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Stress theorem and Hellmann-Feynman relations for the jellium model of interfaces

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Starting with the general stress theorem as the dyadically generalized virial theorem, for metal-metal interfaces within the jellium approximation, a theorem is derived relating the interface stress, i.e., the density derivatives of the interfacial energy, to an appropriate integral of the momentum flux density (local stress or stress field). This interface stress theorem together with other sum rules are tested and illustrated by calculations using the gradient expansion method, i.e., the Thomas-Fermi method with corrections due to (i) exchange and correlation and (ii) gradient expansion both for the kinetic and the exchange and correlation energy. The results include the electron density, electric field, and stress field across the junction, as well as the interfacial energy, interfacial stress (with its parallel and perpendicular components), the adhesive force, and linear force constant for pairs of jellium densities corresponding to all alkali-metal interfaces.

I. INTRODUCTION

Within the electron theory of molecules, clusters, and solids there is a continued interest in total energies and related quantities such as equilibrium structure, binding energies, forces, force constants, elastic constants, etc. In this connection the well-known Hellmann-Feynman theorem and the virial theorem as rigorous theorems are generally of invaluable help.

Recently Nielsen and Martin[1] generalized the virial theorem $3p\Omega=2T+V$ to the so-called stress theorem $-\overleftrightarrow{\sigma}\Omega=2\overleftrightarrow{T}+\overleftrightarrow{V}$, which may be considered as the dyadic generalization of the virial theorem. In the following the basic ideas of this generalization as well as the essential content of the subsequent papers will be briefly summarized.

(i) While the pressure arises from the change of the total ground-state energy due to an isotropic homogeneous scaling of all the nuclei's sites $\mathbf{R}_l$ (which are given parameters within Born-Oppenheimer approximation), i.e., $\mathbf{R}_l \rightarrow \lambda \mathbf{R}_l$, the stress $\overleftrightarrow{\sigma}$ follows similarly from the corresponding energy change due to a more general anisotropic homogeneous scaling $\mathbf{R}_l \rightarrow \overleftrightarrow{\lambda}\mathbf{R}_l$.

(ii) While T, the expectation value of the kinetic energy, arises with the help of the one-particle density matrix $n(\mathbf{r},\mathbf{r}')$ from $\mathbf{p}^2/2m$ with $\mathbf{p}=(\hbar/i)\partial/\partial\mathbf{r}$, the tensor $\overleftrightarrow{T}$ follows similarly from the more general expression $\mathbf{p}\circ\mathbf{p}/2m$, where $\circ$ means the dyadic product.

(iii) While V, the expectation value of the potential energy, arises with the help of the pair distribution $n(\mathbf{r}_1;\mathbf{r}_2)$ for pure Coulombic systems from ϵ^2/r_{12}, with $\mathbf{r}_{12}=\mathbf{r}_1-\mathbf{r}_2$, the tensor $\overleftrightarrow{V}$ follows similarly from the more general expression $(\epsilon^2/r_{12})\mathbf{e}_{12}\circ\mathbf{e}_{12}$, where $\mathbf{e}_{12}=\mathbf{r}_{12}/r_{12}$. The stress theorem contains with $\mathrm{tr}\overleftrightarrow{\sigma}=-3p$, $\mathrm{tr}\overleftrightarrow{T}=T$, $\mathrm{tr}\overleftrightarrow{V}=V$ the virial theorem as a special case. With integration by parts and with a certain identity[2] the stress theorem can be reformulated as

$$\overleftrightarrow{\sigma}=\int\frac{d^3r}{\Omega}\overleftrightarrow{\sigma}(\mathbf{r}) \, ,$$

where the negative momentum current density or stress field $\overleftrightarrow{\sigma}(\mathbf{r})$ is defined in such a way that it satisfies the local momentum balance

$$\frac{\partial}{\partial\mathbf{r}}\overleftrightarrow{\sigma}(\mathbf{r})=\mathbf{f}(\mathbf{r})$$

with $\mathbf{f}(\mathbf{r})$ being the Hellmann-Feynman force density exerted on the positive background (the nuclei). Of course, due to the fundamental position-momentum uncertainty of quantum mechanics the stress field $\overleftrightarrow{\sigma}(\mathbf{r})$ has no direct physical meaning, i.e., it can be gauged, but the gauge has to be left unchanged for the following quantities.

(i) the volume integral $\int d^3r\overleftrightarrow{\sigma}(\mathbf{r})$, which provides via the stress theorem with the possibility to calculate stresses $\overleftrightarrow{\sigma}$ directly (avoiding differentiations of the total energy).

(ii) The surface integrals $\oiint d\mathbf{S}\,\overleftrightarrow{\sigma}(\mathbf{r})$, which provide via the momentum balance with an alternative possibility of force calculations.

The advantage of the stress theorem reformulated in terms of the stress field is its direct applicability to extended crystalline systems, which arise from finite systems through the thermodynamic limit. Then, the bulk stress follows from the above-described scaling of the bulk energy (per unit cell) and the stress field is averaged over the unit cell Ω_0.

While in Ref. 1 the stress field $\overleftrightarrow{\sigma}(\mathbf{r})$ has been expressed in terms of many-body wave functions, in Refs. 3–8 consequent use of reduced density matrices has been made and the somewhat intuitive considerations given in Ref. 1 with respect to the transition from the many-body to the effective one-particle description (density-functional theory, Kohn-Sham equation) were formally completed. In Refs. 9–11 the considerations have been extended beyond the local-density approximation; i.e., to the density gradient dependent exchange and correlation (XC) of the Kohn-Sham (KS) equation as well as gradient expansion method (GEM) for the kinetic and XC energies. Furthermore, in Refs. 12 and 13 the generalization to relativistic systems is given. Other papers dealing with this subject are Refs. 14–19.

In Ref. 20 the general stress theorem has been specified for surfaces of half-space crystals and a surface stress theorem has been derived, where the surface stress arises from a scaling of the surface energy[21] and the integrand on the right-hand side is now $\overleftrightarrow{\sigma}(\mathbf{r})-\theta(-z)\overleftrightarrow{\sigma}^b(\mathbf{r})$ instead of only the first term $\overleftrightarrow{\sigma}(\mathbf{r})$ which approaches as $z\rightarrow-\infty$ (bulk region) to the bulk stress field $\overleftrightarrow{\sigma}^b(\mathbf{r})$ and vanishes for $z\rightarrow+\infty$ (vacuum region). If applied to half-space jellia the surface virial theorem[22] is decomposed into two components, a parallel or lateral one and a perpendicular or vertical one. The corresponding Hellmann-Feynman relations lead to the rederivation of a theorem found by Vannimenus and Budd[23] and a new theorem between the density derivative of the surface energy and the electronic structure of a quarter-space jellium. Other papers dealing with the concept of surface stress and its applications are Refs. 24 and 25.

Here the stress theorem is specified for the jellium model of metal-metal interfaces ("bijellic" interfaces), especially with zero separation between the background edges. Such systems are models for metal-metal junctions, the properties of which are of great theoretical interest and have, as is well known, many applications in technology (electrical contacts, adhesion, thin-film deposition, grain boundary energetics, friction and wear, brittle and ductile fracture, crack propagation, etc.). In analogy with the attempts to understand surface properties in terms of the surface stress,[21,24,25] here the concept of the interface stress is developed, which arises from the interface energy again by an appropriate scaling. Its relation to a certain integral of the stress field across the junction is the content of the interface stress theorem obtained in Ref. 26, mentioned in Ref. 8, and presented in detail in here, and it generalizes the surface stress theorem mentioned above. The corresponding Hellmann-Feynman relations between density derivatives of the interfacial energy and the electric field across the junction generalize the above-mentioned Vannimenus-Budd theorem for jellium surfaces: two such relations appear (because of the two background densities), and their sum yields a rederivation of a theorem obtained by Swingler and Inkson.[27]

For the purpose of illustration, numerical calculations are performed for ten pairs of background densities which correspond to all interfaces of the alkali metals. They are based on the gradient expansion method (GEM),[28–31] which means the Thomas-Fermi method with corrections due to XC and gradient expansion for the kinetic and the XC energy, and which has been developed and applied in Refs. 32–38. In this way, for each interface of densities n_1,n_2 the following quantities are calculated: The electron density $n(z)$; the electric field $E(z)$; $\sigma_\parallel(z)$ and $\sigma_\perp(z)$, the components of the stress field using the results of Ref. 10, and integrals of them; the interfacial energy $\mathcal{E}^{12}$, density derivatives of it and $\sigma_\parallel^{12}$ and $\sigma_\perp^{12}$, the components of the interfacial stress; four different but equivalent expressions for the adhesive force; the force constant. Some of these numbers thus produced in principle have to coincide because of the stress theorem, of the Hellmann-Feynman relation, and of force sum rules. Note that if the theorems or sum rules are not satisfied, the results are not satisfactory due to the approximations used in the calculations. However, when the theorems or the sum rules are well satisfied, we cannot necessarily conclude that we have obtained a result very close to the true ones.

The paper is organized as follows. Section II lists the characteristic quantities of a bijellic interface in terms of reduced density matrices. Section III presents rigorous theorems or sum rules. Section IV describes GEM together with the two versions (variational *Ansatz* and linearization of Euler equation) we used in our calculations. Section V gives the results. Finally, Sec. VI contains conclusions and an outlook.

II. CHARACTERISTIC QUANTITIES OF A BIJELLIC INTERFACE

Bijellic interfaces with zero separation between the half-space jellia "1" and "2" are characterized by the following quantities:

(1) A positive background charge density

$$\rho(z)=n_1\theta(-z)+n_2\theta(z), \quad \text{with } n_1>n_2 .$$

(2) A ground-state electron density $n(z)$ with the asymptotic behavior $n(-\infty)=n_1$, $n(+\infty)=n_2$, and with the neutrality condition

$$\int_{-\infty}^{+\infty} dz[\rho(z)-n(z)]=0 .$$

(3) An electric field (times $|e|$ for convenience)

$$E(z)=4\pi\epsilon^2\int_{-\infty}^{z} dz'[\rho(z')-n(z')]$$

following from Gauss's law, $E'(z)=4\pi\epsilon^2[\rho(z)-n(z)]$, $\epsilon^2=e^2/4\pi\varepsilon_0$; due to the jump of $\rho(z)$ at $z=0$ and $n_1>n(0)>n_2$, the field $E(z)$ has a sharp cusp at the interface, and due to the neutrality condition we have $\lim_{z\rightarrow\pm\infty}E(z)=0$.

