

## On the order of magnitude of the gradient-of-density dependent part of an elastic potential in liquids(\*)

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AN APPROXIMATE equation of equilibrium and an expression for the gradient-of-density dependent isothermal elastic potential is derived for nonlocal media with central interactions. The surface tension on vapour-liquid interface for gradient-sensitive media is expressed in terms of bulk properties of the substance. The order of magnitude of the gradient-dependent term is estimated starting both from intermolecular forces and from known surface tension. Both methods lead to the same order of magnitude of the specific length characterizing relative contribution of the gradient-dependent term to the elastic potential which appears to be equal to  $10^{-8}$ – $10^{-7}$  cm.

Wyprowadzono przybliżone równanie równowagi oraz wyrażenie na zależny od gradientu gęstości izotermiczny potencjał sprężysty dla ośrodka z nielokalnymi oddziaływaniami centralnymi. Znalaziono wyrażenie dla napięcia powierzchniowego na granicy ciecz-para w zależności od charakterystyk materiałowych substancji gradientowo-czułej. Oszacowano rząd wielkości gradientowego członu potencjału, zarówno z sił międzycząsteczkowych jak i z rzeczywistej wartości napięcia powierzchniowego. Obie metody doprowadziły do oszacowań tego samego rzędu ( $10^{-8}$ – $10^{-7}$  cm) dla długości charakterystycznej opisującej względny wkład członu gradientowego do potencjału sprężystego.

Выведено приближенное уравнение равновесия, а также выражение на зависимый от градиента плотности изотермический упругий потенциал для среды с нелокальными центральными взаимодействиями. Найдена зависимость поверхностного натяжения на границе пар-жидкость от материальных характеристик градиентно-чувствительного вещества. Исходя, как из межмолекулярных сил, так из реальной величины поверхностного натяжения, производятся оценки градиентного члена упругого потенциала. Оба подхода ведут к результатам одного порядка для характерной длины описывающей относительный вклад градиентного члена в упругий потенциал, которая оказывается равной  $10^{-8}$ – $10^{-7}$  см.

### 1. Introduction

DESPITE the well-known fact that the real behaviour of fluids depends on nonlocal intermolecular forces, to the best of the author's knowledge, no experimental evidence for invalidity of the classical (i.e. based on the concept of the contact forces) approach can, as regards problems of single phase flow, be demonstrated. On the other hand, there is no doubt that if interfacial phenomena are to be considered, it should be assumed that the behaviour of liquids in the interfacial region differs in some way from the bulk behaviour.

For many applications, an interface can be considered as a separate two-dimensional phase ruled by its own intrinsic constitutive equation. In the simplest model due to Young and Laplace (for reference see [1, 2]), the interface can be represented as a constant tension membrane. More sophisticated models include surface viscosity [3] and the possible

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dependence of interfacial tension on the curvature of the interface [4]. These models, being very useful for practical problems, cannot, however, provide any information about the nature of the interfacial region and about the connection between the bulk and surface properties of liquids.

Another approach which can also be traced from the works of YOUNG and LAPLACE (c.f. [1, 2]) and which was developed by Rayleigh [5] and later by VAN der WAALS' school [6, 7, 8], is based on the concept of nonlocal forces and employs quasi-continual methods (in the sense of LAPLACE). More general approaches of modern statistic mechanics use very similar concepts for obtaining the partition function by cell methods (c.f. [9]).

In addition to the two approaches mentioned above<sup>(1)</sup>, still another, different one is possible. It can be assumed that the stress tensor, or the elastic potential of the fluid (we shall see later that within the framework of this method there is no significant difference between the gas and the liquid phase) depends not on the density alone, but also on the first, and possibly higher gradients of density. This consideration, which yields the same or similar results as the previous one, was employed as early as 1901 by KORTEWEG [12].

During the last two decades, many attempts at a generalization of classical continuum mechanics have been made. Several papers may be indicated [13, 14, 15, 16, 17, 18] devoted to the concepts of gradient-dependent elastic potential and its application for the description of interfacial phenomena<sup>(2)</sup>.

The object of the present paper consists in estimating the order of magnitude of the gradient-dependent terms of an elastic potential in fluids. We shall consider here a simple model of fluid, admitting symmetric, central and finite range nonlocal interactions dependent on the densities and the distance only. We shall show the possibility of existence of a transition zone similar to Van der Waals' liquid-vapour transition in an infinite medium. We shall also show that the simplest gradient-dependent potential theory can provide an approximate description for the nonlocal interactions. An expression for surface tension will be obtained in terms of the gradient theory.

Thus we shall be able to estimate the terms under consideration in two ways: (a) starting from their physical origin due to intermolecular forces and (b) comparing predicted results with the experimental data for surface tension.

As far as possible we will use here continuum mechanics methods only. Considering infinite media we will avoid all difficulties connected with the generalized boundary tractions (see e.g. [14, 15, 16, 17, 18]) the physical meaning of which is yet far from clear in the existing gradient-dependent theories.

## 2. Nonlocal interactions and the elastic potential

Let us consider an infinite body with finite and sufficiently smooth density field  $\zeta(X)$ . We assume that the following balance of forces holds for every material particle  $X(\mathbf{x})$ :

$$(2.1) \quad \int_E \psi[\zeta(\mathbf{x}), \zeta(\mathbf{y}), R] \frac{\mathbf{R}}{R} dV_{\mathbf{y}} + \mathbf{b}(\mathbf{x}) \zeta(\mathbf{x}) = \frac{\partial^2 \mathbf{x}(\mathbf{X}, t)}{\partial t^2} \zeta(\mathbf{x}),$$

<sup>(1)</sup> We shall not discuss here Gibbs' [10] and more recently Buff's [11] approaches which, containing some mechanical concepts, are based mainly on thermodynamic considerations.

<sup>(2)</sup> See also [19].

where  $\mathbf{b}(\mathbf{x})$  denotes the density of the external body forces  $\mathbf{R} \equiv \mathbf{y} - \mathbf{x}$ ,  $R \equiv |\mathbf{R}|$ ,  $\zeta(\mathbf{x})$  and  $\zeta(\mathbf{y})$  are densities at space point  $\mathbf{x}(\mathbf{X})$  and  $\mathbf{y}(\mathbf{Y})$ , respectively, and the integral is taken over the whole space  $E$ .

It is not difficult to see that the expression (2.1) already contains certain assumption on the nature of nonlocal forces acting between two material particles  $\mathbf{X}(\mathbf{x})$  and  $\mathbf{Y}(\mathbf{y})$  which are assumed to be central, additive and dependent on densities in  $\mathbf{x}$  and  $\mathbf{y}$  and the distance  $|\mathbf{y} - \mathbf{x}|$  only.

