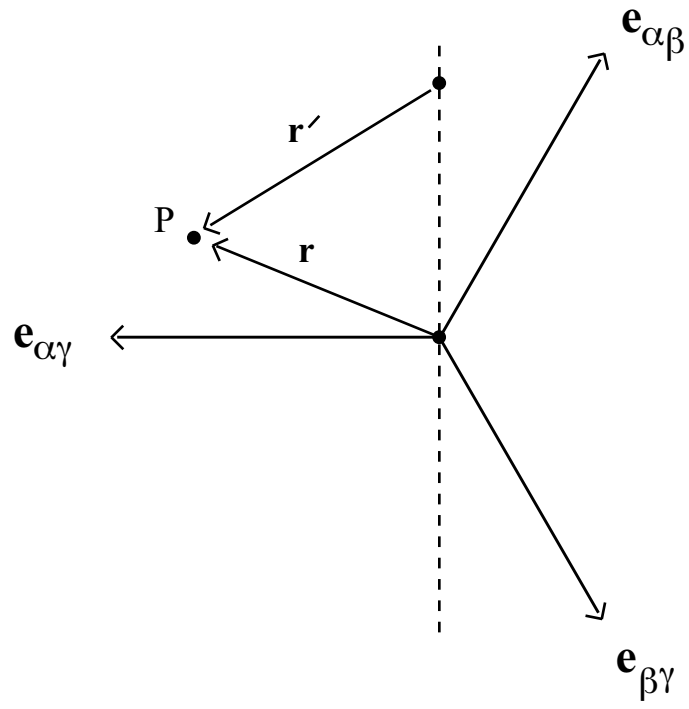


Fig. 6

$$\sigma_{\alpha\beta} d\mathbf{e}_{\alpha\beta} + \sigma_{\beta\gamma} d\mathbf{e}_{\beta\gamma} + \sigma_{\alpha\gamma} d\mathbf{e}_{\alpha\gamma}$$

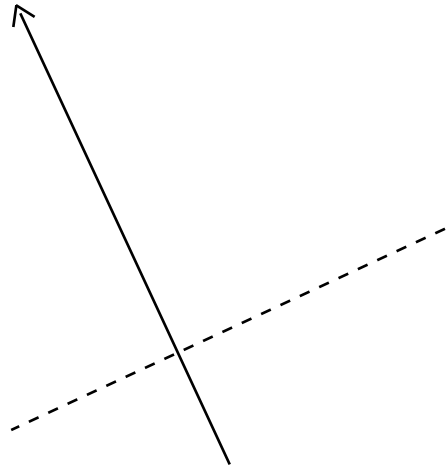


Fig. 7