(4) A one-particle density matrix $n(\mathbf{r},\mathbf{r}')=n(\mathbf{a}-\mathbf{a}'|z,z')$, with $\mathbf{a}=x\mathbf{e}_z+y\mathbf{e}_y$ and $n(0|z,z)=n(z)$, and $n(\mathbf{a}-\mathbf{a}'|z,z')$ approaching the homogeneous bulk density matrices $n(\mathbf{r}-\mathbf{r}')$ of "1" or "2" for $z,z'\rightarrow-\infty$ and $+\infty$, respectively.

(5) A kinetic energy density

$$t(z)=\frac{1}{2m}\tilde{\mathbf{p}}^2 n(\mathbf{r},\mathbf{r}) \qquad (1)$$

with $\tilde{\mathbf{p}}=\frac{1}{2}(\mathbf{p}'^{*}+\mathbf{p})$ and $\mathbf{p}=(\hbar/i)/(\partial/\partial\mathbf{r})$. The operator $\tilde{\mathbf{p}}$ is symmetrized with respect to the variables of $n(\mathbf{r},\mathbf{r}')$. Note that $\mathbf{r}'=\mathbf{r}$ is set only after the action of $\tilde{\mathbf{p}}^2$ on $n(\mathbf{r},\mathbf{r}')$; $t(z)$ can be considered as to consist of "components"

$$t_{\parallel}(z)=\frac{1}{2m}\,\tfrac{1}{2}(\tilde{\mathbf{p}}_x^2+\tilde{\mathbf{p}}_y^2)n(\mathbf{a}-\mathbf{a}'|z,z)|_{\mathbf{a}'=\mathbf{a}}\ , \qquad (2)$$

$$t_{\perp}(z)=\frac{1}{2m}\tilde{\mathbf{p}}_z^2 n(0|z,z')|_{z'=z} \qquad (3)$$

with $t(z)=2t_{\parallel}(z)+t_{\perp}(z)$.

(6) A pair distribution function $n(\mathbf{r}_1;\mathbf{r}_2)=n(a_{12}|z_1;z_2)$, with $a_{12}=[(x_1-x_2)^2+(y_1-y_2)^2]^{1/2}$, with the perfect screening sum rule

$$\int d^2a_2\int dz_2[n(a_{12}|z_1;z_2)-n(z_1)n(z_2)]=-n(z_1) \qquad (4)$$

and with $n(a_{12}|z_1;z_2)$ approaching the homogeneous bulk pair distributions $n(r_{12})$ of "1" or "2" for $z_{1,2}\rightarrow-\infty$ and $+\infty$, respectively. From $n(\mathbf{r}_1;\mathbf{r}_2)$ follows the total pair distribution function given by

$$\nu(a_{12}|z_1;z_2)=\rho(z_1)\rho(z_2)-\rho(z_1)n(z_2)$$
$$-n(z_1)\rho(z_2)+n(a_{12}|z_1;z_2)\ .$$

(7) A potential energy density

$$v(z)=\tfrac{1}{2}\int d^3r_1\int d^3r_2\,\nu(a_{12}|z_1;z_2)$$
$$\times\frac{1}{4\pi\epsilon^2}\mathbf{E}_1(0,0,z)\mathbf{E}_2(0,0,z) \qquad (5)$$

with $\mathbf{E}_i(x,y,z)=(\epsilon^2/|\mathbf{r}-\mathbf{r}_i|^2)(\mathbf{r}-\mathbf{r}_i)/|\mathbf{r}-\mathbf{r}_i$, $i=1,2$; $v(z)$ can be considered as to consist of "components"

$$v_{\parallel}(z)=\tfrac{1}{2}\int d^3r_1\int d^3r_2\,\nu(a_{12}|z_1;z_2)\frac{\epsilon^2}{4\pi}\frac{(z-z_1)(z-z_2)}{([a_1^2+(z-z_1)^2][a_2^2+(z-z_2)^2])^{3/2}}\ , \qquad (6)$$

$$v_{\perp}(z)=\tfrac{1}{2}\int d^3r_1\int d^3r_2\,\nu(a_{12}|z_1;z_2)\frac{\epsilon^2}{4\pi}\frac{\mathbf{a}_1\mathbf{a}_2-(z-z_1)(z-z_2)}{([a_1^2+(z-z_1)^2][a_2^2+(z-z_2)^2])^{3/2}} \qquad (7)$$

with $v(z)=2v_{\parallel}(z)+v_{\perp}(z)$. The decomposition is chosen in such a way that the components $v_{\parallel}(z)$ and $v_{\perp}(z)$ can be used for the definition of $\sigma_{\parallel}(z)$ and $\sigma_{\perp}(z)$ in Eqs. (11) and (12) according to the general definition of $\overleftrightarrow{\sigma}(\mathbf{r})$; see Eq. (26) in Ref. 5.

(8) An interfacial energy $\mathscr{E}^{12}(n_1,n_2)$ with $\mathscr{E}^{12}(n_1,n_1)=0$ and $\mathscr{E}^{12}(n_1,0)=\mathscr{E}^{1}(n_1)$, where $\mathscr{E}^{1}(n_1)$ means the surface energy of the half-space jellium "1" only ("interface" between "1" and vacuum). Note that $\mathscr{E}^{12}(n_1,n_2)$ arises from $E_{L_1,L_2}(n_1,n_2)$, the ground-state energy of a finite bijellic system (with two finite, e.g., cylindrical jellia "1" and "2" in contact characterized by electron numbers N_1 and N_2, cylinder lengths L_1 and L_2, and a common cross-sectional area S) by considering the difference $E^{12}_{L_1,L_2}(n_1,n_2)=E_{L_1,L_2}(n_1,n_2)-N_1\varepsilon(n_1)-N_2\varepsilon(n_2)$ with $\varepsilon(n)$ being the bulk energy (per particle) of the homogeneous jellium and by taking the thermodynamic limit of $E^{12}_{L_1,L_2}(n_1,n_2)/S$ for $S\rightarrow\infty$ and $L_{1,2}\rightarrow\infty$.

(9) An interface stress tensor

$$\overleftrightarrow{\sigma}^{12}=\sigma_{\parallel}^{12}(\mathbf{e}_x\circ\mathbf{e}_x+\mathbf{e}_y\circ\mathbf{e}_y)+\sigma_{\perp}^{12}\mathbf{e}_z\circ\mathbf{e}_z$$

with

$$\sigma_{\parallel}^{12}=\left[-n_1\frac{\partial}{\partial n_1}-n_2\frac{\partial}{\partial n_2}+1\right]\mathscr{E}^{12}\ , \qquad (8)$$

$$\sigma_{\perp}^{12}=\left[-n_1\frac{\partial}{\partial n_1}-n_2\frac{\partial}{\partial n_2}\right]\mathscr{E}^{12} \qquad (9)$$

and $\overleftrightarrow{\sigma}^{12}(n_1,n_1)=0$; for $n_2=0$ the interface stress tensor $\overleftrightarrow{\sigma}^{12}(n_1,n_2)$ becomes the surface stress tensor of the half-space jellium "1." Note that the origin of Eqs. (8) and (9) is the scaling of the interfacial energy per particle, i.e., $S\mathscr{E}^{12}$ (instead of $\mathscr{E}^{12}$, the interfacial energy per unit area), according to

$$\overleftrightarrow{\sigma}^{12}=\frac{1}{S}\frac{\partial}{\partial\overleftrightarrow{\lambda}}S_{\overleftrightarrow{\lambda}}\mathscr{E}^{12}_{\overleftrightarrow{\lambda}}|_{\overleftrightarrow{\lambda}=\overleftrightarrow{1}}$$

or, in detail

$$\sigma_{\parallel}^{12}=\frac{1}{S}\frac{\partial}{\partial\lambda}\lambda S\mathscr{E}^{12}(\lambda^{-1}n_1,\lambda^{-1}n_2)|_{\lambda=1}\ ,$$

$$\sigma_{\perp}^{12}=\frac{\partial}{\partial\lambda}\mathscr{E}^{12}(\lambda^{-1}n_1,\lambda^{-1}n_2)|_{\lambda=1}\ ,$$

from which Eqs. (8) and (9) follow.

(10) By an adhesive force and force constant

$$F(D)=\frac{d\mathscr{E}^{12}(n_1,n_2;D)}{dD},\quad F'(D)=\frac{dF(D)}{dD}\ ,$$

where $\mathscr{E}^{12}(n_1,n_2;D)$ is the interfacial energy for the half-space background edges of "1" and "2" separated by a distance D. In the following only the zero separation values $F=F(0)$ and $A=F'(0)$ are considered. From $t(z)$ and $v(z)$ follows an interfacial energy density

$$e(z)=t(z)+v(z)\ , \qquad (10)$$

and from $t_{\parallel}(z),t_{\perp}(z)$ and $v_{\parallel}(z),v_{\perp}(z)$ an interfacial stress field

$$\overleftrightarrow{\sigma}(z)=\sigma_{\parallel}(z)(\mathbf{e}_x\circ\mathbf{e}_x+\mathbf{e}_y\circ\mathbf{e}_y)+\sigma_{\perp}(z)\mathbf{e}_z\circ\mathbf{e}_z$$

with

$$\sigma_{\parallel}(z)=-[2t_{\parallel}(z)+v_{\parallel}(z)]\ , \tag{11}$$

$$\sigma_{\perp}(z)=-[2t_{\perp}(z)+v_{\perp}(z)] \tag{12}$$

can be constructed. The fields $e(z)$ and $\overleftrightarrow{\sigma}(z)$ constructed in this way have no direct physical meaning. They can be gauged arbitrarily leaving integrals over $e(z)$ and $\overleftrightarrow{\sigma}(z)$ [see the right-hand sides of Eqs. (13) and (14)] as well as differences of $\sigma_{\perp}(z)$ at different positions z unchanged.

III. RIGOROUS THEOREMS OR SUM RULES

Now the following theorems or sum rules are valid.