We assume also

$$(2.2) \quad \psi(\zeta(\mathbf{x}), \zeta(\mathbf{y}), R) = \psi(\zeta(\mathbf{y}), \zeta(\mathbf{x}), R)$$

i.e., we assume the symmetry of interactions.

Let us note here that (2.1) contains another hidden assumption that the integral over the whole space exists for every bounded density distribution — i.e., we do not consider, for example, mutual gravitational interactions. The above assumptions are essential to our considerations.

Our next assumptions which we shall impose for the sake of simplicity of further analysis can be omitted or replaced if we employ more sophisticated mathematical methods. However, in the author's opinion, they are quite reasonable from the physical point of view.

Thus we assume that the force function  $\psi[\zeta(\mathbf{x}), \zeta(\mathbf{y}), R]$  can be expressed as

$$(2.3) \quad \psi[\zeta(\mathbf{x}), \zeta(\mathbf{y}), R] = A(R)\varphi[\zeta(\mathbf{x}), \zeta(\mathbf{y})] + [1 - A(R)]\Phi(R)\zeta(\mathbf{x})\zeta(\mathbf{y}),$$

where

$$\begin{aligned} A(R) &= 1 & \text{for } R < C^2, \\ A(R) &= 0 & \text{for } R > C_2, \\ \Phi(R) &= 0 & \text{for } R > C_1; C_2 \ll C_1, \end{aligned}$$

and where  $\Phi(R)$ ,  $\varphi[\zeta(\mathbf{x}), \zeta(\mathbf{y})]$  and derivatives of  $\varphi[\zeta(\mathbf{x}), \zeta(\mathbf{y})]$  are bounded — i.e., we assume that the force function can be expressed as a sum of an extremely short range force, which does not depend on the distance, and a long (but finite) range force proportional to the product of densities. We confine ourselves to the case of the static equilibrium

with the absence of external forces and to such density distributions for which  $\left| \overset{i}{\nabla} \zeta \right| \leq \frac{D}{C_1^i}$ ,

for every  $i = 0, 1, 2, \dots$ , where symbol  $\overset{i}{\nabla}$  denotes the  $i$ -th spatial gradient and  $D$  is some constant.

Under the above assumptions, we can write:

$$(2.4) \quad A(R)\varphi[\zeta(\mathbf{x}), \zeta(\mathbf{y})] = \varphi[\zeta(\mathbf{x}), \zeta(\mathbf{x})] + \frac{\partial \varphi[\zeta(\mathbf{x}), \zeta(\mathbf{y})]}{\partial \zeta(\mathbf{y})} \Big|_{\mathbf{y}=\mathbf{x}} \nabla \zeta(\mathbf{x}) \cdot \mathbf{R} + \sigma \left( \frac{C_2^2}{C_1^2} \right),$$

where  $\sigma \left( \frac{C_2^2}{C_1^2} \right)$  is of the order of

$$\varphi[\zeta(\mathbf{x}), \zeta(\mathbf{x})] \left( \frac{C_2}{C_1} \right)^2.$$

Expanding  $\zeta(\mathbf{y})$  in power series, and disregarding small terms, we can rewrite (2.1) in the form:

$$(2.5) \quad \varphi[\zeta(\mathbf{x}), \zeta(\mathbf{x})] \int_{K(C_2)} \frac{\mathbf{R}}{R} dV_y + \left. \frac{\partial \varphi[\zeta(\mathbf{x}), \zeta(\mathbf{y})]}{\partial \zeta(\mathbf{y})} \right|_{\mathbf{y}=\mathbf{x}} \nabla \zeta(\mathbf{x}) \cdot \int_{K(C_2)} \frac{\mathbf{R} \otimes \mathbf{R}}{R} dV_y \\ + \zeta(\mathbf{x}) \int_{K(C_1)} \frac{\Phi(R)}{R} \sum_{i=1}^{\infty} \left[ \frac{1}{i!} \nabla^i \zeta(\mathbf{x}) \cdot \otimes_{k=1}^{i+1} \mathbf{R}_{(k)} \right] dV_y = \mathbf{0},$$

where  $K(C_2)$  and  $K(C_1)$  denote interiors of the spheres of radii  $C_2$  and  $C_1$  respectively, and dots stand for the product with contraction over all the indices of  $\nabla^i \zeta(\mathbf{x})$ . The first and the third terms are by symmetry equal to zero, and after rearrangement we can write:

$$(2.6) \quad \left. \frac{\partial \varphi[\zeta(\mathbf{x}), \zeta(\mathbf{y})]}{\partial \zeta(\mathbf{y})} \right|_{\mathbf{y}=\mathbf{x}} \nabla \zeta(\mathbf{x}) \cdot \int_{\varkappa} \mathbf{n} \otimes \mathbf{n} dS \int_0^{C_2} R^3 dR \\ + \zeta(\mathbf{x}) \sum_{i=1}^{\infty} \frac{1}{i!} \nabla^i \zeta(\mathbf{x}) \cdot \int_{\varkappa} \otimes_{k=1}^{i+1} \mathbf{n}_{(k)} dS \int_0^{C_1} \Phi(R) R^{i+2} dR = \mathbf{0},$$

where  $\varkappa$  is the unit sphere,  $\mathbf{n}$  denotes the outward unit normal vector.

Integrating, we obtain:

$$(2.7) \quad \int_{\varkappa} \mathbf{n} \otimes \mathbf{n} dS = \frac{4\pi}{3} \mathbf{1},$$

$$(2.8) \quad \int_{\varkappa} \otimes_{k=1}^{i+1} \mathbf{n}_{(k)} dS = \mathbf{0} \quad \text{for } i = 2m, \quad m = 1, 2, 3, \dots,$$

$$(2.9) \quad \frac{1}{3!} \nabla^3 \zeta(\mathbf{x}) \cdot \int_{\varkappa} \mathbf{n} \otimes \mathbf{n} \otimes \mathbf{n} \otimes \mathbf{n} dS = \frac{2}{15} \pi \nabla \Delta \zeta(\mathbf{x}),$$

$$(2.10) \quad \frac{1}{5!} \nabla^5 \zeta(\mathbf{x}) \cdot \int_{\varkappa} \mathbf{n} \otimes \mathbf{n} \otimes \mathbf{n} \otimes \mathbf{n} \otimes \mathbf{n} \otimes \mathbf{n} dS = \frac{1}{210} \pi \nabla \Delta^2 \zeta(\mathbf{x})^{(3)}.$$

It can be shown (see Appendix I) that the expansion (2.6) is, under our assumptions, convergent.

