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ELASTIC INTERACTIONS OF POINT DEFECTS IN A SEMI-INFINITE MEDIUM *

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Two problems involving the elastic interactions of point defects in a semi-infinite, isotropic elastic medium, bounded by a planar, stress-free surface, have been solved. The first is the determination of the energy of interaction of a point defect with the surface. The point defect is represented by the superposition of three, mutually perpendicular, double forces without moment, of unequal strength, one of which is perpendicular to the plane of the surface. The interaction energy is negative and decreases as the inverse third power of the distance of the defect from the surface. The second problem solved is the determination of the energy of interaction of two such defects. In the case that both defects are isotropic (the three double forces without moments have equal strengths) there is no interaction at a distance between these two defects in an infinitely extended medium. In the presence of a surface, however, they interact with an energy that varies as the inverse cube of the function

$$[(\boldsymbol{x}_{\parallel}^{(1)} - \boldsymbol{x}_{\parallel}^{(2)})^2 + (x_3^{(1)} + x_3^{(2)})^2]^{1/2},$$

where

$$(\boldsymbol{x}_{\parallel}^{(1)}, x_3^{(1)}) \quad \text{and} \quad (\boldsymbol{x}_{\parallel}^{(2)}, x_3^{(2)})$$

are the positions of the two defects, and which can be attractive or repulsive depending on the relative orientation of the two defects. In both cases the results are obtained analytically, in closed form, by a Green function approach.

1. Introduction

There has been considerable interest recently in the interaction of adatoms on a solid surface. This interaction can be direct and it can also be indirect, through the substrate. The direct, dipole–dipole, interaction between two adatoms on a metal surface has been determined by Kohn and Lau [1]. The indirect interaction between two adatoms on a metal substrate, mediated by the conduction electrons, has been discussed by Grimley [2,3] and by Einstein and Schrieffer [4]. The

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indirect interaction of two adatoms through the phonon field of the substrate has been studied by Schick and Campbell [5] and by Cunningham et al. [6,7]. Recently Lau and Kohn [8] have investigated the interaction between two adatoms mediated by the elastic distortion of the isotropic substrate to which they give rise, to which the interaction studied by Cunningham et al. is the leading quantum correction. Lau and Kohn have shown that the interaction caused by the elastic distortion of the substrate is three or four orders of magnitude larger than that arising from the phonon field. More recently the interaction between two adatoms mediated by the elastic distortion of the substrate has also been studied by Stoncham [9], who obtains results qualitatively similar to those of Lau and Kohn. An extension of the earlier work of Lau and Kohn [8] to the case of two adatoms on a cubic substrate bounded by a stress-free (001) surface has been carried out by Lau [10].

In this paper we consider a somewhat different, but related type of problem. We study the elastic interaction of a point defect with the stress-free, planar boundary of the semi-infinite elastic medium in which the point defect is situated; and we consider the elastic interaction of two point defects in a semi-infinite elastic medium, bounded by a planar, stress-free surface.

The elastic interaction of point defects in an infinitely extended medium has been studied extensively in the past [11]. In contrast, few studies have been carried out of such interactions in the presence of a surface, or of the interaction of a defect with a surface. The elastic interaction energy between a point defect that can be described as a bubble with pressure and a stress-free, planar surface of an isotropic elastic medium was calculated by Bullough [12], and found to vary as the inverse cube of the distance of the defect from the surface. Bacon [13] calculated the elastic interaction energy between a center of dilation in an isotropic medium, created by inserting an oversized or undersized sphere into a spherical cavity of a different radius, and a surface layer of finite thickness on the planar surface of the medium. After the present calculations were completed a paper by Michel [14] appeared in which the elastic interaction energy between a center of dilation and a stress-free surface in an isotropic medium was obtained, and found to agree with the appropriate limit of Bacon's earlier result. Michel also calculated the energy of interaction of two centers of dilation in the vicinity of a stress-free surface.

In addition to these studies there have been a few determinations of defect-surface interactions mediated by the phonon field in a semi-infinite crystal [15], but none of defect–defect interactions. These interactions represent the first quantum corrections to the elastic interaction energies discussed in the preceding paragraph [8]. Thus, for example, the zero point energy of interaction of an isotopic impurity with a free surface has been found to vary as the inverse fourth power of its distance from the surface; it is attractive if the impurity is lighter than the atom it replaces and repulsive if it is heavier. A vacancy has been found to be attracted to a free surface and the energy of interaction varies as the inverse square of its distance from the surface.

The approach to the calculation of the elastic interaction of a point defect with

a stress-free surface or of two defects in the vicinity of such a surface taken in this paper is different from that of Bacon and Michel. It is based on the use of the static Green's tensor for a semi-infinite elastic medium bounded by a planar, stress-free surface. It has the attractive feature that once the elements of this tensor have been calculated for a particular solid, it can be used for a variety of different defect problems without the necessity of having to solve a boundary value problem anew for each different model of a point defect or system of defects. These Green tensors have now been obtained for a semi-infinite, isotropic elastic medium (see the Appendix), for an hexagonal medium bounded by a planar, stress-free surface normal to the axis of six-fold symmetry [16], and effectively for a cubic elastic medium bounded by a stress-free (001) surface [17]. Their existence makes it possible to solve a variety of defect problems in anisotropic media as well as in isotropic media. We model the point defects we study by distributions of body force. Together with our Green function approach this makes it possible to treat anisotropic defects as easily as isotropic (spherically symmetric) defects.

We have remarked in the preceding that in this work we consider a semi-elastic medium, that we assume to be elastically isotropic, occupying the half-space $x_3 > 0$, and bounded by a stress-free, planar surface at $x_3 = 0$. The assumption of a stress-free surface means that we are assuming the absence of an oxide layer, or any surface layer formed by deposition, that would lead to nonvanishing stresses at the surface of the semi-infinite medium, as well as the absence of residual stresses due to mechanical deformation of the surface, as in an unannealed, cold worked surface. The interaction of a point defect with a surface subjected to nonvanishing stresses will be treated in a subsequent paper.

In section 2 the elastic strain energy of interaction of a single point defect with the surface will be obtained, while in section 3 the energy of interaction of two point defects in the semi-infinite medium will be obtained. The results will be discussed in section 4.

2. Interaction of a point defect with a stress-free surface

In this section we obtain the strain energy of interaction of a point defect with the stress-free, planar boundary of an isotropic elastic medium, which we assume fills the half-space $x_3 \geqslant 0$. As we have indicated in the Introduction, the point defect will be modeled by a distribution of body force. We will denote by $\boldsymbol{F}$ the body force per unit mass, so that $\rho \boldsymbol{F}$ gives the body force per unit volume, where ρ is the mass density of the elastic medium.

In the presence of a body force the equations of equilibrium of an elastic body are given by

$$\sum_{\beta\mu\nu} C_{\alpha\beta\mu\nu} \frac{\partial^2 u_\mu}{\partial x_\beta \partial x_\nu} + \rho F_\alpha = 0 , \quad \alpha = 1, 2, 3 , \tag{2.1}$$

where $\boldsymbol{u}(\boldsymbol{x})$ is the displacement of the medium at the point $\boldsymbol{x}$, and the $\{C_{\alpha\beta\mu\nu}\}$ are the elements of the elastic modulus tensor. Equations (2.1) are to be supplemented by boundary conditions that express the assumption that the surface $x_3 = 0$ is free of stresses acting on it:

$$\sum_{\mu\nu} C_{\alpha 3\mu\nu} \left.\frac{\partial u_\mu}{\partial x_\nu}\right|_{x_3=0} = 0 , \quad \alpha = 1, 2, 3 , \tag{2.2}$$

and that the stresses vanish at infinity.