(a) It holds that

$$\begin{aligned}&\mathcal{E}^{12}=\int_{-\infty}^{+\infty}dz\, e^{12}(z)\ ,\\ &e^{12}(z)=[e(z)-\theta(-z)n_1\varepsilon(n_1)-\theta(z)n_2\varepsilon(n_2)]\ .\end{aligned} \tag{13}$$

(b) It holds that

$$\begin{aligned}&\overleftrightarrow{\sigma}^{12}=\int_{-\infty}^{+\infty}dz\, \overleftrightarrow{\sigma}^{12}(z)\ ,\\ &\overleftrightarrow{\sigma}^{12}(z)=[\overleftrightarrow{\sigma}(z)-\theta(-z)\sigma(n_1)\overleftrightarrow{1}-\theta(z)\sigma(n_2)\overleftrightarrow{1}]\end{aligned} \tag{14}$$

with $\sigma(n)=-n^2d\varepsilon(n)/dn$ being the (isotropic) stress of a homogeneous jellium. Equation (13) connects $\mathcal{E}^{12}$ and $e(z)$, and may be referred to as the "interface energy theorem." Its derivation starts with the many-body Schrödinger equation and the ground-state energy $E=(\phi,H\phi)$ defined thereby. Integration by parts and use of the identity given at the end of footnote 2 allows the rewriting $E=\int d^3re(\mathbf{r})$ which, along with taking the thermodynamic limit described above, yields Eq. (13). Equation (14) connects $\overleftrightarrow{\sigma}^{12}$ and $\overleftrightarrow{\sigma}(z)$, and is referred to as "interface stress theorem." It generalizes dyadically the interface virial theorem, which follows from Eq. (14) by taking the trace

$$\begin{aligned}\left[-3n_1\frac{\partial}{\partial n_1}-3n_2\frac{\partial}{\partial n_2}+2\right]\mathcal{E}^{12}&\\ =\int dz\{-2t(z)-v(z)&-\theta(-z)[-3p(n_1)]\\ &-\theta(z)[-3p(n_2)]\}\ ,\end{aligned} \tag{15}$$

where $p(n)=n^2d\varepsilon(n)/dn$ is the bulk pressure of a homogeneous jellium. The interface stress theorem (14) can be proved in a similar manner as the surface stress theorem in Ref. 20 (for the details, see Appendix A). The components of the interface stress theorem (14) are

$$\left[-n_1\frac{\partial}{\partial n_1}-n_2\frac{\partial}{\partial n_2}+1\right]\mathcal{E}^{12}=\int_{-\infty}^{+\infty}dz\sigma_{\parallel}^{12}(z)\ , \tag{14a}$$

$$\left[-n_1\frac{\partial}{\partial n_1}-n_2\frac{\partial}{\partial n_2}\right]\mathcal{E}^{12}=\int_{-\infty}^{+\infty}dz\sigma_{\perp}^{12}(z)\ . \tag{14b}$$

The weighted sum of Eq. (14b) and two times Eq. (14a) gives Eq. (15). In addition to the "total" perpendicular stress theorem (14b), the following "partial" perpendicular stress theorems hold:

$$-n_1\frac{\partial}{\partial n_1}\mathcal{E}^{12}=\int_{-\infty}^{0}dz\,\sigma_{\perp}^{12}(z)\ , \tag{14b'}$$

$$-n_2\frac{\partial}{\partial n_2}\mathcal{E}^{12}=\int_{0}^{\infty}dz\,\sigma_{\perp}^{12}(z) \tag{14b''}$$

as shown also in Appendix A. Their sum obviously gives Eq. (14b). Note

$$\int_{-\infty}^{+\infty}dz[4t_{\parallel}^{12}(z)+3v_{\parallel}^{12}(z)]=\int_{-\infty}^{+\infty}dzt_{\perp}^{12}(z)$$

as a consequence of Eqs. (11), (12), (14a), and (14b).

(c) The Hellmann-Feynman relations

$$\frac{\partial\mathcal{E}^{12}}{\partial n_1}=\int_{-\infty}^{0}dz\,zE(z)\ , \tag{16}$$

$$\frac{\partial\mathcal{E}^{12}}{\partial n_2}=\int_{0}^{\infty}dz\,zE(z) \tag{17}$$

connect the derivatives of $\mathcal{E}^{12}$ with the electric field and follow simply from a generalized Hellmann-Feynman theorem (for the details, see Appendix B).

(d) As a consequence of Eqs. (9), (16), and (17) it is evident that

$$\sigma_{\perp}^{12}=-\int_{-\infty}^{+\infty}dz\,\rho(z)zE(z)\ . \tag{18}$$

The difference of Eq. (16) and Eq. (17) leads to another theorem. If its right-hand side is expressed in terms of $\phi(z)$, the electrostatic potential (times $|e|$), instead of $E(z)=-\phi'(z)$, then the above-mentioned theorem given by Swingler and Inkson[27] [their Eq. (3)] arises.

(e) The adhesive force in terms of Hellmann-Feynman relations is given by

$$F=n_1\int_{-\infty}^{0}dz\,E(z)-p(n_1) \tag{19}$$

or

$$F=-n_2\int_{0}^{\infty}dz\,E(z)-p(n_2)\ . \tag{20}$$

(f) Because of the local momentum balance,

$$F=\sigma_{\perp}(0) \tag{21}$$

is also valid (see Appendix C).

(g) Moreover, F can also be expressed rigorously by bulk quantities of "1" and "2":[39]

$$F=\frac{\Delta\varepsilon}{\Delta n^{-1}}\ . \tag{22}$$

(h) Finally the force constant is to be found as[33]

$$A=-\frac{E(0)}{\Delta n^{-1}}\ , \tag{23}$$

where $E(0)$ means the electric field (times $|e|$) at the interface.

Because the many-body quantities $n(\mathbf{a}-\mathbf{a}'|z,z')$ and $n(a_{12}|z_1;z_2)$ as ingredients for the calculation of interfacial energy $\mathcal{E}^{12}$ and interfacial stress $\overleftrightarrow{\sigma}^{12}$ are not available, the density-functional theory (DFT) will be used in what follows.

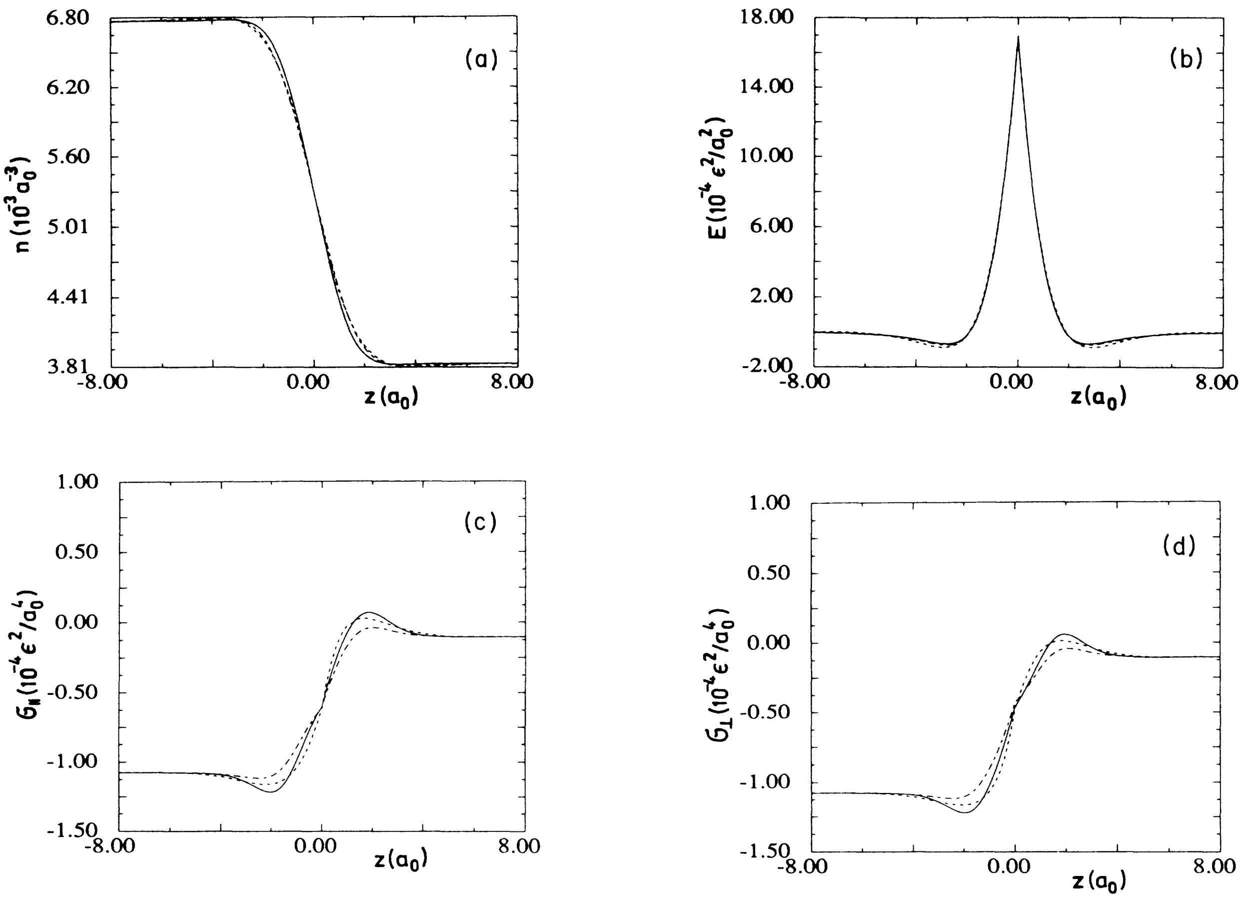

FIG. 1. Jellium model of the Li-Na interface with (a) density profile, (b) electric field, (c) parallel, and (d) perpendicular component of the stress field as functions of z, the distance from the interfacial plane. The solid and dotted-dashed lines refer to the *Ansatz* method using the gradient XC correction due to Langreth-Mehl and Lau-Kohn, respectively. The dotted line refers to the linearization method using the Lau-Kohn correction.

IV. DENSITY-FUNCTIONAL THEORY

DFT rests (for the system under consideration) upon the existence of a functional $\mathcal{E}^{12}[\rho,n]$, which arises within the gradient expansion method (GEM) from

$$e(z)=\frac{1}{2}\frac{E^2(z)}{4\pi\epsilon^2}+g[n(z),s(z)],\quad s(z)=\tfrac{1}{2}[n'(z)]^2 . \qquad (24)$$

$g(n,s)$ comprises both the kinetic-energy density $t(z)$ and the exchange and correlation (XC) part of the potential-energy density [arising from the XC part of the pair distribution function $n_{\mathrm{XC}}(a_{12}|z_1;z_2)=n(a_{12}|z_1;z_2)-n(z_1)n(z_2)$]. The first term of $e(z)$ is the Hartree or electrostatic part of the potential-energy density. Inserting Eq. (24) into Eq. (13) a functional $\mathcal{E}^{12}[\rho,n]$ arises. Now, for any given approximation of $g(n,s)$, the electron density $n(z)$ is obtained from the minimization of $\mathcal{E}^{12}[\rho,n]$ with respect to the variation of $n(z)$ under the constraint of fixed $\rho(z)$ and of the neutrality condition. Having in this way determined $n(z)$ variationally via an

TABLE I. Alkali metals and densities of their conduction electrons n (in units of $10^{-3}a_0^{-3}$) and the corresponding dimensionless density parameter r_s.