Denoting

$$(2.11) \quad \Phi_3 \equiv \frac{2\pi}{15} \int_0^{C_1} \Phi(R) R^5 dR,$$

(<sup>3</sup>) For every  $i = 2m+1$  ( $m = 0, 1, 2, \dots$ ):  $\nabla^i \zeta(\mathbf{x}) \cdot \int_{\varkappa} \otimes_{k=1}^{i+1} \mathbf{n}_{(k)} dS = \frac{4\pi}{i+2} \nabla \Delta^{\frac{i-1}{2}} \zeta(\mathbf{x})$ .

(This relation has been recently proven by K. Żak MS Thesis, Warsaw University, 1973).

( $15\Phi_3/2\pi$  can be referred to as the fifth moment of the long range part of the force function), and

$$(2.12) \quad -\frac{\partial P(\zeta)}{\partial \zeta} \equiv \frac{4\pi}{3} \left( \frac{C_2^4}{4} \frac{\partial \varphi[\zeta(\mathbf{x}), \zeta(\mathbf{y})]}{\partial \zeta(\mathbf{y})} \Big|_{\mathbf{y}=\mathbf{x}} + \zeta(\mathbf{x}) \int_0^{C_1} \Phi(R) R^3 dR \right),$$

dropping out small terms containing higher gradients, we obtain:

$$(2.13) \quad -\nabla P[\zeta(\mathbf{x})] + \zeta(\mathbf{x}) \Phi_3 \nabla \Delta \zeta(\mathbf{x}) = \mathbf{0}.$$

It is not difficult to show (Appendix II) that in the case of a uniform density function,  $P(\zeta)$  is equal to the pressure defined as the total force acting between two semispaces per unit area of the dividing plane (compare [5]). The equation of the mechanical equilibrium (2.13) can be obtained also by an entirely different approach, as follows. Let us assume that there exists an elastic (e.g. isothermal) potential density function  $w(\zeta, \nabla \zeta)$ , which depends on the density and the first gradient of density<sup>(\*)</sup>; we assume also that the following law of conservation is valid for every material region  $V$  and every velocity field  $\mathbf{v}$ :

$$(2.14) \quad \int_V \dot{\zeta} w dV = \int_V \zeta \mathbf{b} \cdot \mathbf{v} dV + \int_{\partial V} \mathbf{n} \cdot \mathbf{T} \cdot \mathbf{v} dS + \int_{\partial V} \mathbf{n} \cdot \mathbf{Q} \cdot \nabla \mathbf{v} dS - \int_V \zeta \frac{\mathbf{v} \cdot \mathbf{v}}{2} dV,$$

where  $\mathbf{T}$  is a symmetric stress tensor and  $\mathbf{Q}$  is some hyperstress tensor of rank 3. We shall not discuss here a possible physical meaning of the tensor  $\mathbf{Q}$ , which plays here only a transitory role and will not appear in the further analysis, because no dynamic boundary conditions are considered (for discussion of hyperstress and hypertractions see, e.g., [14, 15, 17, 18]).

Using the following identity, which holds for every material region  $V$

$$(2.15) \quad \int_V \dot{\zeta} w dV = \int_V \zeta \dot{w} dV = \int_V \zeta \left( \frac{\partial w}{\partial \zeta} \dot{\zeta} + \frac{\partial w}{\partial (\nabla \zeta)} \cdot \dot{\nabla \zeta} \right) dV,$$

and expressing  $\dot{\zeta}$  and  $\dot{\nabla \zeta}$  by the velocity gradients

$$(2.16) \quad \dot{\zeta} = -\zeta \nabla \cdot \mathbf{v}, \quad \dot{\nabla \zeta} = -\nabla \mathbf{v} \cdot \nabla \zeta - \nabla \zeta (\nabla \cdot \mathbf{v}) - \zeta \nabla (\nabla \cdot \mathbf{v}),$$

and changing the surface integrals into volume integrals, we can perform the standard procedure on (2.14): making use of the fact that (2.14) should be valid for every velocity field and every material region, we are able to obtain the following equilibrium conditions (in the absence of body forces):

$$(2.17) \quad \nabla \cdot \mathbf{T} = \mathbf{0},$$

$$(2.18) \quad \mathbf{T} = - \left[ \left( \zeta^2 \frac{\partial w}{\partial \zeta} + \zeta \frac{\partial w}{\partial (\nabla \zeta)} \cdot \nabla \zeta \right) \mathbf{1} + \zeta \frac{\partial w}{\partial (\nabla \zeta)} \otimes \nabla \zeta - \nabla \cdot \left( \zeta^2 \frac{\partial w}{\partial (\nabla \zeta)} \otimes \mathbf{1} \right) \right].$$

It should be mentioned here that condition (2.18), which can be considered as a constitutive equation for  $\mathbf{T}$ , has been obtained as a consequence of the fact that (2.14) does not contain any higher order inertial terms (for details see [19]).

(\*) In the thermodynamic approach,  $w$  can be referred to as a generalized form of Helmholtz free energy.

It is not difficult to see now that, if we assume

$$(2.19) \quad w(\zeta, \nabla\zeta) = \int \frac{P(\zeta)}{\zeta^2} d\zeta + \Phi_3 \frac{\nabla\zeta \cdot \nabla\zeta}{2\zeta},$$

then we obtain for  $\mathbf{T}$ :

$$(2.20) \quad \mathbf{T} = \left( -P(\zeta) + \frac{1}{2} \Phi_3 \nabla\zeta \cdot \nabla\zeta + \Phi_3 \zeta \Delta\zeta \right) \mathbf{1} - \Phi_3 \nabla\zeta \otimes \nabla\zeta$$

and (2.17) can be rewritten as

$$(2.21) \quad \nabla \cdot \mathbf{T} = -\frac{\partial P(\zeta)}{\partial \zeta} \nabla\zeta + \Phi_3 \zeta \nabla \Delta\zeta = \mathbf{0}$$

which is exactly the same as (2.13).

Thus, starting from entirely different assumptions, we obtain the same equation of equilibrium (if we did not assume  $\mathbf{v} = \mathbf{0}$ ,  $\mathbf{b} = \mathbf{0}$ , we would get in both cases the same equation of motion). It is evident, however, that (2.19) is by no means the only possible form of potential  $w$  which can yield (2.21) or (2.13). If we demand, however,  $w$  to be an isotropic function of  $\zeta$  and  $\nabla\zeta$ , we can prove (see Appendix III) that if any particular  $w(\zeta, \nabla\zeta)$  yields (2.21) then the stress tensor has to be equal to those given by (2.20). Thus (2.19) is one of the simplest potential density functions which is compatible with the expression (2.13) which has been obtained as an approximate equation for nonlocal central interactions.