To solve eqs. (2.1)–(2.2) we introduce the Green function $D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}')$ which is the solution of the equation

$$\frac{1}{\rho}\sum_{\beta\mu\nu} C_{\alpha\beta\mu\nu} \frac{\partial^2}{\partial x_\beta \partial x_\nu} D_{\mu\gamma}(\boldsymbol{x};\boldsymbol{x}') = \delta_{\alpha\gamma}\delta(\boldsymbol{x}-\boldsymbol{x}') , \tag{2.3}$$

$\alpha, \gamma = 1, 2, 3 , \quad x_3, x_3' \geqslant 0 ,$

together with the boundary conditions

$$\frac{1}{\rho}\sum_{\mu\nu} C_{\alpha 3\mu\nu} \frac{\partial}{\partial x_\nu} D_{\mu\gamma}(\boldsymbol{x};\boldsymbol{x}') \Big|_{\substack{x_3=0 \\ |\boldsymbol{x}|\to\infty,\ x_3>0}} = 0 , \tag{2.4}$$

$\alpha, \gamma = 1, 2, 3 .$

With the aid of this function the solution of eqs. (2.1)–(2.2) can be written in the form

$$u_\alpha(\boldsymbol{x}) = -\sum_\beta \int \mathrm{d}^3x' D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}') F_\beta(\boldsymbol{x}') . \tag{2.5}$$

To obtain the elastic energy associated with the introduction of the point defect, we note that in the presence of a distribution of body force the elastic energy in a volume V of material is given by

$$U_S = \int_V \mathrm{d}^3x \left\{ \tfrac{1}{2} \sum_{\alpha\beta\mu\nu} C_{\alpha\beta\mu\nu} \frac{\partial u_\alpha(\boldsymbol{x})}{\partial x_\beta} \frac{\partial u_\mu(\boldsymbol{x})}{\partial x_\nu} - \sum_\alpha \rho F_\alpha(\boldsymbol{x})\, u_\alpha(\boldsymbol{x}) \right\} . \tag{2.6}$$

The equations of equilibrium (2.1) are just the Euler equations that result when we seek the minimum of the elastic energy (2.6) subject to the condition that the boundary S of the volume V be stress-free. We can simplify eq. (2.6) in the following way. We multiply (2.1) by $u_\alpha(\boldsymbol{x})$, sum on α and integrate over the volume of the elastic medium (the region $x_3 \geqslant 0$). In this way we obtain

$$\sum_{\alpha\beta\mu\nu} \int_V \mathrm{d}^3x u_\alpha(\boldsymbol{x})\, C_{\alpha\beta\mu\nu} \frac{\partial^2 u_\mu(\boldsymbol{x})}{\partial x_\beta \partial x_\nu} = -\rho \sum_\alpha \int \mathrm{d}^3x u_\alpha(\boldsymbol{x})\, F_\alpha(\boldsymbol{x}) . \tag{2.7}$$

The left hand side of this equation can be rewritten in the following way:

$$\sum_{\alpha\beta\mu\nu} \int_V \mathrm{d}^3x u_\alpha(\boldsymbol{x})\, C_{\alpha\beta\mu\nu} \frac{\partial^2 u_\mu(\boldsymbol{x})}{\partial x_\beta \partial x_\nu}$$

$$= -\sum_{\alpha\beta\mu\nu} \int_V \mathrm{d}^3x \, \frac{\partial u_\alpha(\boldsymbol{x})}{\partial x_\beta} C_{\alpha\beta\mu\nu} \frac{\partial u_\mu(\boldsymbol{x})}{\partial x_\nu}$$

$$+ \sum_{\alpha\beta\mu\nu} \int_V \mathrm{d}^3x \, \frac{\partial}{\partial x_\beta} \left(u_\alpha(\boldsymbol{x}) \, C_{\alpha\beta\mu\nu} \frac{\partial u_\mu(\boldsymbol{x})}{\partial x_\nu} \right)$$

$$= -\sum_{\alpha\beta\mu\nu} \int_V \mathrm{d}^3x \, \frac{\partial u_\alpha(\boldsymbol{x})}{\partial x_\beta} C_{\alpha\beta\mu\nu} \frac{\partial u_\mu(\boldsymbol{x})}{\partial x_\nu}$$

$$+ \sum_\alpha \int_S \mathrm{d}S u_\alpha(\boldsymbol{x}) \left(\sum_{\beta\mu\nu} \hat{n}_\beta C_{\alpha\beta\mu\nu} \frac{\partial u_\mu(\boldsymbol{x})}{\partial x_\nu} \right), \tag{2.8}$$

where $\hat{n}$ is the outward normal unit vector at each point of the boundary of the elastic medium. The expression in parentheses in the integrand of the surface integral is recognized as the α component of the stress acting on the bounding surface of the medium ($=\Sigma_\beta T_{\alpha\beta}\hat{n}_\beta$, where $T_{\alpha\beta}$ is the stress tensor). The surface integral vanishes because the boundary is stress-free. It therefore follows from eqs. (2.7) and (2.8) that for a displacement field satisfying the equations of equilibrium (2.1) within a solid body, and stress-free boundary conditions on its surface

$$\sum_{\alpha\beta\mu\nu} \int_V \mathrm{d}^3x C_{\alpha\beta\mu\nu} \frac{\partial u_\alpha(\boldsymbol{x})}{\partial x_\beta} \frac{\partial u_\mu(\boldsymbol{x})}{\partial x_\nu} = \rho \sum_\alpha \int_V \mathrm{d}^3x u_\alpha(\boldsymbol{x}) \, F_\alpha(\boldsymbol{x}) \, . \tag{2.9}$$

Under these conditions we find on combining eqs. (2.6) and (2.9) that the elastic energy in the body is given by

$$U_S = -\tfrac{1}{2}\rho \sum_\alpha \int \mathrm{d}^3x u_\alpha(\boldsymbol{x}) \, F_\alpha(\boldsymbol{x})$$

$$= \tfrac{1}{2}\rho \sum_{\alpha\beta} \int \mathrm{d}^3x \int \mathrm{d}^3x' F_\alpha(\boldsymbol{x}) \, D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}') \, F_\beta(\boldsymbol{x}') \, . \tag{2.10}$$

The Green function $D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}')$ has been obtained for an isotropic elastic medium in ref. [18]. It is shown there that because the unperturbed medium is invariant against arbitrary displacements parallel to the surface $D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}')$ can be Fourier analyzed with respect to the coordinates in the plane of the surface,

$$D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}') = \int \frac{\mathrm{d}^2k_{/\!/}}{(2\pi)^2} D_{\alpha\beta}(\boldsymbol{k}_{/\!/}|x_3x_3') \exp[\mathrm{i}\boldsymbol{k}_{/\!/} \cdot (\boldsymbol{x}_{/\!/} - \boldsymbol{x}'_{/\!/})] \, , \tag{2.11}$$

where $\boldsymbol{x}_{/\!/} = \hat{x}_1 x_1 + \hat{x}_2 x_2$ and $\boldsymbol{k}_{/\!/} = \hat{x}_1 k_1 + \hat{x}_2 k_2$. The Fourier coefficients $\{D_{\alpha\beta}(\boldsymbol{k}_{/\!/}|x_3x_3')\}$ in turn can be expressed in terms of a simpler set of functions $\{d_{\alpha\beta}(k_{/\!/}|x_3x_3')\}$, which depend on the vector $\boldsymbol{k}_{/\!/}$ only through its magnitude, through the relation

$$D_{\alpha\beta}(\boldsymbol{k}_{/\!/}|x_3x_3') = \sum_{\mu\nu} S^{-1}_{\alpha\mu}(\hat{k}_{/\!/}) \, D_{\mu\nu}(k_{/\!/}|x_3x_3') \, S_{\nu\beta}(\hat{k}_{/\!/}) \, . \tag{2.12}$$