Interface	n	r_s
Li	6.765	3.28
Na	3.844	3.96
K	1.956	4.96
Rb	1.669	5.23
Cs	1.338	5.63

TABLE II. Density ratios of the alkali-metal interfaces.

Interface	n_2/n_1	$2(n_1-n_2)/(n_1+n_2)$
Li-Na	0.5682	0.5506
Li-K	0.2892	1.1027
Li-Rb	0.2467	1.2085
Li-Cs	0.1977	1.3396
Na-K	0.5089	0.6509
Na-Rb	0.4341	0.7892
Na-Cs	0.3480	0.9674
K-Rb	0.8530	0.1587
K-Cs	0.6838	0.3756
Rb-Cs	0.8016	0.2202

appropriate *Ansatz* or via an approximate solution of the Euler equation, the question then arises as how to calculate the stress field $\vec{\sigma}(z)$ from $n(z)$. This task has been solved in Ref. 10 (or 11) for the general case of an arbitrary background density $\rho(\mathbf{r})$. In our case, i.e., for $\rho(z)$ it takes the form of

$$\sigma_{\parallel}(z) = -\frac{1}{4\pi\epsilon^2}\tfrac{1}{2}E^2(z) + [g - ng_n + n(n'g_s)']_{n(z)} , \tag{25}$$

$$\sigma_{\perp}(z) = \frac{1}{4\pi\epsilon^2}\tfrac{1}{2}E^2(z) + [g - ng_n + n(n'g_s)' - (n')^2 g_s]_{n(z)} . \tag{26}$$

g_n and g_s mean the derivatives with respect to n and s. With this result, i.e., Eqs. (25) and (26) as well as Eq. (24), all the quantities appearing in the theorems or sum rules (13)–(23) can be calculated within the GEM. As shown in Ref. 10 these sum rules are exactly satisfied for any chosen approximation of $g(n,s)$, assuming the corresponding Euler equation has been solved exactly. This means the violation of the sum rules measures only the approximations made in solving the Euler equation.

Here, for the purpose of performing the following GEM calculations the above-mentioned two approaches are used.

(i) The *Ansatz*

$$n(z) = \frac{n_1}{1+e^{\beta z}} + \frac{n_2}{1+e^{-\beta z}} - 2\alpha\frac{\sinh(\beta z)}{1+\cosh^2(\beta z)} \tag{27}$$

is described and used in Refs. 32–34 and 38. Here, by considering the work-function energetics, it is assumed that aside from the usual quantum-mechanical leakage of charges from metallic surfaces some charges flow from the low-density region (bulk density $=n_2$) to the high-density side (bulk density $=n_1$). The parameters α and β are determined from the minimization of $\mathcal{E}^{12}$ obtained from Eq. (27) via Eqs. (24) and (13). The $g(n,s)$ has been specified as follows:

$$g(n,s) = n\varepsilon(n) + \frac{1}{72}\frac{(n')^2}{n}\epsilon^2 a_0 + a\,[2e^{[-b(|n'|/n^{7/6})]} - \tfrac{7}{9}]\frac{(n')^2}{n^{4/3}}\epsilon^2 . \tag{28}$$

The constants a and b are given by

$$a = \frac{\pi}{16(3\pi^2)^{4/3}} = 2.144\times 10^{-3} ,$$

$$b = (9\pi)^{1/6} f = 0.2618 \text{ (for } f = 0.15) .$$

$\varepsilon(n)$, the bulk energy of the homogeneous jellium, is given by

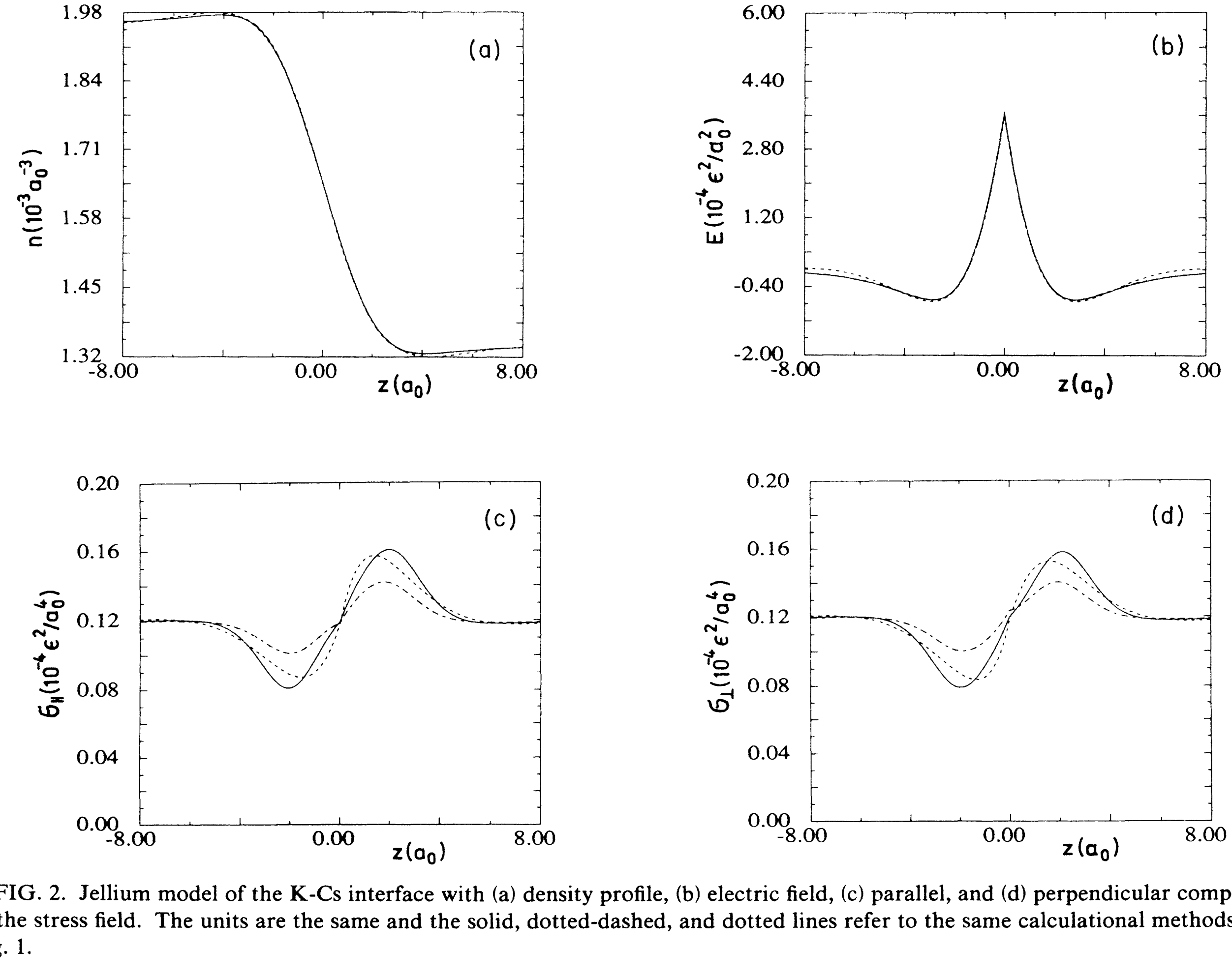

FIG. 2. Jellium model of the K-Cs interface with (a) density profile, (b) electric field, (c) parallel, and (d) perpendicular component of the stress field. The units are the same and the solid, dotted-dashed, and dotted lines refer to the same calculational methods as in Fig. 1.

$$\varepsilon(n)=\frac{3}{10\alpha^2 r_s^2}\frac{e^2}{a_0}-\frac{3}{4\pi\alpha r_s}\frac{e^2}{a_0}+\varepsilon_c(n)\ ,$$
$$\alpha=\left[\frac{4}{9\pi}\right]^{1/3},\ \frac{1}{n}=\frac{4\pi}{3}(r_s a_0)^3\ , \tag{29}$$

where the correlation energy has been taken from the interpolation of the Ceperley-Alder Quantum Monte Carlo data due to Vosko *et al.*[40] The first gradient term (the correction to the kinetic energy) is due to Kirshnits and the second gradient term is the XC correction due to Langreth and Mehl.[29] Also the XC correction of Lau and Kohn[31] (instead of Langreth and Mehl), i.e.,

$$\frac{e^2}{2}\left[\frac{3}{4\pi}\right]^{4/3}\left[0.0216+\frac{0.0130}{r_s}+\frac{0.0349}{r_s^2}\right]\frac{(n')^2}{n^{4/3}} \tag{30}$$

has been tried.

(ii) The linearization of the Euler equation under the assumption

$$\left|n(z)-\frac{n_1+n_2}{2}\right| \ll \frac{n_1+n_2}{2} \tag{31}$$

is described and used in Refs. 35 and 36. This linearized Euler equation allows, for an XC correction proportional

TABLE III. Interfacial energy [according to Eq. (13)] and interface stress [according to Eqs. (8), (9), and (14)], in units of $10^{-6}e^2/a_0^3$. The first and second numbers in each box refer to the *Ansatz* method with the Vosko *et al.* interpolation formula for $\varepsilon(n)$ using (i) Langreth and Mehl gradient XC correction and (ii) the Lau-Kohn gradient XC correction term, respectively. The third number in each box refers to the linearization method with the same interpolation formula for $\varepsilon(n)$ and the same gradient XC correction as in (ii). The missing numbers in the fourth and sixth columns are identical to the corresponding numbers given in the columns for $\sigma_\parallel^{12}$ and $\sigma_\perp^{12}$, respectively.