Now, we can see the other interpretation of  $P(\zeta)$  which is equal to the negative derivative of the potential density function over the specific volume  $v = 1/\zeta$  (in the case of uniform density).

### 3. One-dimensional case, the surface tension at the plane vapour-liquid interface

For the one-dimensional case the Eq. (2.13) has the form:

$$(3.1) \quad -\frac{\partial P(\zeta)}{\partial \zeta} \zeta' + \Phi_3 \zeta \zeta''' = 0.$$

The trivial solution of (3.1) is  $\zeta = \text{const}$ , which corresponds to the single phase case. The problem of the stability of this solution, as well as the problem of the existence of any nontrivial solution, cannot be solved without at least qualitative information about the function  $P(\zeta)$ , and will not be discussed here.

Let us seek, however, the conditions necessary for the existence of an inhomogeneous solution with gradients vanishing at infinity. Integrating (3.1) by parts, we obtain

$$(3.2) \quad -P(\zeta) + \Phi_3 \left( \zeta \zeta'' - \frac{1}{2} \zeta'^2 \right) = \alpha_1.$$

Integration of (3.2) after some rearrangement gives:

$$(3.3) \quad -\int \frac{P(\zeta)}{\zeta^2} d\zeta + \frac{1}{2} \Phi_3 \frac{\zeta'^2}{\zeta} = -\frac{\alpha_1}{\zeta} + \alpha_2.$$

Let us impose the following conditions:

$$(3.4) \quad \begin{aligned} \lim_{x \rightarrow -\infty} \zeta &= \zeta_1, & \lim_{x \rightarrow \pm\infty} \zeta' &= 0, \\ \lim_{x \rightarrow \infty} \zeta &= \zeta_2, & \lim_{x \rightarrow \pm\infty} \zeta'' &= 0. \end{aligned}$$

From (3.4) and (3.2), we obtain the following necessary condition:

$$(3.5) \quad -P(\zeta_1) = -P(\zeta_2) \equiv \alpha_1$$

and from (3.4) and (3.3), we have:

$$(3.6) \quad \int_{\zeta_1}^{\zeta_2} \frac{P(\zeta) + \alpha_1}{\zeta^2} d\zeta = 0.$$

It can be shown that (3.5) and (3.6) are also the necessary conditions for the existence of the one-dimensional solution of any-order differential equation which can be obtained from (2.6) with higher gradient terms preserved under the condition of vanishing of all derivatives at infinity (see Appendix IV).

Now we have, sufficiently far from the transition region, almost uniform density, and  $P(\zeta)$  can there be considered as a pressure. If the density transition under consideration is to be considered as a liquid-vapour transition (cf. VAN DER WAALS [6, 20]) then  $\alpha_1 = -P_s$ , where  $P_s$  denotes the saturated vapour pressure and  $\zeta_1, \zeta_2$  are correspondingly saturated vapour and liquid densities.

As already indicated, we shall not discuss here the necessary conditions for the existence of the solution of (3.1). We shall only point out that if for some particular case  $P(\zeta)$  can be approximated within some range of  $\zeta$  as a virial equation of state without linear terms

$$(3.7) \quad P(\zeta) = B\zeta^2 + C\zeta^3 + D\zeta^4,$$

then the solution of the problem under consideration (subject to certain restrictions imposed on coefficients  $B, C, D$ ) can be obtained in the form:

$$(3.8) \quad \zeta = a + b \tanh(cx),$$

where  $a, b, c$  are functions of  $B, C, D$  and  $\Phi_3$ . The representation (3.7), however, does not seem to be very realistic, because it leads for low densities to

$$\lim_{\zeta \rightarrow 0} \frac{\partial P(\zeta)}{\partial \zeta} = 0,$$

by contrast with the well-known behaviour of diluted gases for which

$$\lim_{\zeta \rightarrow 0} \frac{\partial P(\zeta)}{\partial \zeta} = \frac{RT}{M},$$

where  $R$  is the gas constant,  $T$  is the temperature and  $M$  denotes molecular weight.

Let us assume, however, that  $w(\zeta, \nabla\zeta)$  is not an isothermal, but an adiabatic potential [in this case  $w(\zeta, \nabla\zeta)$  can no longer be identified with the Helmholtz free energy, but still it has sufficient thermodynamic explanation as an internal energy]; then for diluted gases we have:

$$P(\zeta) / \left( \frac{\zeta}{\zeta_0} \right)^\alpha = \text{constant},$$

where  $\alpha > 1$  and  $\zeta_0$  is some arbitrary density. In this case, (3.7) can represent the first three terms of the power expansion of the isentropic equation of state. Now, the value

$$\frac{\partial P(\zeta)}{\partial \zeta} = 0$$

for  $\zeta = 0$  does not stand in contraction with the physical behaviour of gases. It is not difficult to see that all the above considerations remain valid and, as in the case of isothermal potential conditions, (3.5) and (3.6) are the necessary conditions of mechanical (but not necessarily thermal) equilibrium.

Let us adhere, however, to the Van der Waals viewpoint and assume that there exists a proper solution of (3.10) [with the conditions (3.4)], then, taking one of the common definitions of surface tension (see e.g. [21]):

$$(3.9) \quad \sigma = \int_{-\infty}^{\infty} \left( T_{yy} - \frac{1}{3} \text{tr} \mathbf{T}_{\infty} \right) dx,$$

where  $y$  is a suitable second principle direction. From (2.20), we obtain:

$$(3.10) \quad T_{yy} = P(\zeta) + \Phi_3 \left( \zeta \zeta'' + \frac{\zeta'^2}{2} \right).$$

Bearing in mind that  $-\frac{1}{3} \text{tr} \mathbf{T}_{\infty} = P_S$ , and substituting (3.10) and (3.2) into (3.9), we obtain the familiar result (cf. [20]):

$$(3.11) \quad \sigma = \Phi_3 \int_{-\infty}^{\infty} \zeta'^2 dx.$$

We have obtained here the expression (3.11) using concepts of stresses and forces for  $\sigma$  as a tension of some fictitious membrane stretched perpendicular to the  $x$  axis. Let us observe here that GIBBS'S [10] definition of  $\sigma$  as a surface energy also remains valid. Let us consider density distribution  $\zeta(x)$  satisfying (3.1) and (3.4), and some other distribution  $\zeta^*(x)$ , where

$$\zeta^*(x) = \zeta_2 \quad \text{for } x > a, \quad \text{and} \quad \zeta^*(x) = \zeta_1 \quad \text{for } x \leq a.$$