The matrix $S(\hat{k}_{/\!/})$ appearing in this equation is given by

$$S(\hat{k}_{/\!/}) = \begin{bmatrix} \hat{k}_1 & \hat{k}_2 & 0 \\ -\hat{k}_2 & \hat{k}_1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad S^{-1}(\hat{k}_{/\!/}) = \begin{bmatrix} \hat{k}_1 & -\hat{k}_2 & 0 \\ \hat{k}_2 & \hat{k}_1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \tag{2.13}$$

where $\hat{k}_\alpha = (k_\alpha/k_{/\!/})$ ($\alpha = 1, 2$). The nonzero elements of the tensor $d_{\mu\nu}(k_{/\!/}|x_3x_3')$ are presented in the Appendix.

Combining eqs. (2.10) (2.12) we find that we can express the strain energy associated with the point defect conveniently as

$$U_S = \frac{1}{2\rho}\sum_{\mu\nu}\frac{d^2k_{/\!/}}{(2\pi)^2}\int_0^\infty dx_3\int_0^\infty dx_3' f_\mu(\boldsymbol{k}_{/\!/}|x_3)\, d_{\mu\nu}(k_{/\!/}|x_3x_3')\, f_\nu^*(\boldsymbol{k}_{/\!/}|x_3'), \tag{2.14}$$

where

$$f_\mu(\boldsymbol{k}_{/\!/}|x_3) = \sum_\alpha S_{\mu\alpha}(\hat{k}_{/\!/})\int d^2x_{/\!/}\,\rho F_\alpha(\boldsymbol{x})\exp(i\boldsymbol{k}_{/\!/}\cdot\boldsymbol{x}_{/\!/}). \tag{2.15}$$

We must now specify the distribution of body force we will use to describe the point defect. We will represent the defect by the superposition of three mutually perpendicular double forces without moment centered at the point $\boldsymbol{x}_0$. That is, we express $\rho F_\alpha(\boldsymbol{x})$ as

$$\rho F_\alpha(\boldsymbol{x}) = -A_\alpha\frac{\partial}{\partial x_\alpha}\delta(\boldsymbol{x}-\boldsymbol{x}_0), \quad \alpha = 1, 2, 3, \tag{2.16}$$

where A_α is a constant with the dimensions of force times length. The quantities $f_\mu(\boldsymbol{k}_{/\!/}|x_3)$ obtained from eqs. (2.13), (2.15), and (2.16) are

$$f_1(\boldsymbol{k}_{/\!/}|x_3) = ik_{/\!/}\delta(x_3 - x_{03})(\hat{k}_1^2A_1 + \hat{k}_2^2A_2)\exp(i\boldsymbol{k}_{/\!/}\cdot\boldsymbol{x}_{/\!/}^{(0)}), \tag{2.17a}$$

$$f_2(\boldsymbol{k}_{/\!/}|x_3) = ik_{/\!/}\delta(x_3 - x_{03})\,\hat{k}_1\hat{k}_2(-A_1 + A_2)\exp(i\boldsymbol{k}_{/\!/}\cdot\boldsymbol{x}_{/\!/}^{(0)}), \tag{2.17b}$$

$$f_3(\boldsymbol{k}_{/\!/}|x_3) = -A_3\frac{d}{dx_3}\delta(x_3 - x_{03})\exp(i\boldsymbol{k}_{/\!/}\cdot\boldsymbol{x}_{/\!/}^{(0)}), \tag{2.17c}$$

where we have set $\boldsymbol{x}_{/\!/}^{(0)} = \hat{x}_1x_{01} + \hat{x}_2x_{02}$. We see that each of these expressions is of the form

$$f_\alpha(\boldsymbol{k}_{/\!/}|x_3) = \hat{f}_\alpha(\boldsymbol{k}_{/\!/}|x_3x_{03})\exp(i\boldsymbol{k}_{/\!/}\cdot\boldsymbol{x}_{/\!/}^{(0)}), \tag{2.18}$$

which defines the $\{\hat{f}_\alpha(\boldsymbol{k}_{/\!/}|x_3x_{03})\}$. Since $\hat{f}(\boldsymbol{k}_{/\!/}|x_3x_{03})$ is independent of $\boldsymbol{x}_{/\!/}^{(0)}$, it follows from eq. (21.4) that the strain energy

$$U_S(x_{03}) = \frac{1}{2\rho}\sum_{\mu\nu}\int\frac{d^2k_{/\!/}}{(2\pi)^2}\int_0^\infty dx_3\int_0^\infty dx_3'\hat{f}_\mu(\boldsymbol{k}_{/\!/}|x_3x_{03})$$

$$\times d_{\mu\nu}(k_{/\!/}|x_3x_3')\,\hat{f}_\nu^*(\boldsymbol{k}_{/\!/}|x_3'x_{03}) \tag{2.19}$$

is independent of $\boldsymbol{x}_{/\!/}^{(0)}$, as would be expected from translational invariance considerations, and depends on the position of the point defect only through the coordinate x_{03}. We have indicated this dependence explicitly in writing eq. (2.19).

The energy of interaction of the point defect with the surface $U_{\mathrm{I}}(x_{03})$ is defined as the difference between the strain energy $U_{\mathrm{S}}(x_{03})$ when the defect is at a distance x_{03} from the surface and the strain energy $U_{\mathrm{S}}(\infty)$ when the defect has been removed to infinity where the elastic effects to which it gives rise are insensitive to the presence of the surface.

The function $U_{\mathrm{I}}(x_{03})$ can be solved for directly. This results from the following circumstance. The Fourier coefficient $d_{\mu\nu}(k_{/\!/}|x_3x_3')$ can be written as the sum of a part $d_{\mu\nu}^{(\infty)}(k_{/\!/}|x_3x_3')$, corresponding to the Green function for an infinitely extended medium, and a part $d_{\mu\nu}^{(\mathrm{s})}(k_{/\!/}|x_3x_3')$ which reflects the presence of a stress-free surface at the plane $x_3 = 0$.