Interface	$\mathcal{E}^{12}$	$\sigma_\parallel^{12}$	$\int_{-\infty}^{\infty} dz\ \sigma_\parallel^{12}(z)$	$\sigma_\perp^{12}$	$\int_{-\infty}^{+\infty} dz\ \sigma_\perp^{12}(z)$
Li-Na	2.27	15.60		13.33	
	1.88	15.03		13.16	
	1.81	15.07	15.10	13.26	13.22
Li-K	17.65	44.29		26.63	
	19.29	43.24		23.95	
	18.98	43.40	43.69	24.42	23.56
Li-Rb	22.70	49.96		27.26	
	25.57	49.05		23.47	
	25.16	49.25	49.69	24.09	22.76
Li-Cs	30.00	56.74		26.74	
	35.18	56.28		21.10	
	34.63	56.59	57.26	21.97	19.74
Na-K	7.56	7.65		0.08	
	7.14	7.25		0.12	
	7.10	7.26	7.29	0.16	0.09
Na-Rb	11.10	10.20		−0.90	
	10.74	9.71		−1.03	
	10.67	9.71	9.79	−0.96	−1.12
Na-Cs	16.63	13.54		−3.08	
	16.64	13.01		−3.63	
	16.53	13.02	13.19	−3.51	−3.90
K-Rb	0.40	0.20		−0.21	
	0.36	0.18		−0.18	
	0.35	0.18	0.18	−0.18	−0.18
K-Cs	2.11	0.91		−1.20	
	2.19	0.82		−1.10	
	1.90	0.81	0.82	−1.09	−1.10
Rb-Cs	0.69	0.27		−0.43	
	0.62	0.23		−0.39	
	0.61	0.23	0.23	−0.38	−0.39

to $(n')^2$ with a prefactor depending only on the electron density (in contrast to the Langreth-Mehl prefactor which contains n', too), an analytic solution. Therefore here the XC correction of Lau-Kohn has been used only. $\varepsilon_c(n)$ is taken again from Ref. 40. If for $\varepsilon_c(n)$ the data of Aguilera-Navarro *et al.*[41] are used, the results are changed only slightly.

The above-mentioned two approaches have been applied to ten combinations of n_1 and n_2 values corresponding to all interfaces between the 5 alkali metals, whose densities n and density parameters r_s are given in Table I.

V. NUMERICAL RESULTS

The results for $n(z)$, $E(z)$, $\sigma_\parallel(z)$, and $\sigma_\perp(z)$ obtained with the methods described above are plotted in Figs. 1 and 2 for two illustrating cases of Li-Na (Fig. 1) and K-Cs (Fig. 2) interfaces. The solid and dashed lines refer to the *Ansatz* method using the XC gradient correction due to the Langreth-Mehl and Lau-Kohn corrections, respectively. The dotted line refers to the linearization method using the Lau-Kohn correction. Note that the jellium model of an interface has its artificial aspects. Because the background density is kept fixed, the system is not in its equilibrium, and this is reflected in the stress field not being zero. As Figs. 1 and 2 show, and in agreement with the general characteristics of the bijellic interfaces mentioned in Sec. II, the cusp in the electric field changes into a kink for the two components of the stress field. The results of *Ansatz* and linearization methods both show that the change of the cusp to the kink occurs for all the bialkali interfaces with the exception of Li-Cs. Since the ratio of the bulk density differences of bialkali interfaces to their corresponding sum (see Table II) is largest for the Li-Cs interface, the GEM is not expected to lead to reasonable results in this special case.

Tables III–V show the results for the following: (i) In-

TABLE IV. Density derivatives of the interfacial energy $\mathcal{E}^{12}$ in comparison with the integrated stress field and the moments of the electric field (in units of $10^{-6}e^2/a_0^3$). The three numbers in each box refer to the same calculations as in Table III.

Interface	$n_1 \frac{\partial \mathcal{E}^{12}}{\partial n_1}$	$-\int_{-\infty}^{0} dz\, \sigma_\perp^{12}(z)$	$n_1 \int_{-\infty}^{0} dz\, zE(z)$	$n_2 \frac{\partial \mathcal{E}^{12}}{\partial n_2}$	$-\int_{0}^{+\infty} dz\, \sigma_\perp^{12}(z)$	$n_2 \int_{0}^{+\infty} dz\, zE(z)$
Li-Na	−1.04	−6.41	7.52	−12.29	−6.91	−4.27
	−0.91	−6.05	13.57	−12.25	−7.11	−7.71
	−1.23	−2.08	6.90	−12.03	−11.13	−3.92
Li-K	4.11	−6.06	37.15	−30.74	−20.58	−10.74
	13.56	−1.00	84.42	−37.13	−22.95	−24.41
	12.56	6.41	39.30	−56.95	−29.96	−11.36
Li-Rb	5.24	−5.20	44.45	−32.50	−22.07	−10.97
	17.91	0.33	106.01	−41.38	−23.80	−26.15
	16.70	8.64	47.47	−40.78	−31.39	−11.71
Li-Cs	6.47	−3.47	54.67	−33.21	−23.27	−10.81
	24.11	1.88	137.51	−45.22	−22.98	−27.19
	22.60	11.56	58.28	−44.57	−31.30	−11.52
Na-K	20.64	17.53	41.62	−20.72	−17.61	−21.18
	20.62	17.66	46.85	−20.74	−17.78	−23.84
	20.45	19.64	27.40	−20.61	−19.73	−13.94
Na-Rb	24.51	20.69	51.49	−23.61	−19.79	−22.35
	25.56	21.56	61.73	−24.53	−20.53	−26.80
	25.32	23.93	35.01	−24.36	−22.81	−15.19
Na-Cs	29.18	24.55	64.40	−26.09	−21.47	−22.41
	32.24	26.45	84.06	−28.61	−22.82	−29.25
	31.91	29.40	45.45	−28.41	−25.50	−15.81
K-Rb	5.12	4.85	8.88	−4.92	−4.65	−7.57
	4.56	4.34	8.06	−4.38	−4.16	−6.87
	4.53	4.54	4.82	−4.35	−4.36	−4.11
K-Cs	11.42	10.73	20.99	−10.22	−9.53	−14.36
	10.59	10.04	20.36	−9.50	−8.95	−13.92
	10.53	10.46	11.91	−9.44	−9.36	−8.14
Rb-Cs	6.41	6.11	11.43	−5.98	−5.68	−9.16
	5.78	5.54	10.55	−5.39	−5.15	−8.45
	5.75	5.73	6.17	−5.36	−5.35	−4.95

terfacial energy $\mathcal{E}^{12}$, calculated with the help of the interface energy theorem (13); (ii) two sides of the stress theorem [(14a), (14b), (14b′), (14b″)]; (iii) two sides of the Hellmann-Feynman relations (16) and (17); (iv) adhesive force F, calculated by means of Eqs. (19)–(22); and (v) force constant A, calculated via Eq. (23). The three numbers in each box refer to the same calculational methods mentioned in the caption of Table III.

The numbers for $\sigma_{\parallel}^{12}$ [from Eq. (8)] and $\int dz\, \sigma_{\parallel}^{12}(z)$ given in Table III and calculated within the *Ansatz* method as well as those for $\sigma_{\perp}^{12}$ [from Eq. (9)] and $\int dz \sigma_{\perp}^{12}(z)$ coincide for any choice of $g(n,s)$ assuming the minimum is found correctly (see Appendix D). Note that when the bulk density difference for an interface is relatively large, the interfacial energies given in Table III, in the case of the *Ansatz* method employing the Langreth-Mehl XC correction, differ from the corresponding ones given in Ref. 34. This is due to their assumption that the expression $\exp(-b \ldots)$ in Langreth-Mehl XC correction only weakly depends on β. The interfacial energies in Table III are calculated without invoking this assumption and as a result the above-mentioned sum rules are identically satisfied. Within the linearization method the stress theorem is better satisfied the better condition (31) is fulfilled by the interface under consideration.

With respect to the Hellmann-Feynman relations (see Table IV) only for the interfaces K-Rb, K-Cs, Rb-Cs a reasonable agreement is obtained. The same is true for the four in principle equivalent expressions of adhesive force, Eqs. (19)–(22) (see Table V). On the other hand, the most striking disagreement appears for Li-Cs [note once more that the numbers obtained by using Eq. (22) can be considered as "exact" ones for the true bulk energies].

Altogether Tables III–V show that the linearization method satisfies the sum rules best for the interfaces K-Rb, K-Cs, and Rb-Cs, but worst for Li-Cs. This is to be expected because of assumption (31): The third column

TABLE V. Adhesive forces F (in units of $10^{-6}\epsilon^2/a_0^4$). The three numbers in each box refer to the same calculational methods as in Table III. The missing numbers for each interface are the same as the one given.

	F				A
Interface	Eq. (19)	Eq. (20)	Eq. (21)	Eq. (22)	Eq. (23)
Li-Na	−44.94	−46.27	−45.87	−44.15	15.04
	−46.05	−45.63	−46.84		15.11
	−45.50	−45.80	−48.35		15.00
Li-K	−15.70	−14.68	−9.51	−9.59	7.51
	−20.85	−13.19	−16.46		7.78
	−13.64	−15.21	−21.66		7.69
Li-Rb	−13.37	−10.88	−4.07	−5.33	6.36
	−19.48	−9.38	−12.63		6.65
	−9.80	−11.70	−18.86		6.57
Li-Cs	−12.37	−6.94	2.08	−0.98	5.03
	−19.31	−5.57	−8.44		5.35
	−5.85	−8.18	−16.18		5.27
Na-K	2.72	5.17	5.06	5.87	4.41
	1.89	5.59	4.12		4.44
	4.45	4.34	3.30		4.41
Na-Rb	3.25	6.39	6.88	7.53	3.73
	1.95	6.96	5.21		3.79
	5.59	5.42	4.06		3.76
Na-Cs	2.92	7.22	8.89	8.96	2.94
	0.82	7.95	5.98		3.04
	6.33	6.07	4.28		3.01
K-Rb	11.81	12.50	12.19	12.27	1.97
	11.82	12.49	12.20		1.91
	12.20	12.20	12.18		1.90
K-Cs	11.05	12.53	12.00	12.25	1.55
	10.97	12.58	11.92		1.52
	11.94	11.94	11.83		1.51
Rb-Cs	11.65	12.51	12.14	12.24	1.34
	11.65	12.51	12.14		1.29
	12.14	12.14	12.11		1.28

of Table II shows small numbers for the "good" interfaces, but larger numbers for the "bad" ones, and for Li-Cs the ratio is the largest. A detailed consideration of Tables III–V with respect to the *Ansatz* method seems to indicate that the *Ansatz* (27) is "good" again for the last three interfaces, but not as "good" for the others.

Comparing, in Table III, the results for the interfacial energy $\mathcal{E}^{12}$ obtained for the three calculational methods mentioned above, one finds a reasonable agreement. The force constant A even depends less sensitively on these calculational methods (see Table V).

VI. CONCLUSIONS AND OUTLOOK

Within the only approximately solved many-body problem, rigorous theorems are a very useful tool. In our case—jellium model for interfaces between alkali metals treated within the gradient expansion method—from improved *Ansätze* or improved solutions of the Euler equation a better fulfillment of the interface stress theorem and other sum rules should be expected. Also, the study of self-consistent solutions of the corresponding Kohn-Sham equation in terms of these theorems and rules is of interest. The inclusion of pseudopotentials similarly, as this has been done for surfaces, would make the model more realistic.