Introducing the following condition for  $a$

$$(3.12) \quad \int_{-\infty}^{\infty} [\zeta(x) - \zeta^*(x)] dx = 0$$

which can be considered as a condition of preservation of total mass, we can find the difference  $\Delta W$  between the total elastic potential associated with both distributions (per unit area of the  $yz$  plane):

$$(3.13) \quad \Delta W = \int_{-\infty}^{\infty} \left[ \zeta(x) \left( \int_{\zeta_0}^{\zeta(x)} \frac{P(t)}{t^2} dt + \frac{1}{2} \Phi_3 \frac{\zeta'^2(x)}{\zeta(x)} \right) - \zeta^*(x) \left( \int_{\zeta_0}^{\zeta^*(x)} \frac{P(t)}{t^2} dt + \frac{1}{2} \frac{\zeta^{*2}(x)}{\zeta^*(x)} \right) \right] dx,$$



where  $\zeta_0 \leq \zeta_1$  denotes some arbitrary density, or, using (3.3)

(3.14)

$$\Delta W = \int_{-\infty}^{\infty} \Phi_3 \zeta'^2(x) dx + \int_{-\infty}^{\infty} \left[ \alpha_1 - \alpha_2 \zeta(x) - w(\zeta_0) - \zeta^*(x) \int_{\zeta_0}^{\zeta^*(x)} \frac{P(t)}{t^2} dt + \frac{1}{2} \Phi_3 \frac{\zeta^{*2}(x)}{\rho^*(x)} \right] dx,$$

but  $\zeta^{*'}(x) = 0$ , and by (3.3) and by our definition of  $\zeta^*(x)$ , we have:

$$\zeta^*(x) \int_{\zeta_0}^{\zeta^*(x)} \frac{P(t)}{t^2} dt = \alpha_1 - \zeta_1 \alpha_2 - w(\zeta_0) \quad \text{for } x \leq a, \quad (3.15)$$

$$\zeta^*(x) \int_{\zeta_0}^{\zeta^*(x)} \frac{P(t)}{t^2} dt = \alpha_1 - \zeta_2 \alpha_2 - w(\zeta_0) \quad \text{for } x > a,$$

or

$$\zeta^*(x) \int_{\zeta_0}^{\zeta^*(x)} \frac{P(t)}{t^2} dt = \alpha_1 - \zeta^*(x) \alpha_2 - w(\zeta_0).$$

Substituting (3.16) into (3.14), we arrive at:

$$\Delta W = \int_{-\infty}^{\infty} \Phi_3 \zeta'^2(x) dx - \alpha_2 \int_{-\infty}^{\infty} [\zeta(x) - \zeta^*(x)] dx. \quad (3.16)$$

In view of (3.12), the second right-hand side term is equal to zero and in virtue of (3.11), we have:

$$\Delta W = \sigma. \quad (3.17)$$

Thus we can consider the surface tension as an excessive Helmholtz free energy associated with the existence of the gradient zone. The plane  $x = a$  at which our reference density distribution  $\zeta^*(x)$  is discontinuous has been defined by GIBBS [10] as the surface of tension.

Changing the variable of integration, we can rewrite (3.11) in the form:

$$\sigma = \Phi_3 \int_{\zeta_1}^{\zeta_2} \zeta' d\zeta, \quad (3.18)$$

or substituting for  $\zeta'$  the expression obtained from (3.3), we are able to write:

$$\sigma = \sqrt{2\Phi_3} \int_{\zeta_1}^{\zeta_2} \sqrt{\zeta \int_{\zeta_1}^{\zeta} \frac{P(\xi)}{\xi^2} d\xi + P_S - \frac{P_S}{\zeta_1} \zeta} d\zeta. \quad (3.19)$$

Thus, in principle, knowing  $\sigma$ ,  $P_S$ ,  $\zeta_1$ ,  $\zeta_2$  and  $P(\zeta)$  we are able to find  $\Phi_3$ . However, our description somewhat being simplified can hardly be applied for any particular substance. Moreover, it is well-known that  $P(\zeta)$  cannot be experimentally found for the entire interval  $\zeta_1 < \zeta < \zeta_2$ . Thus in the next section we shall use cruder methods based on the Eq. (3.11) for the estimation of  $\Phi_3$ .

#### 4. Numerical evaluation

For further considerations, we shall introduce now the characteristic length  $l$  defined as

$$(4.1) \quad l = \sqrt{\frac{\Phi_3 \zeta}{\frac{\partial P(\zeta)}{\partial \zeta}}} = \sqrt{\frac{\Phi_3}{M}} = \sqrt{\frac{\Phi_3 \zeta}{c^2}},$$

where  $M$  is the bulk modulus and  $c$  is the sound velocity.

It is not difficult to see the physical meaning of  $l$  as that length with which certain length characteristics for the particular problem under consideration (e.g. ratio  $\zeta/|\nabla\zeta|$  or wavelength) should be compared in order to decide whether or not the term  $\Phi_3$  introduces any detectable contribution to the solution.

According to (3.11) we have

$$(4.2) \quad \Phi_3 = \frac{\sigma}{\int_{-\infty}^{\infty} \zeta'^2 dx}$$

Now, let  $2\delta$  denote the width of the zone within which the major density change takes place. We shall omit here the proof of the rather obvious fact that

$$(4.3) \quad \int_{-\delta}^{\delta} \left[ \frac{\zeta(\delta) - \zeta(-\delta)}{2\delta} \right]^2 dx \leq \int_{-\infty}^{\infty} \zeta'^2 dx.$$

If we take now sufficiently large  $\delta$ , we have:

$$\zeta(\delta) \approx \zeta_2, \quad \zeta(-\delta) \approx \zeta_1,$$

and we can write

$$(4.4) \quad \Phi_3 \leq \frac{2\delta\sigma}{(\zeta_2 - \zeta_1)}.$$

Up to this point we have used exclusively considerations of continuum mechanics. Now, we shall try to expand our field, borrowing certain concepts from molecular theory. Our function  $\psi(\zeta(\mathbf{x}), \zeta(\mathbf{y}), R)$  in (2.1) describes all possible interactions, including both static forces and dynamic forces due to momentum exchange between moving particles (compare RAYLEIGH [5]).