The function $d_{\mu\nu}^{(\infty)}(k_{/\!/}|x_3x_3')$ depends on the coordinates x_3 and x_3' only through their difference. Consequently, the contribution to the strain energy associated with the point defect from this part of the total function $d_{\mu\nu}(k_{/\!/}|x_3x_3')$ is a constant independent of x_{03}. This contribution in fact is the one we have denoted by $U_{\mathrm{S}}(\infty)$, because the contribution to $U_{\mathrm{S}}(x_{03})$ coming from the function $d_{\mu\nu}^{(\mathrm{s})}(k_{/\!/}|x_3x_3')$ is a function of x_{03} that tends to zero as $x_{03} \to \infty$. It follows, therefore, that the interaction strain energy of the point defect with the stress-free surface is given by

$$U_{\mathrm{I}}(x_{03}) = -\frac{1}{2\rho}\sum_{\mu\nu}\int\frac{\mathrm{d}^2k_{/\!/}}{(2\pi)^2}\int_0^\infty \mathrm{d}x_3\int_0^\infty \mathrm{d}x_3'\,\hat{f}_\mu(\boldsymbol{k}_{/\!/}|x_3x_{03})$$

$$\times d_{\mu\nu}^{(\mathrm{s})}(k_{/\!/}|x_3x_3')\,\hat{f}_\nu^*(\boldsymbol{k}_{/\!/}|x_3'x_{03})\,. \tag{2.20}$$

In evaluating the integral over the magnitude of $\boldsymbol{k}_{/\!/}$ in eq. (2.20) we cut it off at a value of $k_{/\!/} = k_{\mathrm{D}}$, where k_{D}, the Debye radius, is of the order of the reciprocal of an interatomic spacing or lattice parameter. Such a cutoff arises naturally in lattice theories of surface properties of solids, because in such theories the wave vector $\boldsymbol{k}_{/\!/}$ is restricted to lie inside the two-dimensional first Brillouin zone associated with the periodicity of the lattice in directions parallel to the surface. In a continuum theory such as we are employing here k_{D} strictly speaking is infinite, because in continuous media the lattice parameter is zero. Imposing a cutoff on the integral over $k_{/\!/}$ therefore takes us beyond the limits of elasticity theory. This step, however, has the desirable consequences that it yields a finite value for the interaction energy $U_{\mathrm{I}}(x_{03})$ as $x_{03} \to 0$, and in the limit of large x_{03}, where the use of continuum theory is valid, it gives rise to an interaction energy that is independent of k_{D}. Nevertheless, it should be kept in mind that in the immediate vicinity of a crystal surface the discreteness of the crystal plays an important role, together with the details of its structure, in determining the interaction energy. Consequently, in view of this and of the measure of uncertainty surrounding the value of the Debye radius k_{D}, too much reliance should not be placed on the values of the interaction energy

obtained below in the limit as $x_{03} \to 0$. They are likely to be correct only as to their order of magnitude.

With the use of the expression for $d^{(s)}_{\mu\nu}(k_{/\!/}|x_3 x_3')$ given in the Appendix the sums over μ and ν, and the integrals over x_3, x_3' and $\boldsymbol{k}_{/\!/}$ in eq. (2.20) can be carried out with the result that

$$
\begin{aligned}
U_I(x_{03}) = {} & \frac{1}{256\pi\rho c_t^2 c_Q^2}\frac{1}{x_{03}^3}\left\{\frac{1}{c_Q^2 - c_t^2}\,[\tfrac{1}{4}(5c_Q^4 - 2c_Q^2c_t^2 + 3c_t^4)(A_1^2 + A_2^2)\right. \\
& + 2(c_Q^4 - 4c_Q^2c_t^2 + 5c_t^4)\,A_3^2 - (c_Q^4 - 2c_Q^2c_t^2 - c_t^4) \\
& \times(\tfrac{1}{2}A_1A_2 + 2A_2A_3 + 2A_3A_1)]\,I_2(\xi) + [-\tfrac{3}{4}(c_Q^2 + c_t^2)(A_1^2 + A_2^2) \\
& - 2(c_Q^2 - 3c_t^2)\,A_3^2 - \tfrac{1}{2}(c_Q^2 + c_t^2)\,A_1A_2 + 2(c_Q^2 - c_t^2)(A_2A_3 + A_3A_1)]\,I_3(\xi) \\
& \left. + (c_Q^2 - c_t^2)[\tfrac{3}{8}(A_1^2 + A_2^2) + A_3^2 + \tfrac{1}{4}A_1A_2 - A_2A_3 - A_3A_1]\,I_4(\xi)\right\}. \qquad (2.21)
\end{aligned}
$$

In writing this result we have introduced the following notation

$$
I_n(\xi) = \int_0^{\xi} \mathrm{d}u\, u^n \mathrm{e}^{-u}, \qquad \xi = 2k_D x_{03}. \qquad (2.22)
$$

We have explicitly that

$$
I_n(\xi) = n! - n!\,\mathrm{e}^{-\xi}\sum_{p=0}^{n}\xi^p/p! \qquad (2.23)
$$

It follows from these results that the interaction energy takes the following forms in the limits as $x_{03} \to 0$ and $x_{03} \to \infty$, respectively:

$$
\begin{aligned}
U_I(x_{03}) \xrightarrow[x_{03}\to 0]{} {} & \frac{-k_D^3}{384\pi\rho c_t^2 c_Q^2(c_Q^2 - c_t^2)}\,\{(5c_Q^4 - 2c_Q^2c_t^2 + 3c_t^4)(A_1^2 + A_2^2) \\
& + 8(c_Q^4 - 4c_Q^2c_t^2 + 5c_t^4)\,A_3^2 - 2(c_Q^4 - 2c_Q^2c_t^2 - c_t^4)\,A_1A_2 \\
& - 8(c_Q^4 - 2c_Q^2c_t^2 - c_t^4)\,A_3(A_1 + A_2)\}, \qquad (2.24a)
\end{aligned}
$$

$$
\begin{aligned}
U_I(x_{03}) \xrightarrow[x_{03}\to\infty]{} {} & \frac{-1}{256\pi\rho c_t^2 c_Q^2(c_Q^2 - c_t^2)}\,\frac{1}{x_{03}^3} \\
& \{(7c_Q^4 - 19c_Q^2c_t^2 + 15c_t^4)(A_1^2 + A_2^2) + 8(2c_Q^4 - 2c_Q^2c_t^2 + c_t^4)\,A_3^2 \\
& + 2(c_Q^4 - 5c_Q^2c_t^2 + 5c_t^4)\,A_1A_2 - 8(2c_Q^4 - 4c_Q^2c_t^2 + c_t^4)\,A_3(A_1 + A_2)\}. \qquad (2.24b)
\end{aligned}
$$

These results simplify in various limiting cases. For example, in the limit as $x_{03} \to \infty$, we have in the case that $A_1 = A_2 \neq A_3$

$$
\begin{aligned}
U_I(x_{03}) = {} & \frac{-1}{32\pi\rho c_t^2 c_Q^2(c_Q^2 - c_t^2)}\,\frac{1}{x_{03}^3}\,\{(2c_Q^4 - 6c_Q^2c_t^2 + 5c_t^4)\,A_1^2 \\
& - 2(2c_Q^4 - 4c_Q^2c_t^2 + c_t^4)\,A_1A_3 + (2c_Q^4 - 2c_Q^2c_t^2 + c_t^4)\,A_3^2\}, \qquad (2.25)
\end{aligned}
$$

while in the case that $A_1 = A_2 = A_3$ we find that

$$U_I(x_{03}) = -\frac{1}{8\pi\rho}\frac{c_t^2 A_1^2}{c_\ell^2(c_\ell^2 - c_t^2)}\frac{1}{x_{03}^3} . \tag{2.26}$$

We will show in section 4 how the coefficient A_1 can be evaluated for a particular defect system.

The result given by eq. (2.25) could apply for example, to the case of a carbon impurity present interstitially in bcc iron, since such a defect can be regarded as possessing tetragonal symmetry [19].

The result given by eq. (2.26) agrees with the corresponding results of Bacon [13] and Michel [14], who modeled the defect by a center of dilation. In order to make the comparison the volume change due to the introduction of the defect is required. This is given, for example, in the review article of Eshelby [11].