Within the jellium model the theorems presented above should be completed by adding that appropriate moment of the Hellmann-Feynman forces which corresponds to the "parallel" interface stress theorem (14a), i.e., the theorem corresponding to formula (18), as well as the pendants to Eqs. (14b′), (14b″), (16), and (17): A semi-infinite interface or two just touching quarter-space jellia (i.e., an extended interface cleaved perpendicular to the interface) enter the scene.[26] Also a finite (nonzero) separation including the problem of ideal fracture strength should be of interest to study. Finally, it would be worthwhile to give the interface stress theorem and related sum rules for interfaces between crystals (instead of jellia)[26] and to study to which extent the concept of interface stress is useful.

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APPENDIX A: PROOF OF THE INTERFACE STRESS THEOREM (14)

First the proof of the surface stress theorem is briefly summarized. We start with the general stress theorem (Sec. I), which is valid for a finite system with volume Ω, and specialize it to a jellium cylinder with radius $\mathcal{A}$ and thickness $2L$ [hence $\Omega=2\pi\mathcal{A}^2L$, its background density is given by $\rho_{\mathcal{A},L}(a,z)=n\theta(L-|z|)\theta(\mathcal{A}-a)$, $n=N/\Omega$]:

$$\left[\mathcal{A}\frac{\partial}{\partial\mathcal{A}}\right]_{N,L}\mathcal{E}_{\mathcal{A},L}=\frac{2}{N}\int d^2a\int dz\,\sigma_{\mathcal{A},L,\parallel}(a,z)\ , \tag{A1}$$

$$\left[L\frac{\partial}{\partial L}\right]_{N,\mathcal{A}}\mathcal{E}_{\mathcal{A},L}=\frac{1}{N}\int d^2a\int dz\,\sigma_{\mathcal{A},L,\perp}(a,z)\ . \tag{A2}$$

$N=2\pi\mathcal{A}^2Ln$ is the number of electrons, $\mathcal{E}_{\mathcal{A},L}=E_{\mathcal{A},L}/N$ is the ground-state energy per particle, $\parallel$ means the xx (or yy) component, $\perp$ corresponds to the zz component, and $a=(x^2+y^2)^{1/2}$. In the limit of an extended slab ($N,\mathcal{A}\to\infty$, $N/\mathcal{A}^2=\text{const}$), Eqs. (A1) and (A2) along with the new variables n,L (instead of $n,L,\mathcal{A}$) and with $\mathcal{E}_{\mathcal{A},L}\to\mathcal{E}_L$ take the form

$$-n\frac{\partial}{\partial n}\mathcal{E}_L=\frac{1}{n}\int\frac{dz}{2L}\sigma_{L,\parallel}(z)\ , \tag{A3}$$

$$\left[L\frac{\partial}{\partial L}-n\frac{\partial}{\partial n}\right]\mathcal{E}_L=\frac{1}{n}\int\frac{dz}{2L}\sigma_{L,\perp}(z)\ . \tag{A4}$$

Here use is made of $\int d^2a/\pi\mathcal{A}^2\to 1$. Next the surface energy

$$\begin{aligned}-\mathcal{E}^s_L&=Ln[\mathcal{E}_L-\varepsilon(n)]\\&=\int dz\,[e_L(z)-\theta(L-|z|)n\varepsilon(n)]\end{aligned} \tag{A5}$$

and surface stress field

$$\sigma^s_{L,\parallel}(z)=\sigma_{L,\parallel}(z)-\theta(L-|z|)\sigma(n)\ , \tag{A6}$$

$$\sigma^s_{L,\perp}(z)=\sigma_{L,\perp}(z)-\theta(L-|z|)\sigma(n) \tag{A7}$$

are introduced and with the help of $-n^2\varepsilon(n)/dn=\sigma(n)$ from Eqs. (A3) and (A4) one obtains

$$\left[-n\frac{\partial}{\partial n}+1\right]\mathcal{E}^s_L=\int_0^\infty dz\,\sigma^s_{L,\parallel}(z)\ , \tag{A8}$$

$$\left[L\frac{\partial}{\partial L}-n\frac{\partial}{\partial n}\right]\mathcal{E}^s_L=\int_0^\infty dz\,\sigma^s_{L,\perp}(z)\ . \tag{A9}$$

In the limit of a semi-infinite jellium ($L\to\infty$, $n=\text{const}$), the *surface stress theorem*

$$\left[-n\frac{\partial}{\partial n}+1\right]\mathcal{E}^s=\int dz\,\sigma^s_{\parallel}(z)\ , \tag{A10}$$

$$-n\frac{\partial}{\partial n}\mathcal{E}^s=\int_{-L}^{+\infty}dz\sigma^s_{\perp}(z) \tag{A11}$$

results, where

$$\mathcal{E}^s_L\to\mathcal{E}^s,\quad L\frac{\partial}{\partial L}\mathcal{E}^s_L\to 0\ ,$$

$$\int_{-L}^{+\infty}dz'\,\sigma^s_{L,\ldots}(z')\to\int_{-\infty}^{+\infty}dz'\,\sigma^s_{L,\ldots}(z')$$

has been assumed [$\sigma^s_{L,\ldots}(z')$ results from redenoting of $\sigma^s_{L,\ldots}(z'+L)$ due to the shift of the origin from the middle of the slab to its surface at $z=+L$, which means $z'=0$].

Analogously we derive the interface stress theorem and start with two cylindrical slabs of radius $\mathcal{A}$ and of thicknesses $2L_1$ and $2L_2$, respectively, and with different background densities n_1 (for $-2L_1<z<0$ and $a<\mathcal{A}$) and n_2 (for $0<z<2L_2$ and $a<\mathcal{A}$), which are just touching each other (zero separation) with a common interface of size $\pi\mathcal{A}^2$ situated at $z=0$. Thus the background density is given by

$$\rho_{\mathcal{A},L_{1,2}}(a,z)=[n_1\theta_{-2L_1,0}(z)+n_2\theta_{0,2L_2}(z)]\theta(\mathcal{A}-a)$$

with the abbreviation $\theta_{z_1,z_2}(z)=\theta(z-z_1)\theta(z_2-z)$, $z_1<z_2$. The stress theorem (Sec. I) applied to this case now reads

$$\left[\mathcal{A}\frac{\partial}{\partial\mathcal{A}}\right]_{N,L_{1,2}}\mathcal{E}_{\mathcal{A},L_{1,2}}=\frac{2}{N}\int d^2a\int dz\,\sigma_{\mathcal{A},L_{1,2},\parallel}(a,z)\ ,\tag{A12}$$

$$\left[L_1\frac{\partial}{\partial L_1}+L_2\frac{\partial}{\partial L_2}\right]_{N,\mathcal{A}}\mathcal{E}_{\mathcal{A},L_{1,2}}=\frac{1}{N}\int d^2a\int dz\,\sigma_{\mathcal{A},L_{1,2},\perp}(a,z)\tag{A13}$$

with $N=\pi\mathcal{A}^2(2L_1n_1+2L_2n_2)$. In the slab limit ($N,\mathcal{A}\to\infty, N/\mathcal{A}^2=\text{const}$), Eqs. (A12) and (A13) take the form

$$\left[-n_1\frac{\partial}{\partial n_1}-n_2\frac{\partial}{\partial n_2}\right]\mathcal{E}_{L_{1,2}}=\frac{1}{2(L_1n_1+L_2n_2)}\int dz\,\sigma_{L_{1,2},\parallel}(z)\ ,\tag{A14}$$

$$\left[L_1\frac{\partial}{\partial L_1}+L_2\frac{\partial}{\partial L_2}-n_1\frac{\partial}{\partial n_1}-n_2\frac{\partial}{\partial n_2}\right]\mathcal{E}_{L_{1,2}}=\frac{1}{2(L_1n_1+L_2n_2)}\int dz\,\sigma_{L_{1,2},\perp}(z)\ .\tag{A15}$$

Next these equations are multiplied by $2(L_1n_1+L_2n_2)$ and rewritten with the help of

$$-n_i^2\frac{d\varepsilon(n_i)}{dn_i}=\sigma(n_i)\ .$$

Then surface energies

$$\mathcal{E}^1_{L_{1,2}}=\int_{-\infty}^{-L_1}dz\,[e_{L_{1,2}}(z)-\theta_{-2L_1,-L_1}(z)n_1\varepsilon(n_1)]\ ,$$

$$\mathcal{E}^2_{L_{1,2}}=\int_{+L_2}^{+\infty}dz\,[e_{L_{1,2}}-\theta_{L_2,2L_2}(z)n_2\varepsilon(n_2)]$$

and the interfacial energy

$$\mathcal{E}^{12}_{L_{1,2}}=\int_{-L_1}^{L_2}dz[e_{L_{1,2}}(z)-\theta_{-L_1,0}(z)n_1\varepsilon(n_1)-\theta_{0,L_2}(z)n_2\varepsilon(n_2)]$$

are introduced in such a way that

$$2(L_1n_1+L_2n_2)\mathcal{E}_{L_{1,2}}-2L_1n_1\varepsilon(n_1)-2L_2n_2\varepsilon(n_2)=\mathcal{E}^1_{L_{1,2}}+\mathcal{E}^{12}_{L_{1,2}}+\mathcal{E}^2_{L_{1,2}}$$

holds. The right-hand sides of Eqs. (A14) and (A15) are also rewritten in the same manner. In the limit of two semi-infinite jellia ($L_{1,2}\to\infty$, $n_{1,2}=\text{const}$) the stress theorems are

$$\left[-n_1\frac{\partial}{\partial n_1}-n_2\frac{\partial}{\partial n_2}+1\right](\mathcal{E}^1+\mathcal{E}^{12}+\mathcal{E}^2)=\int dz[\sigma^1_\parallel(z)+\sigma^{12}_\parallel(z)+\sigma^2_\parallel(z)]\ ,\tag{A16}$$

$$\left[-n_1\frac{\partial}{\partial n_1}-n_2\frac{\partial}{\partial n_2}\right](\mathcal{E}^1+\mathcal{E}^{12}+\mathcal{E}^2)=\int dz\,[\sigma^1_\perp(z)+\sigma^{12}_\perp(z)+\sigma^2_\perp(z)]\ .\tag{A17}$$

Finally, subtracting the surface stress theorems (A10) and (A11) for $n\to n_i$, $\mathcal{E}^s\to\mathcal{E}^i$, $\sigma^s_{\dots}(z)\to\sigma^i_{\dots}(z)$ with $i=1,2$, the *interface stress theorem* (14) or (14a) and (14b) results, QED.