However, it is reasonable to assume that the long range part of

$$\psi(\zeta(\mathbf{x}), \zeta(\mathbf{y}), R)$$

— i.e.,  $\Phi(R)\zeta(\mathbf{x})\zeta(\mathbf{y})$  — is insensitive to the relative molecular velocities. Thus, if the force between two similar molecules separated by the distance  $R$  is equal to some value  $f(R)$ , we can express  $\Phi(R)$  as

$$(4.5) \quad \Phi(R) = \frac{f(R)}{m^2},$$

where  $m$  denotes the mass of the molecule. From (2.11), we obtain for  $\Phi_3$ :

$$(4.6) \quad \Phi_3 = \frac{2\pi}{15} \int_0^{c_1} \frac{f(R)}{m^2} R^5 dR.$$

Many valuable results in molecular theory were obtained with the use of Lennard-Jones [6–12] potential function (see e.g. [9]).

$$(4.7) \quad A(R) = 4\varepsilon \left[ \left( \frac{d}{R} \right)^{12} - \left( \frac{d}{R} \right)^6 \right],$$

where  $\varepsilon$  and  $d$  are certain constants. In our sign convention, where the outward directed force is considered as positive, we obtain for the total force  $f(R)$ :

$$(4.8) \quad f(R) = 4\varepsilon \left[ 6 \frac{d^6}{R^7} - 12 \frac{d^{12}}{R^{13}} \right].$$

Now, we are faced with the problem as to which part of  $f(R)$  has to be referred to as the long distance force  $\Phi_3(R)$ . It can easily be shown, however, that for any choice of  $C_1$  and  $C_2$ , we shall obtain:

$$(4.9) \quad \Phi_3 \leq \frac{2\pi}{15} \int_{\sqrt[6]{2d}}^{\infty} \frac{4\varepsilon}{m^2} \left[ 6 \frac{d^6}{R^7} - 12 \frac{d^{12}}{R^{13}} \right] R^5 dR < \frac{8\pi\varepsilon}{15m^2} 6 \frac{d^5}{\sqrt[6]{2}} < \frac{10\varepsilon d^5}{m^2},$$

thus from (4.1) and (4.9) we obtain:

$$(4.10) \quad l < \sqrt{\frac{10\varepsilon d^5 \zeta}{m^2 c^2}},$$

as an estimation from molecular forces. And from (4.4) and (4.1) we obtain:

$$(4.11) \quad l \leq \sqrt{\frac{2\delta\sigma}{(\zeta_2 - \zeta_1)^2} \frac{\zeta}{c^2}},$$

as an estimation from the surface tension. Now, the only problem is the choice of the proper value for  $2\delta$  in (4.11). Available estimations of  $2\delta$  vary from "Several molecular diameters" [22], to 100 Å [21, 23].

Thus we hope that we do not underestimate in taking  $2\delta = 200$  Å. If we now take data for such a typical molecular substance as  $\text{CCl}_4$ , where

$$\varepsilon = 3.27 \cdot 1.3806 \cdot 10^{-14} \text{ gcm}^2, \quad d = 5.881 \cdot 10^{-8} \text{ cm}, \quad m = 153.81 \cdot 1.66 \cdot 10^{-24} \text{ g},$$

$$\zeta = 1.595 \text{ g/cm}^3, \quad \sigma = 27 \frac{\text{dyna}}{\text{cm}}$$

(cf. [9, 24]), we obtain from (4.10):

$$l < 3 \cdot 10^{-8} \text{ cm},$$

and from (4.11):

$$l \leq 4.45 \cdot 10^{-8} \text{ cm}.$$

For reference we may mention here that the linearized Eq. (3.1) completed with dynamic terms yields the following expression for the relative contribution of gradient sensitive terms to the velocity of sound waves in liquids:

$$(4.12) \quad \frac{v-c}{c} \approx 2\pi^2 \frac{l^2}{\lambda^2},$$

where  $c$  is the classical sound velocity,  $v$  is the velocity obtained by taking into consideration the term  $\Phi_3$ , and  $\lambda$  is the wavelength. For  $\text{CCl}_4$  under normal conditions and frequency as high as  $10^2$  MHz we obtain for  $(v-c)/c$  the order of magnitude of  $10^{-8}$ , which is evidently far beyond the range of any possible experimental verification.

## 5. Conclusions

In the foregoing sections, we have shown that the concept of gradient-dependent elastic potential can be used for approximate continuous description of fluids with nonlocal interactions.

We have also pointed out that for certain forms of the equation of state the simplest gradient-dependent theory can yield a solution with a density transition analogous to Van der Waals's vapour-liquid transition. By obtaining an expression for the surface tension at the plane vapour-liquid interface, we were able to show that the gradient approach yields in this case the same result as the VAN DER WAALS and BAKKER approach, and agrees with the widely-used Gibbs' energetic approach.

Despite the crude assumptions and rough approximations, we have obtained, by two independent ways, essentially the same estimation for the gradient-dependent part of the elastic potential.

Our extremely simplified model can hardly provide an accurate quantitative description of any real fluid, but even if it is assumed that in some cases the value of parameter  $l$  can exceed our estimation by one or (which does not seem very probable) two orders of magnitude, it is still evident that for any particular problem which does not involve discontinuities or phase boundaries the gradient-dependent term can be disregarded without detectable loss of accuracy.

It may be supposed that the term under consideration may provide some information on the behaviour of materials within the transition regions of shock waves. It should be mentioned here, however, that the first gradient term alone, with positive constant  $\Phi_3$  likely, does not yield a continuous solution for high amplitude shock wave. Thus if it is desired to apply the gradient theory to shock wave problems, viscosity and/or thermal conductivity effects leading to high but finite gradient solutions (cf. [25]) should be taken into consideration.

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## Appendix I

Introducing some characteristic pressure  $P_0$  and characteristic density  $\zeta_0$ , denoting

$$(I.A) \quad \bar{\Phi}(\bar{R}) \equiv \frac{C_1^3}{P_0} \zeta_0^2 \Phi(R), \quad \bar{R} \equiv \frac{R}{C_1}, \quad \bar{P} \equiv \frac{P}{P_0}; \quad \bar{\zeta} \equiv \frac{\zeta}{\zeta_0}, \quad \bar{V} \equiv C_1^i \bar{V},$$

and using (2.9) and (2.12), we are able to rewrite (2.6) as follows:

$$(I.B) \quad -\bar{V} \varrho + \bar{\zeta} \sum_{i=1}^{\infty} \frac{1}{2i+1} \bar{V}^{2i+1} \cdot \int_{\Sigma} \otimes_{k=1}^{2i+1} \mathbf{n}(k) dS \int_0^1 \bar{\Phi}(\bar{R}) \bar{R}^{2i+3} d\bar{R} = \mathbf{O}.$$

Under our assumptions listed in section 2  $\bar{\zeta}$ ,  $\bar{V}$  and  $\bar{\Phi}(\bar{R})$  are bounded. Now, if we use the following inequalities:

$$(I.C) \quad \|\mathbf{A} \cdot \mathbf{B}\| \leq \|\mathbf{A}\| \cdot \|\mathbf{B}\|; \quad \left\| \int_S \mathbf{A} dS \right\| \leq S \sup \|\mathbf{A}\|$$

$$\int_0^1 \bar{\Phi}(\bar{R}) \bar{R}^{2i+3} d\bar{R} \leq |\bar{\Phi}(\bar{R})| \frac{1}{2i+4},$$

we are able to write:

$$(I.D) \quad \left| \frac{1}{(2i+1)!} \left( \frac{2i+1}{\bar{V}} \bar{\zeta} \cdot \int_{\Sigma} \otimes_{k=1}^{2i+2} \mathbf{n}(k) dS \right) \int_0^1 \bar{\Phi}(\bar{R}) \bar{R}^{2i+3} d\bar{R} \right| < \frac{M}{(2i+1)!} \sqrt{3^{2i+2}(2i+2)} < \frac{3M\sqrt{2}}{i!},$$

where  $M$  is a certain positive number. The constant term series in (I.D), which is an absolute majorant of the expansion under consideration, is convergent. Thus the expansion in (2.6) is uniformly convergent over the whole space.