From an examination of the principal minors of the matrices of the quadratic forms in the $\{A_\alpha\}$ in eqs. (2.24b), (2.25), and (2.26), we conclude that for all values of the ratio c_t/c_ℓ allowed by the requirements of elastic stability ($0 < c_t^2/c_\ell^2 < 0.75$) the expression in braces in each of these equations is a positive definite quadratic form in the $\{A_\alpha\}$. This means that a point defect of the kind considered in this section is always attracted to a stress-free surface, regardless of the signs and magnitudes of the $\{A_\alpha\}$.

It appears to be a well known result that a soft layer on a crystal will attract a defect and that a thick, hard layer will repel it [13]. Here "soft" and "hard" refer to layers whose elastic moduli are smaller or larger than those of the medium containing the defect, respectively. The results of the present section are in agreement with this general result, since a medium bounded by a stress-free surface is a limiting case of a medium in contact with a soft layer. However, to obtain the dependence of the interaction energy on the parameters characterizing the point defect and the host medium, and on the distance of the defect from the surface, requires the kind of detailed calculation presented here.

3. Interaction of two point defects in a semi-infinite elastic medium

We now turn to a discussion of the strain energy of interaction of a pair of point defects in a semi-infinite elastic medium bounded by a planar, stress-free surface.

In this case the strain energy in the system is again given by eq. (2.10), except that the density of body force characterizing the defect is now the sum of two contributions,

$$\boldsymbol{F}(\boldsymbol{x}) = \boldsymbol{F}^{(1)}(\boldsymbol{x}|\boldsymbol{x}^{(1)}) + \boldsymbol{F}^{(2)}(\boldsymbol{x}|\boldsymbol{x}^{(2)}) , \tag{3.1}$$

each of which is associated with one of the point defects. In eq. (3.1), $\boldsymbol{x}^{(1)}$ and $\boldsymbol{x}^{(2)}$ are the positions of the two defects which, in general, need not be identical. The interaction strain energy is defined as the difference between the total strain energy

and the sum of the self-strain energies of the individual defects:

$$U_{\mathrm{I}}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) = \tfrac{1}{2}\rho \sum_{\alpha\beta} \int \mathrm{d}^3x \int \mathrm{d}^3x' \{F_\alpha^{(1)}(\boldsymbol{x}|\boldsymbol{x}^{(1)})\, D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}')$$

$$\times F_\beta^{(2)}(\boldsymbol{x}'|\boldsymbol{x}^{(2)}) + F_\alpha^{(2)}(\boldsymbol{x}|\boldsymbol{x}^{(2)})\, D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}')\, F_\beta^{(1)}(\boldsymbol{x}'|\boldsymbol{x}^{(1)})\} \,. \tag{3.2}$$

The Green function $D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}')$ can be shown to possess the summetry property

$$D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}') = D_{\beta\alpha}(\boldsymbol{x}';\boldsymbol{x}) \,. \tag{3.3}$$

Consequently the two terms on the right hand side of eq. (3.2) are equal, and we can write compactly

$$U_{\mathrm{I}}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) = \frac{1}{\rho} \sum_{\alpha\beta} \int \mathrm{d}^3x \int \mathrm{d}^3x' \rho F_\alpha^{(1)}(\boldsymbol{x}|\boldsymbol{x}^{(1)})$$

$$\times D_{\alpha\beta}(\boldsymbol{x};\boldsymbol{x}')\, \rho F_\beta^{(2)}(\boldsymbol{x}'|\boldsymbol{x}^{(2)}) \,. \tag{3.4}$$

With the use of eqs. (2.11)–(2.13) we can rewrite eq. (3.4) in the form

$$U_{\mathrm{I}}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) = \frac{1}{\rho} \sum_{\mu\nu} \int \frac{\mathrm{d}^2k_{/\!/}}{(2\pi)^2} \int_0^\infty \mathrm{d}x_3 \int_0^\infty \mathrm{d}x_3' f_\mu^{(1)}(\boldsymbol{k}_{/\!/}|x_3)$$

$$\times d_{\mu\nu}(k_{/\!/}|x_3x_3')\, f_\nu^{(2)}(\boldsymbol{k}_{/\!/}|x_3')^* \,, \tag{3.5}$$

where

$$f_\mu^{(j)}(\boldsymbol{k}_{/\!/}|x_3) = \sum_\alpha S_{\mu\alpha}(\hat{k}_{/\!/}) \int \mathrm{d}^2x_{/\!/} \rho F_\alpha^{(j)}(\boldsymbol{x}|\boldsymbol{x}^{(j)}) \exp(\mathrm{i}\boldsymbol{k}_{/\!/}\cdot\boldsymbol{x}_{/\!/}) \,, \quad j = 1, 2 \,. \tag{3.6}$$

For the distribution of body force representing each point defect we use the model of the preceding section and set

$$\rho F_\alpha^{(j)}(\boldsymbol{x}|\boldsymbol{x}^{(j)}) = -A_\alpha^{(j)} \frac{\partial}{\partial x_\alpha} \delta(\boldsymbol{x} - \boldsymbol{x}^{(j)}) \,, \quad j = 1, 2, \quad \alpha = 1, 2, 3 \,. \tag{3.7}$$

It follows that the transform $f_\mu^{(j)}(\boldsymbol{k}_{/\!/}|x_3)$ has the form

$$f_\mu^{(j)}(\boldsymbol{k}_{/\!/}|x_3) = \hat{f}_\mu^{(j)}(\boldsymbol{k}_{/\!/}|x_3x_3^{(j)}) \exp(\mathrm{i}\boldsymbol{k}_{/\!/}\cdot\boldsymbol{x}_{/\!/}^{(j)}) \,, \tag{3.8}$$

where

$$\hat{f}_1^{(j)}(\boldsymbol{k}_{/\!/}|x_3x_3^{(j)}) = \mathrm{i}k_{/\!/}\delta(x_3 - x_3^{(j)})(\hat{k}_1^2A_1^{(j)} + \hat{k}_2^2A_2^{(j)}) \,, \tag{3.9a}$$

$$\hat{f}_2^{(j)}(\boldsymbol{k}_{/\!/}|x_3x_3^{(j)}) = \mathrm{i}k_{/\!/}\delta(x_3 - x_3^{(j)})\,\hat{k}_1\hat{k}_2(-A_1^{(j)} + A_2^{(j)}) \,, \tag{3.9b}$$

$$\hat{f}_3^{(j)}(\boldsymbol{k}_{/\!/}|x_3x_3^{(j)}) = -A_3^{(j)} \frac{\mathrm{d}}{\mathrm{d}x_3} \delta(x_3 - x_3^{(j)}) \,. \tag{3.9c}$$

