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Correlation functions of crystal atoms as a function of the distance to a free surface

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We consider the correlation functions between two crystal atoms situated in the vicinity of a free surface. Using an isotropic elastic continuum, we find that the difference between these correlation functions when one introduces a free surface into an infinite solid is proportional to the inverse of the depth, and argue that the derived coefficient should be accurate to within a few percent even one layer below the surface.

We demonstrated recently¹ that the difference between the surface mean-square displacement (MSD) and the bulk one is proportional to the inverse of the depth c . However, this result was obtained from a well-defined model² not rotationally invariant for surface atoms. Therefore the coefficient of the $1/c$ term could not exhibit the right dependence on the modulus of rigidity and the Poisson's ratio. This suggested that such a result can be obtained in the frame of elasticity theory. We give here this coefficient for an isotropic solid bounded by a free surface, as well as the difference due to a free surface. The result also applies to certain correlation functions.

We use for this purpose a solution given by Mindlin³ of the elasticity equations for a homogeneous isotropic solid for the case of a concentrated force acting in the inside of a semi-infinite solid. Let us first show how these two problems are connected.

When a force \vec{P} is applied at a point \vec{r}_1 , this point experiences a displacement $\langle \vec{u}_1 \rangle$ and another point \vec{r}_2 of the medium has a displacement $\langle \vec{u}_2 \rangle$. This displacement $\langle \vec{u}_2 \rangle$ is related to the force \vec{P} acting at \vec{r}_1 by the tensor $G(\vec{r}_2, \vec{r}_1)$ usually called the Green's function:

$$\langle \vec{u}_2 \rangle = G(\vec{r}_2, \vec{r}_1) \vec{P}. \quad (1)$$

In linear-response theory, this tensor is related to the correlation function $\langle \vec{u}_2, \vec{u}_1 \rangle$. This relation is obtained easily in the following manner. Let H_0 and H be the Hamiltonians of the system, respectively, without the force \vec{P} and with this force

$$H = H_0 - \vec{P} \cdot \vec{u}_1. \quad (2)$$

Let us introduce the partition function

$$Z(\vec{P}) = \langle e^{-\beta H} \rangle, \quad (3)$$

where $\langle \rangle$ denotes the expectation value, and

$$\beta = (k_B T)^{-1}, \quad (4)$$

k_B being the Boltzmann constant and T the absolute temperature.

The mean value of \vec{u}_2 is then

$$\langle \vec{u}_2 \rangle = \langle \vec{u}_2 e^{-\beta H} \rangle / Z. \quad (5)$$

To first order in $\beta \vec{u}_1 \cdot \vec{P}$ (expansion valid at high temperatures), this mean value is

$$\langle \vec{u}_2 \rangle = \frac{\langle e^{-\beta H_0} (1 + \beta \vec{u}_1 \cdot \vec{P}) u_2 \rangle}{\langle e^{-\beta H_0} (1 + \beta \vec{u}_1 \cdot \vec{P}) \rangle}. \quad (6)$$

In the absence of the force \vec{P} , the mean values of \vec{u}_1 and \vec{u}_2 vanish and

$$\langle \vec{u}_2 \rangle = \beta \langle \vec{u}_2 \cdot \vec{u}_1 \rangle \vec{P}. \quad (7)$$

Comparing this result with the definition (1), one obtains the Green's function

$$G(\vec{r}_2, \vec{r}_1) = \beta \langle \vec{u}_2 \cdot \vec{u}_1 \rangle. \quad (8)$$

This classic relation was also introduced in another manner in our recent paper [Eq. (10) in Ref. 1].

A long time ago, Mindlin³ derived the explicit expressions (1) for the displacements due to a force \vec{P} applied at a point $(0, 0, +c)$ of a semi-infinite solid bounded by the plane $z=0$, the positive z axis penetrating into the body (see Fig. 1). He introduced G as the modulus of rigidity, μ as the Poisson's ratio, (u_x, u_y, u_z) as the displacements of the point (x, y, z) , r^2 as $x^2 + y^2 + z^2$, R_1 as the distance between (x, y, z) and $(0, 0, +c)$, and R_2 as the distance between (x, y, z) and $(0, 0, -c)$. He obtained³ the following expressions in the frame of an isotropic elastic approach:

(i) When the force P acts in the positive z direction

$$\langle u_x(x, y, z) \rangle = \langle u_y(x, y, z) \rangle = \frac{Pr}{16\pi G(1-\mu)} \left(\frac{z-c}{R_1^3} + \frac{(3-4\mu)(z-c)}{R_2^3} - \frac{4(1-\mu)(1-2\mu)}{R_2(R_2+z+c)} + \frac{6cz(z+c)}{R_2^5} \right), \quad (9)$$

$$\langle u_z(x, y, z) \rangle = \frac{P}{16\pi G(1-\mu)} \left(\frac{3-4\mu}{R_1} + \frac{8(1-\mu)^2 - (3-4\mu)}{R_2} + \frac{(z-c)^2}{R_1^3} + \frac{(3-4\mu)(z+c)^2 - 2cz}{R_2^3} + \frac{6cz(z+c)^2}{R_2^5} \right). \quad (10)$$

Combining the identities (1) and (8) gives for the correlation functions

$$\langle u_\sigma(x, y, z) u_\sigma(0, 0, c) \rangle = (1/\beta P) \langle u_\sigma(x, y, z) \rangle, \quad \sigma = x, y, z, \quad (11)$$

and these can now be evaluated with (9) and (10).

(ii) When the force P acts in the positive x direction

$$\langle u_x(x, y, z) \rangle = \frac{P}{16\pi G(1-\mu)} \left[\frac{3-4\mu}{R_1} + \frac{1}{R_2} + \frac{x^2}{R_1^3} + \frac{(3-4\mu)x^2}{R_2^3} + \frac{2cz}{R_2^3} \left(1 - \frac{3x^2}{R_2^2} \right) + \frac{4(1-\mu)(1-2\mu)}{R_2+z+c} \left(1 - \frac{x^2}{R_2(R_2+z+c)} \right) \right], \quad (12)$$

$$\langle u_y(x, y, z) \rangle = \frac{Pxy}{16\pi G(1-\mu)} \left(\frac{1}{R_1^3} + \frac{3-4\mu}{R_2^3} - \frac{6cz}{R_2^5} - \frac{4(1-\mu)(1-2\mu)}{R_2(R_2+z+c)^2} \right), \quad (13)$$

$$\langle u_z(x, y, z) \rangle = \frac{Px}{16\pi G(1-\mu)} \left(\frac{z-c}{R_1^3} + \frac{(3-4\mu)(z-c)}{R_2^3} - \frac{6cz(z+c)}{R_2^5} + \frac{4(1-\mu)(1-2\mu)}{R_2(R_2+z+c)} \right). \quad (14)$$

In the same way as above, the correlation function is

$$\langle u_\sigma(x, y, z) u_\sigma(0, 0, c) \rangle = (1/\beta P) \langle u_\sigma(x, y, z) \rangle, \quad \sigma = x, y, z. \quad (15)$$

Let us note that in the above expressions (9)–(15) we have two types of terms: first those that depend on the relative positions of the points (x, y, z) and $(0, 0, +c)$, second those that depend on the relative positions of the point (x, y, z) and of the image point $(0, 0, -c)$.

The first terms give the bulk contribution $\langle \vec{u}_2 \cdot \vec{u}_1 \rangle_B$ to the correlation functions. Let us note that $\langle \vec{u}_2 \cdot \vec{u}_1 \rangle_B$ diverge when $x=y=0$ and $z=c$, because the theory of elasticity is no longer valid in this atomic limit. However let us consider two points, for example, $(0, 0, c)$ and $(r_0, 0, c)$ with $r_0 \ll c$. From Eqs. (10) and (11), one obtains in this limit

$$\langle u_z(0, 0, c) u_z(r_0, 0, c) \rangle = \langle u_z(0, 0, c) u_z(r_0, 0, c) \rangle_B + \frac{8(1-\mu)^2 + 1}{32\pi(1-\mu)} \frac{k_B T}{Gc} + \dots, \quad (16)$$

where

$$\langle u_z(0, 0, c) u_z(r_0, 0, c) \rangle_B = \frac{1}{16\pi} \frac{3-4\mu}{1-\mu} \frac{k_B T}{Gr_0}, \quad (17)$$

and from the Eqs. (12) and (15)

$$\langle u_x(0, 0, c) u_x(r_0, 0, c) \rangle = \langle u_x(0, 0, c) u_x(r_0, 0, c) \rangle_B + \frac{7-12\mu+8\mu^2}{64\pi(1-\mu)} \frac{k_B T}{Gc}, \quad (18)$$

where

$$\langle u_x(0, 0, c) u_x(r_0, 0, c) \rangle_B = \frac{1}{4\pi} \frac{k_B T}{Gr_0}. \quad (19)$$