## Appendix II

We shall calculate here the total force per unit area acting across any plane in the infinite homogeneous body with uniform density.

By virtue of symmetry, the only component of the force to be taken into consideration is a vertical one.

We seek a quantity:

$$(II.A) \quad \mathcal{P} \equiv \lim_{S \rightarrow 0} \frac{F}{S},$$

where  $F$  is the total force acting between the lower semispace and the infinite column  $K$  (Fig. 1), and  $S$  is the cross-section area of the column. We have:

$$(II.B) \quad \mathcal{P} = \int_{V_L} \int_0^{\infty} \psi(\zeta(\mathbf{x}), \zeta(y), R) \cos \alpha dh dV_y,$$

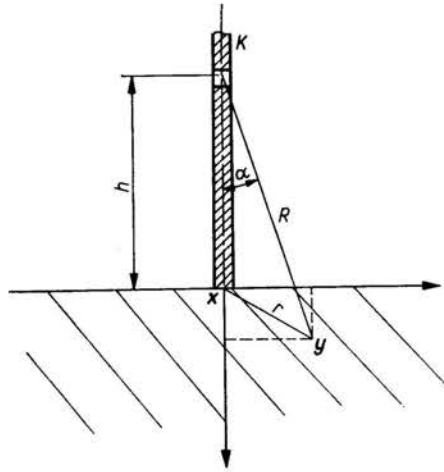


FIG. 1.

where  $V_L$  denotes the lower semispace. In the polar coordinates, we have:

$$(II.C) \quad \int_0^{\frac{\pi}{2}} \int_0^{2\pi} \int_0^{\infty} \left[ \int_r^{\infty} \psi(\zeta(\mathbf{x}), \zeta(\mathbf{y})) dR \right] r^2 \sin\theta dr d\varphi d\theta.$$

Integrating by parts and substituting  $\psi$  given by (2.2), we obtain:

$$(II.D) \quad \mathcal{P} = -\frac{2\pi}{3} \zeta^2 \int_0^{\infty} \Phi(R) R^3 dR - \frac{4\pi}{6} \frac{C_2^4}{4} \varphi(\zeta(\mathbf{x}), \zeta(\mathbf{y})),$$

and

$$(II.E) \quad -\frac{\partial \mathcal{P}}{\partial \zeta} = \frac{4\pi}{3} \zeta \int_0^{\infty} \Phi(R) R^3 dR + \frac{4\pi}{6} \frac{\partial \varphi^*(\zeta)}{\partial \zeta} \frac{C_2^4}{4},$$

where  $\varphi^*(\zeta) \equiv \varphi(\zeta, \zeta)$ .

Let us observe, however, that if  $\varphi(\zeta, \eta)$  is a symmetric function, then

$$(II.F) \quad \left. \frac{\partial \varphi(\xi, \eta)}{\partial \eta} \right|_{\xi=\eta=\zeta} = \frac{1}{2} \frac{\partial \varphi^*(\zeta)}{\partial \zeta}.$$

Now, comparing (II.E) and (2.12), we can see that  $\mathcal{P}(\zeta)$  and  $P(\zeta)$  can differ only by some constant term, which can be chosen to be equal to zero.

### Appendix III

If  $w(\zeta, \nabla\zeta)$  is an isotropic function of  $\nabla\zeta$ , then we have:

$$(III.A) \quad \nabla(\zeta, \nabla\zeta) = w(\zeta, I)$$

where

$$(III.B) \quad I \equiv \nabla_{\zeta} \cdot \nabla_{\zeta};$$

then we have

$$(III.C) \quad \frac{\partial w}{\partial(\nabla\zeta)} = \frac{\partial w}{\partial I} 2\nabla\zeta,$$

and (2.20) can be rewritten as:

$$(III.D) \quad \mathbf{T} = -\left[ \zeta^2 \frac{\partial w}{\partial\zeta} + 2\zeta \frac{\partial w}{\partial I} I \right] \mathbf{1} + 2\zeta \frac{\partial w}{\partial I} \nabla\zeta \otimes \nabla\zeta - \nabla \cdot \left( 2\zeta^2 \frac{\partial w}{\partial I} \nabla\zeta \otimes \mathbf{1} \right) \\ = f_1 \mathbf{1} + f_2 \nabla\zeta \otimes \nabla\zeta + f_3 \nabla\zeta \cdot \nabla\nabla\zeta \cdot \nabla\zeta \mathbf{1} + f_4 \nabla \cdot \nabla\zeta \mathbf{1},$$

where  $f_i$ , ( $i = 1, 2, 3, 4$ ) are some functions of  $\zeta$  and  $I$ . Let us denote now:

$$(III.E) \quad \varphi_1(\zeta, I) \equiv f_1 - (-P(\zeta) + \frac{1}{2} \Phi_3 \nabla\zeta \cdot \nabla\zeta), \\ \varphi_2(\zeta, I) \equiv f_2 + \Phi_3, \quad \varphi_3(\zeta, I) \equiv f_3, \quad \varphi_4(\zeta, I) \equiv f_4 - \Phi_3 \zeta.$$

Now the potential  $w(\zeta, I)$  can provide the Eq. (2.13) if and only if

$$(III.F) \quad \nabla \cdot [\varphi_1 \mathbf{1} + \varphi_2 (\nabla\zeta \otimes \nabla\zeta) + \varphi_3 (\nabla\zeta \cdot \nabla\nabla\zeta \cdot \nabla\zeta) \mathbf{1} + \varphi_4 \nabla \cdot \nabla\zeta \mathbf{1}] = 0,$$

for every density field  $\zeta = \zeta(\mathbf{x})$ .