If we also note the separation of $d_{\mu\nu}(\boldsymbol{k}_{/\!/}|x_3x_3')$ into a part that corresponds to an infinite medium and a part that reflects the presence of a stress-free surface, we can

effect a similar separation of the interaction strain energy:

$$U_{\mathrm{I}}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) = U_{\mathrm{I}}^{(\infty)}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) + U_{\mathrm{I}}^{(\mathrm{s})}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) , \tag{3.10}$$

where

$$U_{\mathrm{I}}^{(\infty)}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) = \frac{1}{\rho}\sum_{\mu\nu}\int \frac{\mathrm{d}^2 k_{/\!/}}{(2\pi)^2} \exp[\mathrm{i}\boldsymbol{k}_{/\!/}\cdot(\boldsymbol{x}_{/\!/}^{(1)} - \boldsymbol{x}_{/\!/}^{(2)})]$$

$$\times \int_0^\infty \mathrm{d}x_3 \int_0^\infty \mathrm{d}x_3' \hat{f}_\mu^{(1)}(\boldsymbol{k}_{/\!/}|x_3 x_3^{(1)})\, d_{\mu\nu}^{(\infty)}(k_{/\!/}|x_3 x_3')\, \hat{f}_\nu^{(2)}(\boldsymbol{k}_{/\!/}|x_3' x_3^{(2)})^* , \tag{3.11a}$$

$$U_{\mathrm{I}}^{(\mathrm{s})}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) = \frac{1}{\rho}\sum_{\mu\nu}\int \frac{\mathrm{d}^2 k_{/\!/}}{(2\pi)^2} \exp[\mathrm{i}\boldsymbol{k}_{/\!/}\cdot(\boldsymbol{x}_{/\!/}^{(1)} - \boldsymbol{x}_{/\!/}^{(2)})]$$

$$\times \int_0^\infty \mathrm{d}x_3 \int_0^\infty \mathrm{d}x_3' f_\mu^{(1)}(\boldsymbol{k}_{/\!/}|x_3 x_3^{(1)})\, d_{\mu\nu}^{(\mathrm{s})}(k_{/\!/}|x_3 x_3')\, \hat{f}_\nu^{(2)}(\boldsymbol{k}_{/\!/}|x_3' x_3^{(2)})^* . \tag{3.11b}$$

Unfortunately, it does not appear to be possible to evaluate the integrals appearing in eq. (3.11) analytically, in closed form, if a cutoff wave vector k_{D} is introduced into the integrations over $\boldsymbol{k}_{/\!/}$. Consequently, to avoid recourse to numerical integration, with the attending inability to obtain the explicit dependence of the interaction energy on the parameters of the problem, we have evaluated the expressions in eq. (3.11) in the limit as $k_{\mathrm{D}} \to \infty$. This means that the results we obtain are those provided by elasticity theory and, consequently, are accurate when the separation between the defects is larger than a few interatomic spacings. At smaller separations our results will overestimate the interaction energy, since they lead to a divergence of the energy as the two defects approach each other, while in a lattice the energy remains finite at the nearest neighbor separation. It should also be noted that the interaction energy remains finite as both defects approch the surface, provided that they maintain a nonzero distance from each other parallel to the surface.

Rather than maintaining complete generality even in the continuum limit we have adopted, we have made two additional simplifying assumptions to render the final expressions less cumbersome. We assume first that the two point defects are identical, i.e. that

$$A_\alpha^{(1)} = A_\alpha^{(2)} , \quad \alpha = 1, 2, 3 . \tag{3.12}$$

We next assume that

$$A_1^{(1)} = A_2^{(1)} = A , \quad A_3^{(1)} = C . \tag{3.13}$$

The latter assumption allows us to treat a pair of identical, parallel impurities of tetragonal symmetry, such as the interstitial carbon atoms in alpha iron mentioned in the preceding section [19]. In addition, by setting $A = C$ in our final expressions

we recover the case of substitutional impurities or vacancies in our medium.

With the preceding assumptions and the results of the Appendix we obtain the following expression for $U_1^{(\infty)}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)})$:

$$U_1^{(\infty)}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) = \frac{-A^2}{\rho c_Q^2}\int\frac{d^3k}{(2\pi)^3}\exp(i\boldsymbol{k}\cdot\boldsymbol{R}) + \frac{2A(A-C)}{\rho c_Q^2}\int\frac{d^3k}{(2\pi)^3}$$

$$\times\exp(i\boldsymbol{k}\cdot\boldsymbol{R})\frac{k_3^2}{k^2} - \frac{(A-C)^2}{\rho c_t^2 c_Q^2}\int\frac{d^3k}{(2\pi)^3}\frac{\exp(i\boldsymbol{k}\cdot\boldsymbol{R})}{k^4}[c_Q^2k_{/\!/}^2k_3^2 + c_t^2k_3^4]\,, \tag{3.14}$$

where $R \equiv \boldsymbol{x}^{(1)} - \boldsymbol{x}^{(2)}$. We have written $U_1^{(\infty)}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)})$ in this form to emphasize the fact that it is only if $A \neq C$, i.e. if the defects are anisotropic, that there is an interaction at a distance between the defects, since the first term yields just the contact interaction term $-A^2\delta(\boldsymbol{R})/(\rho c_Q^2)$ [11]. In what follows we will neglect this interaction. The remaining integrals in eq. (3.14) are readily evaluated, and we obtain the result that

$$U_1^{(\infty)}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) = \frac{(A-C)}{8\pi c_t^2 c_Q^2}\frac{1}{R^3}\left\{[4Ac_t^2 + (A-C)(c_Q^2 - c_t^2)]\right.$$

$$\left. - 6[2Ac_t^2 + (A-C)(2c_Q^2 - 3c_t^2)]\frac{R_3^2}{R^2} + 15(A-C)\frac{R_3^4}{R^4}\right\}. \tag{3.15}$$

We now turn to the contribution $U_1^{(s)}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)})$ associated with the presence of the stress-free surface. With the assumptions made above the evaluation of the integrals in eq. (3.12b) yields the result that

$$U_1^{(s)}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) = \frac{-1}{8\pi\rho c_t^2 c_Q^2}\left\{\frac{1}{c_Q^2 - c_t^2}[8A^2c_t^4 + 4A(A-C)c_t^2(c_Q^2 - 3c_t^2)\right.$$

$$+ (A-C)^2(c_Q^4 - 4c_Q^2c_t^2 + 5c_t^4)]\frac{2}{(R_{/\!/}^2 + \bar{R}_3^2)^{3/2}}P_2\left(\frac{\bar{R}_3}{(R_{/\!/}^2 + \bar{R}_3^2)^{1/2}}\right)$$

$$- (A-C)[4Ac_t^2 + (A-C)(c_Q^2 - 3c_t^2)]\frac{6(x_3^{(1)} + x_3^{(2)})}{(R_{/\!/}^2 + \bar{R}_3^2)^2}P_3\left(\frac{\bar{R}_3}{(R_{/\!/}^2 + \bar{R}_3^2)^{1/2}}\right)$$

$$\left. + (A-C)^2(c_Q^2 - c_t^2)\frac{48x_3^{(1)}x_3^{(2)}}{(R_{/\!/}^2 + \bar{R}_3^2)^{5/2}}P_4\left(\frac{\bar{R}_3}{(R_{/\!/}^2 + \bar{R}_3^2)^{1/2}}\right)\right\}, \tag{3.16}$$

where $\boldsymbol{R}_{/\!/} = \boldsymbol{x}_{/\!/}^{(1)} - \boldsymbol{x}_{/\!/}^{(2)}$, $\bar{R}_3 = x_3^{(1)} + x_3^{(2)}$, and $P_n(x)$ is the nth Legendre polynomial. The interaction energy $U_1^{(s)}(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)})$ does not vanish when $A = C$, in which case it provides the total energy of interaction of the two defects:

$$U_1(\boldsymbol{x}^{(1)};\boldsymbol{x}^{(2)}) = \frac{-1}{\pi\rho c_Q^2}\frac{2A^2c_t^2}{c_Q^2 - c_t^2}\frac{1}{(R_{/\!/}^2 + \bar{R}_3^2)^{3/2}}P_2\left(\frac{\bar{R}_3}{(R_{/\!/}^2 + \bar{R}_3^2)^{1/2}}\right). \tag{3.17}$$

This interaction energy is positive in regions where $\bar{R}_3^2 < \frac{1}{2}R_{/\!/}^2$, and is negative in regions where $\bar{R}_3^2 > \frac{1}{2}R_{/\!/}^2$.