The splitting of the perpendicular interface stress theorem (14b) into its "components" (14b′) and (14b″) can be seen by the following procedure. Instead of a total scaling of the two jellia "1" and "2" along the z axis ($L_1\to\lambda L_1$ and $L_2\to\lambda L_2$), which leads to Eq. (A13), only a corresponding partial scaling of the jellium "1" (only $L_1\to\lambda L_1$) is considered ($D=\lim_{\lambda\to1}\partial/\partial\lambda$):

$$\begin{aligned}N\left[L_1\frac{\partial}{\partial L_1}\right]_{N,\mathcal{A},L_2,n_2}\mathcal{E}_{\mathcal{A},L_{1,2}}&=ND\mathcal{E}_{\mathcal{A},\lambda L_1,L_2}\\&=DE_{\mathcal{A},\lambda L_1,L_2}\\&=\langle D\hat{H}_{\mathcal{A},\lambda L_1,L_2}\rangle\ .\end{aligned}\tag{A18}$$

In the last step the Hellmann-Feynman theorem was used. Because only the potential-energy operator,

$$\hat{V}_{\mathcal{A},L_{1,2}}=\tfrac{1}{2}\int d^3r_1\,\rho_{\mathcal{A},L_{1,2}}(\mathbf{r}_1)\int d^3r_2\,\rho_{\mathcal{A},L_{1,2}}(\mathbf{r}_2)\frac{\epsilon^2}{r_{12}}-\int d^3r_1\,\rho_{\mathcal{A},L_{1,2}}(\mathbf{r}_1)\int d^3r_2\,\hat{n}(\mathbf{r}_2)\frac{\epsilon^2}{r_{12}}+V^{2--}$$

depends on L_1, the following relation holds:

$$\begin{aligned}\langle D\hat{H}_{\mathcal{A},\lambda L_1,L_2}\rangle&=\langle D\hat{V}_{\mathcal{A},\lambda L_1,L_2}\rangle\\&=\int d^3r\,D\rho_{\mathcal{A},\lambda L_1,L_2}(\mathbf{r})\phi_{\mathcal{A},L_{1,2}}(\mathbf{r})\ ,\end{aligned}\tag{A19}$$

where

$$\phi_{\mathcal{A},L_{1,2}}(\mathbf{r})=\int d^3\mathbf{r}'[\rho_{\mathcal{A},L_{1,2}}(\mathbf{r}')-n_{\mathcal{A},L_{1,2}}(\mathbf{r}')]\frac{\epsilon^2}{|\mathbf{r}-\mathbf{r}'|}$$

is the electrostatic potential (times $|e|$) arising from background and electron density. In the next step the identity

$$\begin{aligned}D\rho_{\mathcal{A},\lambda L_1,L_2}(a,z)&=\theta(-z)D\lambda^{-1}\rho_{\mathcal{A},L_{1,2}}(a,\lambda^{-1}z)\\&=\theta(-z)\left[-\frac{\partial}{\partial z}z\right]\rho_{\mathcal{A},L_{1,2}}(a,z)\end{aligned}\tag{A20}$$

is used. Thus

$$N\left[L_1\frac{\partial}{\partial L_1}\right]_{N,\mathcal{A},L_2,n_2}\mathcal{E}_{\mathcal{A},L_{1,2}} = -\int d^2a\int_{-\infty}^{0} dz\, z\rho_{\mathcal{A},L_{1,2}}(a,z)\mathbf{E}_{\mathcal{A},L_{1,2}}(a,z)\mathbf{e}_z\ , \tag{A21}$$

where $\mathbf{E}_{\mathcal{A},L_{1,2}}(\mathbf{r})=-\partial\phi_{\mathcal{A},L_{1,2}}(\mathbf{r})/\partial\mathbf{r}$ means the electric field (times $|e|$). Now the Hellmann-Feynman force density $\rho_{\ldots}(\mathbf{r})\mathbf{E}_{\ldots}(\mathbf{r})$ on the right-hand side of Eq. (A21) can be replaced by means of the local momentum balance (Sec. I):

$$\begin{aligned} N\left[L_1\frac{\partial}{\partial L_1}\right]_{N,\mathcal{A},L_2,n_2}\mathcal{E}_{\mathcal{A},L_{1,2}} &= -\int d^2a\int_{-\infty}^{0} dz\, z\frac{\partial}{\partial\mathbf{r}}\overleftrightarrow{\sigma}_{\mathcal{A},L_{1,2}}(\mathbf{r})\mathbf{e}_z \\ &= \int d^2a\int_{-\infty}^{0} dz\sigma_{\mathcal{A},L_{1,2},\perp}(a,z)\ . \end{aligned} \tag{A22}$$

The surface integral arising from integration by parts does not contribute because of $z=0$ along the xy plane as well as $\overleftrightarrow{\sigma}(a,z\rightarrow-\infty)=0$ and $\overleftrightarrow{\sigma}(a\rightarrow\infty,z)=0$. Finally, Eq. (A22) is divided by $\pi\mathcal{A}^2$ and the slab limit $(N,\mathcal{A}\rightarrow\infty,\ N/\mathcal{A}^2=\text{const})$ is taken:

$$\left[L_1\frac{\partial}{\partial L_1}-n_1\frac{\partial}{\partial n_1}\right]2(L_1n_1+L_2n_2)\mathcal{E}_{L_{1,2}} = \int_{-\infty}^{0} dz\,\sigma_{L_{1,2},\perp}(z)\ . \tag{A23}$$

Subtracting

$$-2L_1n_1^2\frac{d\varepsilon(n_1)}{dn_1}=2L_1\sigma(n_1)$$

and taking the limit $L_{1,2}\rightarrow\infty$ the relation

$$-n_1\frac{\partial}{\partial n_1}(\mathcal{E}^1+\mathcal{E}^{12}+\mathcal{E}^2)=\int_{-\infty}^{0} dz[\sigma_\perp^1(z)+\sigma_\perp^{12}(z)]$$

arises, from which immediately Eq. (14b″) follows, if the surface stress theorem is used once more.

APPENDIX B: PROOF OF THE HELLMANN-FEYNMAN RELATIONS (16) AND (17)

Again a single jellium surface [at $z=0$ with bulk density n for $z<0$, i.e., $\rho(z)=n\theta(-z)$] will be considered first. In this case the local momentum balance (Sec. I) reads

$$\frac{d}{dz}\sigma_\perp(z)=\rho(z)E(z)\ . \tag{B1}$$

Applying the operation $\int_{-\infty}^{0}dz\,z$ and replacing $\sigma_\perp(z)$ by $\sigma_\perp^s(z)=\sigma_\perp(z)-\theta(-z)\sigma(n)$ yields after integration by parts,

$$-\int_{-\infty}^{0} dz\,\sigma_\perp^s(z)-z\sigma_\perp^s(z)|_{z\rightarrow-\infty}=n\int_{-\infty}^{0} dz\,zE(z)\ . \tag{B2}$$

The second term on the left-hand side does not contribute because of

$$\sigma_\perp(z)=\sigma(n)+n\int_{-\infty}^{z} dz'\,\theta(-z')E(z')\ , \tag{B3}$$

which is a consequence of Eq. (B1), and

$$E(z\rightarrow-\infty)\sim\frac{\sin(2k_Fz+\cdots)}{z^2}\ , \tag{B4}$$

see Refs. 42 and 43. Thus

$$\int_{-\infty}^{0} dz\,\sigma_\perp^s(z)=-\int_{-\infty}^{0} dz\,zE(z) \tag{B5}$$

results. Combining this with (A11) yields

$$\frac{d}{dn}\mathcal{E}^s=\int_{-\infty}^{0} dz\,zE(z)\ , \tag{B6}$$

which, by the way, allows the following interpretation as a generalized Hellmann-Feynman theorem. The surface energy $\mathcal{E}^s$ depends on the background density n, the characteristic parameter of the system (i.e., of the Hamiltonian before the limits $\mathcal{A}\rightarrow\infty$ and $L\rightarrow\infty$ are taken). The generalization of the Hellmann-Feynman theorem to such a semi-infinite system would mean that only the explicit dependence of $\mathcal{E}^s$ on n and not the implicit dependence via $n(z)$ should contribute to $d\mathcal{E}^s/dn$. This explicit dependence of

$$\mathcal{E}^s=\int dz[e(z)-\theta(-z)e(-\infty)],\quad e(-\infty)=n\varepsilon(n) \tag{B7}$$

on n is contained only in the Hartree part $v_H(z)=\frac{1}{2}[E^2(z)/4\pi\epsilon^2]$ of the potential-energy density $v(z)$ of $e(z)=t(z)+v(z)$. Note that $e(-\infty)$ does not depend on n explicitly because of $v_H(-\infty)=0$. Thus

$$\frac{d}{dn}\mathcal{E}^s=\int dz\left[\frac{dE(z)}{dn}\right]_{\text{expl}}\frac{E(z)}{4\pi\epsilon^2}\ . \tag{B8}$$

On the other hand, the electric field $E(z)$ follows from the Maxwell equation

$$E'(z)=4\pi\epsilon^2[\rho(z)-n(z)],\quad \rho(z)=n\theta(-z) \tag{B9}$$

and its change due to an explicit change of n has to obey the equation

$$[dE(z)]'=4\pi\epsilon^2dn\,\theta(-z)\ . \tag{B10}$$

The expression

$$\left[\frac{dE(z)}{dn}\right]_{\text{expl}}=4\pi\epsilon^2z\theta(-z) \tag{B11}$$

is in agreement with Eq. (B10) and leads, when inserted into Eq. (B8), immediately to Eq. (B6).

For an interface, i.e., $\rho(z)=n_1\theta(-z)+n_2\theta(z)$, the local momentum balance (B1) leads with arguments similar to Eqs. (B2)–(B4) to

$$\int_{-\infty}^{0} dz\,\sigma_\perp^{12}(z)=-n_1\int_{-\infty}^{0} dz\,zE(z)\ , \tag{B12}$$

$$\int_{0}^{+\infty} dz\,\sigma_\perp^{12}(z)=-n_2\int_{0}^{\infty} dz\,zE(z)\ . \tag{B13}$$

Comparison with Eqs. (14b′) and (14b″) immediately yields Eqs. (16) and (17), which can again be interpreted—with arguments like Eqs. (B7)–(B11)—as generalized Hellmann-Feynman theorems.

Note that in Eq. (B6) there would appear an additional term of the type $[0\cdot\infty]$, if one had started with the corresponding term for a finite system. From the above derivation of Eq. (B6) one should conclude that indeed the above-mentioned additional term vanishes. An analogous problem and conclusion appears for the jellium model of an interface.