We can rewrite (III.F) as follows:

$$(III.G) \quad \frac{\partial\varphi_1}{\partial\zeta} \nabla\zeta + \frac{\partial\varphi_1}{\partial I} 2\nabla\zeta \cdot \nabla\nabla\zeta + \frac{\partial\varphi_2}{\partial\zeta} (\nabla\zeta \cdot \nabla\zeta) \nabla\zeta + 2 \frac{\partial\varphi_2}{\partial I} ((\nabla\zeta \cdot \nabla\nabla\zeta \cdot \nabla\zeta) \nabla\zeta \\ + \varphi_2 (\nabla \cdot \nabla\zeta) \nabla\zeta + \varphi_2 \nabla\zeta \cdot \nabla\nabla\zeta + \frac{\partial\varphi_3}{\partial\zeta} (\nabla\zeta \cdot \nabla\nabla\zeta \cdot \nabla\zeta) \nabla\zeta \\ + \frac{\partial\varphi_3}{\partial I} 2 (\nabla\zeta \cdot \nabla\nabla\zeta \cdot \nabla\zeta) \nabla\zeta \cdot \nabla\nabla\zeta + \varphi_3 \nabla\nabla\zeta \cdot \nabla\nabla\zeta \cdot \nabla\zeta + \varphi_3 \nabla\zeta \cdot \nabla\nabla\nabla\zeta \cdot \nabla\zeta \\ + \varphi_4 \nabla\zeta \cdot \nabla\nabla\zeta \cdot \nabla\nabla\zeta + \frac{\partial\varphi_4}{\partial\zeta} (\nabla \cdot \nabla\zeta) \cdot \nabla\zeta + \frac{\partial\varphi_4}{\partial I} 2 (\nabla \cdot \nabla\zeta) \nabla\zeta \cdot \nabla\nabla\zeta + \varphi_4 \nabla (\nabla \cdot \nabla\zeta) = \mathbf{0}.$$

There are only two terms in (III.G) which depend on the third gradient:

$$\varphi_3 \nabla\zeta \cdot \nabla\nabla\nabla\zeta \cdot \nabla\zeta \quad \text{and} \quad \varphi_4 \nabla (\nabla \cdot \nabla\zeta),$$

but (III.G) should be valid for every density field — i.e., for every local value of its gradients, and the second term does not depend on the first gradient, so both  $\varphi_3$  and  $\varphi_4$  should be equal to zero. If  $\varphi_3 = \varphi_4 = 0$ , then multiplying (III.G) by  $\nabla\zeta$  and denoting  $\nabla\zeta \cdot \nabla\nabla\zeta \cdot \nabla\zeta \equiv J$ , we obtain:

$$(III.H) \quad \frac{\partial\varphi_1}{\partial\zeta} I + \frac{\partial\varphi_1}{\partial I} J + \frac{\partial\varphi_2}{\partial\zeta} I^2 + 2 \frac{\partial\varphi_2}{\partial I} I + \varphi_2 J + \varphi_2 (\nabla \cdot \nabla\zeta) I = 0.$$

For given  $I$  and  $J$ ,  $\nabla \cdot \nabla\zeta$  can be chosen arbitrarily; hence  $\varphi_2 = 0$ , and we are left only with two terms, but  $I$  is independent of  $J$  and consequently

$$(III.I) \quad \frac{\partial\varphi_1}{\partial\zeta} = 0, \quad \frac{\partial\varphi_1}{\partial I} = 0.$$

But if  $\varphi_1 \neq 0$ , then bearing in mind that  $P(\zeta)$  has the meaning of pressure for  $\nabla\zeta = 0$ , we have from (III.E)  $f_1 \neq 0$  for  $\zeta = 0$  and  $\nabla\zeta = 0$  and by (III.D)  $\mathbf{T} \neq 0$ , which is nonsense. Thus, if only (2.13) is valid, then  $\mathbf{T}$  is uniquely determined by (2.20).

## Appendix IV

For the one-dimensional case, substituting (2.12) into (2.6), we can write:

$$(IV.A) \quad -\frac{\partial P}{\partial \zeta} \zeta' + \zeta \sum_{k=1}^{\infty} \Phi_k \zeta^{[2k+1]} = 0,$$

where  $\Phi_1$  are certain constants.

Dividing by  $\zeta$  and integrating the first term by parts, we obtain:

$$(IV.B) \quad -\frac{1}{\zeta} P(\zeta) - \int \frac{P(\zeta)}{\zeta} d\zeta + \sum_{i=1}^{\infty} \frac{\Phi_i}{2i} \zeta_i^{[2i]} = \beta_1.$$

Multiplying by  $\zeta'$  and integrating, we arrive at

$$(IV.C) \quad -\int \frac{1}{\zeta} P(\zeta) d\zeta - \int \int \frac{P(\zeta)}{\zeta^2} d\zeta d\zeta + \int \sum_{i=1}^{\infty} \zeta_i^{[2i]} \zeta' dx = \beta_1 \zeta + \beta_2.$$

Now, integrating many times by parts, we can obtain:

$$(IV.D) \quad \int 2^{[2i]} \zeta' dx = \sum_{k=1}^i (-1)^{k+1} \zeta^{[2i-k]} \zeta^{[k]} - (-1)^i \int \zeta^{[i+1]} \zeta^{[i]} dx \\ = \sum_{k=1}^i (-1)^{k+1} \zeta^{[2i-k]} \zeta^{[k]} - \frac{(-1)^i}{2} (\zeta^{[i+1]})^2.$$

If we demand now  $\zeta^{[i]} = 0$  at  $\zeta = \zeta_1, \zeta_2$  for every  $i \geq 1$ , we obtain from (IV.B), (IV.C), and (IV.D):

$$(IV.E) \quad -\frac{P(\zeta)}{\zeta} - \int \frac{P(\zeta)}{\zeta^2} d\zeta = \beta_1,$$

and

$$(IV.F) \quad -\int \frac{P(\zeta)}{\zeta} d\zeta - \int \int \frac{P(\zeta)}{\zeta^2} d\zeta d\zeta = \beta_1 \zeta + \beta_2$$

for  $\zeta = \zeta_1, \zeta_2$

$$\text{but} \quad \int \int \frac{P(\zeta)}{\zeta^2} d\zeta d\zeta = \zeta \int \frac{P(\zeta)}{\zeta^2} d\zeta - \int \frac{P(\zeta)}{\zeta} d\zeta,$$

and we have from (IV.F)

$$(IV.G) \quad -\zeta \frac{P(\zeta)}{\zeta^2} d\zeta = \beta_1 \zeta + \beta_2 \quad \text{for} \quad \zeta = \zeta_1, \zeta_2,$$

which is equivalent to (3.6). Multiplying (IV.E) by  $\zeta$  and subtracting from (IV.G), we obtain (3.5) with  $\beta = -\alpha_1 = P_5$ .



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