Both contributions to the strain energy of interaction are seen to vary essentially as the inverse cube of the distance between the two defects.

4. Discussion

The theory for the elastic interaction of point defects in the presence of a free surface which has just been developed is based on the model of the body forces acting on the defects given by eq. (2.16). We now obtain a numerical estimate of the constant A_α, assuming isotropy, for the case of a krypton impurity atom in an argon crystal. The result can then be used to estimate the interaction energies given by eqs. (2.24a), (2.26), and (3.17).

Argon crystallizes in the face-centered cubic structure. We assume nearest-neighbor interactions characterized by a 6-12 Lennard–Jones potential

$$\varphi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] , \tag{4.1}$$

where the parameters ϵ, σ for the argon–argon and krypton–krypton interactions are taken from Fender and Halsey [20]. If the indices 1 and 2 refer to the argon–argon and krypton–krypton interactions, respectively, we construct the parameters ϵ_{12} and σ_{12} for the argon–krypton interaction by the prescriptions

$$\epsilon_{12} = 2\epsilon_1\epsilon_2/(\epsilon_1 + \epsilon_2) , \tag{4.2a}$$

$$\sigma_{12} = \tfrac{1}{2}(\sigma_1 + \sigma_2) . \tag{4.2b}$$

It must be recognized, however, that the parameters from ref. [20] are for the gas phase and that the equilibrium nearest-neighbor separation in the crystal is not the same as that giving the minimum value of $\varphi(r)$ when the gas phase parameters are used. Therefore, we modify the values of σ_1 and σ_2 so that $\varphi_1(r)$ and $\varphi_2(r)$ have their minimum values when r takes on the values of the respective nearest-neighbor equilibrium distances in the argon and krypton crystals. The values of ϵ_1 and ϵ_2 are not changed, however.

To determine A_α, let us consider the twelve argon atoms that are nearest neighbors of a krypton impurity atom. We write the force density, $\rho \boldsymbol{F}_A$, on an argon atom as

$$\rho \boldsymbol{F}_A(\boldsymbol{x}) = -\frac{\boldsymbol{x}_A - \boldsymbol{x}_0}{|\boldsymbol{x}_A - \boldsymbol{x}_0|}\varphi'_{12}(r_0)\,\delta(x_1 - x_{A1})\,\delta(x_2 - x_{A2})\,\delta(x_3 - x_{A3}) , \tag{4.3}$$

where $\boldsymbol{x}_A$ is the equilibrium position vector of an argon atom relative to the fixed origin of coordinates, $\boldsymbol{x}_0$ is the equilibrium position vector of the krypton impurity atom, r_0 is the equilibrium nearest-neighbor separation in the argon crystal, and the prime on φ_{12} indicates a derivative with respect to argument. In a face-centered cubic lattice with nearest-neighbor separation r_0, the nearest neighbors of a given lattice site are located at $\boldsymbol{x}_A - \boldsymbol{x}_0 = (\pm r_0/\sqrt{2}, \pm r_0/\sqrt{2}, 0)$, $(\pm r_0/\sqrt{2}, 0, \pm r_0/\sqrt{2})$, and

$(0, \pm r_0/\sqrt{2}, \pm r_0/\sqrt{2})$ relative to that lattice site. Let us now consider the contributions to the x-component of force density on the krypton impurity atom due to the argon atoms at $(+r_0/\sqrt{2}, +r_0/\sqrt{2}, 0)$ and $(-r_0/\sqrt{2}, +r_0/\sqrt{2}, 0)$. Substituting into eq. (4.3) and expanding in power series in r_0, we get for the sum of the two contributions to lowest order,

$$\rho F_{K1}(\boldsymbol{x}) = r_0\varphi'_{12}(r_0)\,\delta'(x_1 - x_{01})\,\delta(x_2 - x_{02})\,\delta(x_3 - x_{03})\,. \tag{4.4}$$

The same contribution is given by three other pairs of nearest neighbor argon atoms. The total x-component of force density is then

$$\rho F_{K1}(\boldsymbol{x}) = 4r_0\varphi'_{12}(r_0)\,\delta'(x_1 - x_{01})\,\delta(x_2 - x_{02})\,\delta(x_3 - x_{03})\,. \tag{4.5}$$

Comparing eq. (4.5) to eq. (2.16), we see that

$$A_1 = -4r_0\varphi'_{12}(r_0)\,. \tag{4.6}$$

If we evaluate $\varphi'_{12}(r_0)$ using the parameters calculated from eqs. (4.2) with the values of ϵ_1, ϵ_2, σ_1 and σ_2 taken from ref. [20] and using the value of r_0 for solid argon taken from ref. [21], we obtain

$$A_1 = 0.231 \text{ eV}\,.$$

We are now in a position to evaluate the coefficients in the expressions for the interaction energy. If we take the values of the density and elastic constants for solid argon from the work of Gewurtz and Stoicheff [22], we find that eq. (2.24a) becomes $U_I = 0.093$ eV, where a value of $k_D = \pi/r_0$ has been used. Eq. (2.26) evaluated at $x_{03} = r_0$ and $10\,r_0$ gives $U_I = 2.2 \times 10^{-3}$ eV and 2.2×10^{-6} eV, respectively. From eq. (3.17) we obtain

$$U_I(\boldsymbol{x}^{(1)}, \boldsymbol{x}^{(2)}) = \frac{-0.0360}{(\rho_{/\!/}^2 + \bar{x}_3^2)^{3/2}}\, P_2\!\left(\frac{\bar{x}_3}{(\rho_{/\!/}^2 + \bar{x}_3^2)^{1/2}}\right), \tag{4.7}$$

in eV, where $\rho_{/\!/} = R_{/\!/}/r_0$ and $\bar{x}_3 = \bar{R}_3/r_0$. We find that the interaction energy is of the order of 0.02 eV for both defects on the surface, when they are separated by a distance r_0, and decreases rapidly as the defects move to the interior of the crystal, and/or increase the separation between them. For example, when both defects are on the surface and are separated by $5r_0$ and $10r_0$ the interaction energies are 1.4×10^{-4} eV and 1.8×10^{-5} eV, respectively. Note that the interaction between the defects is repulsive when both are on the surface, in agreement with the result of Lau and Kohn [8]. When the two defects are both five nearest neighbor distances into the solid and are separated by a distance $5r_0$ the interaction energy is -2.8×10^{-5} eV, and becomes 1.2×10^{-8} eV when the distance between them increases to $10r_0$. The change of sign of the interaction energy is caused by the Legendre polynomial in eq. (4.7). The values for the interaction energy when both defects are at the surface are of the order of one to two orders of magnitude larger than the energy of the indirect interaction of two adatoms through their mutual elastic deformation of the substrate [8].

The values of this interaction energy given above are probably upper limits to the true values when the defects are close together since, as we have already pointed out earlier, our use of continuum theory in obtaining eq. (3.17) should overestimate the interaction energy when the two defects are a nearest neighbor distance apart. However, it should also be noted that solid argon is a rather soft, easily deformable crystal, in which, for this reason, large interaction energies might be expected. A more realistic model for the point defect that treats it as a superposition of finite, rather than infintesimal, double forces without moment might also lead to smaller interaction energies.