APPENDIX C: CALCULATION OF FORCES VIA STRESS FIELD AND SURFACE INTEGRATION

From the local momentum balance (Sec. I) immediately follows the force on the nucleus "l,"

$$\mathbf{F}_l=\oint\!\!\!\!\oint_{\Omega_l} d\mathbf{S}\,\vec{\sigma}(\mathbf{r}) \;, \tag{C1}$$

under the assumption that the volume Ω_l contains that nucleus ($\mathbf{R}_l\epsilon\Omega_l$) and no other nuclei. In principle $\mathbf{F}_l$ does not depend on the special choice of Ω_l, because

$$\oint\!\!\!\!\oint_{\Omega} d\mathbf{S}\,\vec{\sigma}(\mathbf{r})=0 \tag{C2}$$

for each volume Ω not containing any nucleus.

The application of this idea to the adhesive force in a bijellic interface goes as follows. Consider the finite bijellic system of Appendix A and integrate the local momentum balance (Sec. I) over the half-space $z<0$ containing the jellium "1." The force exerted on "1" is—as in Eq. (C1)—similarly given by a corresponding surface integral. Because of $\vec{\sigma}(\infty)=0$ only the integral along the xy plane $z=0$ contributes,

$$F_{\mathcal{A},L_{1,2}}=\int d^2a\,\sigma_{\mathcal{A},L_{1,2},\perp}(a,0)\;. \tag{C3}$$

Dividing this by $\pi\mathcal{A}^2$ and taking the limits $\mathcal{A}\rightarrow\infty$ and $L_{1,2}\rightarrow\infty$, formula (21) for the adhesive force (per unit area) immediately results.

APPENDIX D: THE INTERFACE STRESS THEOREM STUDIED WITHIN THE *ANSATZ* METHOD

For any function $g(n,s)$ and $\varepsilon(n)$ and for any pair of background densities n_1 and n_2 the parameters α and β of the *Ansatz* (27) follow from

$$\frac{\partial\mathcal{E}^{12}}{\partial\alpha}=\int dz\frac{\delta\mathcal{E}^{12}}{\delta n(z)}\frac{\partial n(z)}{\partial\alpha}=0 \tag{D1}$$

and a corresponding equation for $\partial/\partial\beta$ with the interfacial energy $\mathcal{E}^{12}$ calculated via Eqs. (13) and (24), i.e.,

$$\mathcal{E}^{12}=\int dz\{\tfrac{1}{2}[\rho(z)-n(z)]\phi(z)+g(n(z),s(z))$$
$$-\theta(-z)n_1\varepsilon(n_1)-\theta(z)n_2\varepsilon(n_2)\}\;.$$

For convenience the electrostatic or Hartree term has been expressed here by $\phi(z)$, the electrostatic potential (times $|e|$) instead of $E(z)=-\phi'(z)$, the electric field (times $|e|$). Now $\sigma_{\parallel}^{12}$ as defined by Eq. (8) has to be studied term by term:

$$\sigma_{\parallel}^{12}=\int dz\left\{\frac{\delta\mathcal{E}^{12}}{\delta n(z)}\left[\frac{\partial n(z)}{\partial\alpha}\sum_i\left[-n_i\frac{\partial\alpha}{\partial n_i}\right]+\frac{\partial n(z)}{\partial\beta}\sum_i\left[-n_i\frac{\partial\beta}{\partial n_i}\right]\right]+\frac{\delta\mathcal{E}^{12}}{\delta n(z)}\sum_l\left[-n_i\frac{\partial n(z)}{\partial n_i}\right]+\sum_i\left[-n_i\frac{\partial\rho(z)}{\partial n_i}\right]\phi(z)\right.$$
$$\left.-\sum_i\left[-n_l\frac{\partial}{\partial n_i}\right][\theta(-z)n_1\epsilon(n_1)+\theta(z)n_2\epsilon(n_2)]\right\}+\mathcal{E}^{12}\;. \tag{D2}$$

The first two terms vanish because of Eq. (D1). In the next term we use the expression (27) for $n(z)$:

$$\sum_i n_i\frac{\partial n(z)}{\partial n_i}=n(z)-\alpha\frac{\partial n(z)}{\partial\alpha}\;. \tag{D3}$$

The term $\alpha\partial n(z)/\partial\alpha$ does not contribute because of (D1). Furthermore, we use

$$\sum_i n_i\frac{\partial\rho(z)}{\partial n_i}=\rho(z)\;, \tag{D4}$$

$$\sum_i n_i\frac{\partial}{\partial n_i}n_j\varepsilon(n_j)=n_j\varepsilon(n_j)-\sigma(n_j) \tag{D5}$$

as well as

$$\frac{\delta}{\delta n(z)}\int dz'[\rho(z')-n(z')]\phi(z')=-\phi(z) \tag{D6}$$

and

$$\frac{\delta}{\delta n(z)}\int dz'\,g(n(z'),s(z'))$$
$$=\{g_n(n,s)-[n'g_s(n,s)]'\}_{n(z)}\;. \tag{D7}$$

Thus Eq. (D2) takes the form

$$\sigma_{\parallel}^{12}=\int dz\{-[\rho(z)-n(z)]\phi(z)+\tfrac{1}{2}[\rho(z)-n(z)]\phi(z)$$
$$+[g-ng_n+n(n'g_s)']_{n(z)}$$
$$-\theta(-z)\sigma(n_1)-\theta(z)\sigma(n_2)\}\;. \tag{D8}$$

In the first line (Hartree term) arises $-\frac{1}{2}[\rho(z)-n(z)]\phi(z)$ or equivalently $-\frac{1}{2}[E^2(z)/4\pi\epsilon^2]$. So, in the case of the *Ansatz* used in Refs. 32–34, the parallel component of the interface stress $\sigma_{\parallel}^{12}$ is identically equal to $\int dz\,\sigma_{\parallel}^{12}(z)$. This is also true for any *Ansatz* $n(z)$, which is a homogeneous function of n_1 and n_2 and of order 1. Because in that case, in accordance with Euler's theorem, $n(z)$ obeys Eq. (D3) without the last term, therefore the mentioned identity holds again. The degree of agreement between the two sides of this identity measures the extent to which the minimum of $\mathcal{E}^{12}$ according to Eq. (D1) has been really reached.

Within the *Ansatz* method also $\sigma_{\perp}^{12}$ is identically equal to $\int dz\,\sigma_{\perp}^{12}(z)$: Because of Eqs. (8) and (9), leading to $\sigma_{\perp}^{12}=\sigma_{\parallel}^{12}-\mathcal{E}^{12}$, and because of (D8) and (26), their difference is given by

$$\sigma_\perp^{12}-\int dz\,\sigma_\perp^{12}(z)=\int dz\{-\tfrac{3}{2}[\rho(z)-n(z)]\phi(z)-[g-(n')^2g_s]_{n(z)}+\theta(-z)n_1\varepsilon(n_1)+\theta(z)n_2\varepsilon(n_2)\}\ . \tag{D9}$$

The right-hand side vanishes because of the analogy of Eq. (D1) with respect to β, which takes with Eqs. (D6) and (D7) and with

$$\beta\frac{\partial}{\partial\beta}n(z)=z\frac{\partial}{\partial z}n(z) \tag{D10}$$

the form

$$\int dz\{-\phi(z)+[g_n-(n'g_s)']_{n(z)}\}zn'(z)=0\ . \tag{D11}$$

The integration by parts indeed transforms the left-hand side of Eq. (D11) into the right-hand side of Eq. (D9). This is proved in the following. With $z\rho'(z)=0$ one finds

$$\begin{aligned}\int dz\,zn'(z)\phi(z)&=-\int dz[\rho(z)-n(z)]'z\phi(z)\\&=\int dz[\rho(z)-n(z)][\phi(z)+z\phi'(z)]\ .\end{aligned} \tag{D12}$$

On the other hand, with the help of the Poisson equation $-\phi''(z)=4\pi\epsilon^2[\rho(z)-n(z)]$ it can be shown that

$$2\int dz[\rho(z)-n(z)]z\phi'(z)=\int dz[\rho(z)-n(z)]\phi(z)\ . \tag{D13}$$

Thus

$$\int dz\,zn'(z)\phi(z)=\tfrac{1}{2}\int dz[\rho(z)-n(z)]\phi(z) \tag{D14}$$

results. Furthermore, with the help of $g'=g_nn'+g_sn'n''$ it is evident that

$$\begin{aligned}\int dz\,zn'(z)[g_n-(n'g_s)']_{n(z)}&=\int dz\,z[g'-n'n''g_s-n'(n'g_s)']_{n(z)}\\&=\int dz[zg'+(n')^2g_s]_{n(z)}\ .\end{aligned} \tag{D15}$$

Finally, with $g(n,s)=g(n,0)+sg_s(n,0)+\cdots$ one arrives at

$$\begin{aligned}\int_{-L_1}^{L_2}dz\,z\frac{d}{dz}g(n(z),s(z))&=-\int_{-L_1}^{L_2}dz\,g(n(z),s(z))+z[g(n,0)+sg_s(n,0)+\cdots]_{n(z)}\Big|_{-L_1}^{+L_2}\\&=\int_{-L_1}^{L_2}dz[-g(n,s)|_{n(z)}+\theta(-z)g(n(-L_1),0)+\theta(z)g(n(L_2),0)]\\&\quad+zs(z)g_s(n(z),0)\Big|_{-L_1}^{+L_2}+\cdots\ .\end{aligned} \tag{D16}$$

In the limit $L_{1,2}\to\infty$

$$\int dz\,z\frac{d}{dz}g(n(z),s(z))=\int dz\,z[-g(n,s)|_{n(z)}+\theta(-z)g(n_1,0)+\theta(z)g(n_2,0)] \tag{D17}$$

results. Note that $g(n,0)=n\varepsilon(n)$. Thus Eqs. (D17), (D15), (D14), and (D11) make the right-hand side of Eq. (D9) zero, QED.

The proof uses, via Eqs. (D3) and (D10), the peculiarities (or symmetry properties) of the *Ansatz* (27).

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$$\int d^3r\frac{1}{4\pi\epsilon^2}\{[\mathbf{E}_1(\mathbf{r})\mathbf{E}_2(\mathbf{r})]\overleftrightarrow{1}-\mathbf{E}_1(\mathbf{r})\circ\mathbf{E}_2(\mathbf{r})-\mathbf{E}_2(\mathbf{r})\circ\mathbf{E}_1(\mathbf{r})\}=\frac{\epsilon^2}{r_{12}}\mathbf{e}_{12}\circ\mathbf{e}_{12}\ .$$

Taking the trace it takes the form

$$\int d^3r(1/4\pi\epsilon^2)\mathbf{E}_1(\mathbf{r})\mathbf{E}_2(\mathbf{r})=\epsilon^2/r_{12}\ .$$

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