Appendix

We present here the nonzero Fourier coefficients $\{d_{\mu\nu}(k_{/\!/}|x_3x_3')\}$ defined by eqs. (2.3), (2.4) and (2.11)–(2.13) of the text for a semi-infinite isotropic elastic medium occupying the half-space $x_3 > 0$ and bounded by a stress free surface at the plane $x_3 = 0$. They were obtained by taking the limit as $\Omega \to 0$ in the functions denoted by $\{d_{\mu\nu}(k_{/\!/}\Omega\,|x_3x_3')\}$ in ref. [18]. In each case the first term, which is a function of x_3 and x_3' only through their difference, is the Fourier coefficient $d_{\mu\nu}^{(\infty)}(k_{/\!/}|x_3x_3')$ which is obtained for an infinitely extended medium; the second term, which depends on x_3 and x_3' separately, is the contribution $d_{\mu\nu}^{(s)}(k_{/\!/}|x_3x_3')$ reflecting the presence of a stress-free surface at the plane $x_3 = 0$.

$$d_{11}(k_{/\!/}|x_3x_3') = -\frac{1}{4k_{/\!/}c_t^2c_\ell^2}\{\exp(-k_{/\!/}|x_3 - x_3'|)[(c_\ell^2 + c_t^2) - (c_\ell^2 - c_t^2)\,k_{/\!/}|x_3 - x_3'|]\}$$
$$-\frac{\exp[-k_{/\!/}(x_3 + x_3')]}{4k_{/\!/}c_t^2c_\ell^2}\left\{\frac{c_\ell^4 + c_t^4}{c_\ell^2 - c_t^2} - (c_\ell^2 + c_t^2)\,k_{/\!/}(x_3 + x_3') + 2(c_\ell^2 - c_t^2)\,k_{/\!/}^2x_3x_3'\right\}, \tag{A.1a}$$

$$d_{13}(k_{/\!/}|x_3x_3') = \frac{\mathrm{i}}{4k_{/\!/}}\frac{c_\ell^2 - c_t^2}{c_t^2c_\ell^2}\exp(-k_{/\!/}|x_3 - x_3'|)\,k_{/\!/}(x_3 - x_3')$$
$$-\frac{\mathrm{i}}{4k_{/\!/}}\exp[-k_{/\!/}(x_3 + x_3')]\left\{\frac{2}{c_\ell^2 - c_t^2} - \frac{c_\ell^2 + c_t^2}{c_t^2c_\ell^2}\,k_{/\!/}(x_3 - x_3')\right.$$
$$\left.-\frac{2(c_\ell^2 - c_t^2)}{c_t^2c_\ell^2}\,k_{/\!/}^2x_3x_3'\right\}, \tag{A.1b}$$

$$d_{31}(k_{/\!/}|x_3x_3') = \frac{\mathrm{i}}{4k_{/\!/}}\frac{c_\ell^2 - c_t^2}{c_t^2c_\ell^2}\exp(-k_{/\!/}|x_3 - x_3'|)\,k_{/\!/}(x_3 - x_3')$$
$$+\frac{\mathrm{i}}{4k_{/\!/}}\exp[-k_{/\!/}(x_3 + x_3')]\left\{\frac{2}{c_\ell^2 - c_t^2} + \frac{c_\ell^2 + c_t^2}{c_t^2c_\ell^2}\,k_{/\!/}(x_3 - x_3')\right.$$
$$\left.-\frac{2(c_\ell^2 - c_t^2)}{c_t^2c_\ell^2}\,k_{/\!/}^2x_3x_3'\right\}, \tag{A.1c}$$

$$d_{33}(k_{/\!/}|x_3x_3') = -\frac{1}{4k_{/\!/}c_t^2c_Q^2}\{\exp(-k_{/\!/}|x_3 - x_3'|)[(c_Q^2 + c_t^2) + (c_Q^2 - c_t^2)\,k_{/\!/}|x_3 - x_3'|]\}$$

$$-\frac{\exp[-k_{/\!/}(x_3 + x_3')]}{4k_{/\!/}c_t^2c_Q^2}\left\{\frac{c_Q^4 + c_t^4}{c_Q^2 - c_t^2} + (c_Q^2 + c_t^2)\,k_{/\!/}(x_3 + x_3') + 2(c_Q^2 - c_t^2)\,k_{/\!/}^2x_3x_3'\right\}, \tag{A.1d}$$

$$d_{22}(k_{/\!/}|x_3x_3') = -\frac{1}{2k_{/\!/}c_t^2}\exp(-k_{/\!/}|x_3 - x_3'|)$$

$$-\frac{1}{2k_{/\!/}c_t^2}\exp[-k_{/\!/}(x_3 + x_3')]\,. \tag{A.1e}$$

In these expressions c_t and c_Q are the speeds of sound for transverse and longitudinal waves, respectively.

In actual calculations it is convenient to introduce a Fourier integral representation for the function $d_{\mu\nu}^{(\infty)}(k_{/\!/}|x_3x_3')$. In particular, we have that

$$d_{11}^{(\infty)}(k_{/\!/}|x_3x_3') = -\frac{\exp(-k_{/\!/}|x_3 - x_3'|)}{4k_{/\!/}c_t^2c_Q^2}[(c_Q^2 + c_t^2) - (c_Q^2 - c_t^2)\,k_{/\!/}|x_3 - x_3'|]$$

$$= -\frac{1}{c_t^2c_Q^2}\int_{-\infty}^{\infty}\frac{dk_3}{2\pi}\exp[ik_3(x_3 - x_3')]\,\frac{c_Q^2k_3^2 + c_t^2k_{/\!/}^2}{(k_{/\!/}^2 + k_3^2)^2}\,, \tag{A.2a}$$

$$d_{13}^{(\infty)}(k_{/\!/}|x_3x_3') = \frac{i}{4k_{/\!/}}\frac{c_Q^2 - c_t^2}{c_t^2c_Q^2}\exp(-k_{/\!/}|x_3 - x_3'|)\,k_{/\!/}(x_3 - x_3')$$

$$= \frac{c_Q^2 - c_t^2}{c_t^2c_Q^2}\int_{-\infty}^{\infty}\frac{dk_3}{2\pi}\exp[ik_3(x_3 - x_3')]\,\frac{k_{/\!/}k_3}{(k_{/\!/}^2 + k_3^2)^2}\,, \tag{A.2b}$$

$$= d_{31}^{(\infty)}(k_{/\!/}|x_3x_3')\,, \tag{A.2c}$$

$$d_{33}^{(\infty)}(k_{/\!/}|x_3x_3') = -\frac{\exp[-k_{/\!/}|x_3 - x_3'|)}{4k_{/\!/}c_t^2c_Q^2}[(c_Q^2 + c_t^2) + (c_Q^2 - c_t^2)\,k_{/\!/}|x_3 - x_3'|]$$

$$= -\frac{1}{c_t^2c_Q^2}\int\frac{dk_3}{2\pi}\exp[ik_3(x_3 - x_3')]\,\frac{c_Q^2k_{/\!/}^2 + c_t^2k_3^2}{(k_{/\!/}^2 + k_3^2)^2}\,, \tag{A.2d}$$

$$d_{22}^{(\infty)}(k_{/\!/}|x_3x_3') = -\frac{1}{2k_{/\!/}c_t^2}\exp(-k_{/\!/}|x_3 - x_3'|)$$

$$= -\frac{1}{c_t^2}\int_{-\infty}^{\infty}\frac{dk_3}{2\pi}\exp[ik_3(x_3 - x_3')]\,\frac{1}{(k_{/\!/}^2 + k_3^2)}\,. \tag{A.2e}$$

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