The bulk MSD are isotropic $\langle u_x^2 \rangle_B = \langle u_y^2 \rangle_B = \langle u_z^2 \rangle_B$. Owing to the invariance of the trace of the matrix $\langle u_\sigma(0, 0, c) u_\sigma(r_0, 0, c) \rangle$, we have to calculate the bulk mean-square displacements from

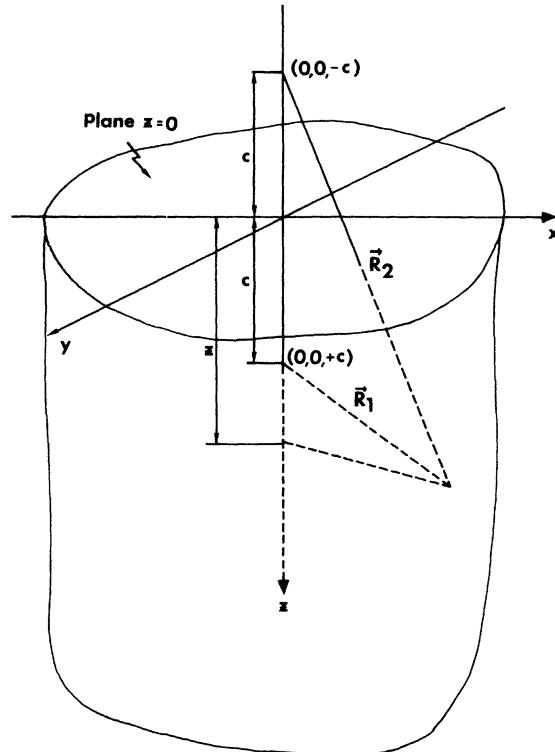


FIG. 1. Geometry and notation used in the text.

$$\langle u_{\sigma}^2 \rangle_B = \frac{2}{3} \langle u_z(0, 0, c) u_z(r_0, 0, c) \rangle_B + \frac{1}{3} \langle u_x(0, 0, c) u_x(r_0, 0, c) \rangle_B, \quad \sigma = x, y, \text{ or } z. \quad (20)$$

Using Eqs. (17) and (19), we have

$$\langle u_{\sigma}^2 \rangle_B = \frac{1}{24\pi} \frac{5 - 6\mu}{1 - \mu} \frac{k_B T}{G r_0}, \quad \sigma = x, y, z. \quad (21)$$

Let us remark that this result can also be obtained from the fundamental Kelvin solution⁴ for a force applied at a point in an infinite solid. Finally this bulk mean-square displacements can also be obtained in the Debye approximation

$$\langle u_{\sigma}^2 \rangle_B = (k_D/6\pi^2) (2/c_t^2 + 1/c_l^2) k_B T/\rho, \quad (22)$$

where c_t and c_l are, respectively, the transverse and longitudinal speeds of sound, ρ the mass density, and k_D the Debye cutoff for the propagation vector. This result is obtained by assuming the elasticity theory valid in the whole three-dimensional Brillouin zone. The summation on the wave vector \vec{k} is stopped at the cutoff $|\vec{k}| = k_D$ such that one has the right number of vibrational modes.

The modulus of rigidity G and the Poisson's ratio μ are related³ to the speeds of sound by

$$\mu = (c_l^2 - 2c_t^2)/2(c_l^2 + c_t^2), \quad (23)$$

$$G = \rho c_t^2, \quad (24)$$

and the Debye cutoff k_D can be related to the lattice parameter a by

$$\frac{4}{3} \pi k_D^3 = (2\pi/a)^3. \quad (25)$$

Using the above expressions, in order to compare Eqs. (21) and (22), one finds the order of magni-

tude of r_0 in function of k_D

$$r_0 = (\frac{1}{8} \pi)^{1/3} \frac{1}{2} a. \quad (26)$$

However our interest is not here in the bulk MSD but rather in the difference between them and the MSD of an atom situated in the vicinity of the surface. This difference is obtained from the Eqs. (16) and (18) to be

$$\langle u_z^2(0, 0, c) \rangle - \langle u_z^2 \rangle_B = \frac{8(1 - \mu)^2 + 1}{32\pi G(1 - \mu)} \frac{1}{c} + \dots, \quad (27)$$

$$\langle u_{\alpha}^2(0, 0, c) \rangle - \langle u_{\alpha}^2 \rangle_B = \frac{7 - 12\mu + 8\mu^2}{64\pi G(1 - \mu)} \frac{1}{c} + \dots, \quad \alpha = x, y. \quad (28)$$

These results are obtained here in the frame of elasticity theory, which, as noticed before,¹ can give only the term of order c^{-1} . We saw¹ that when the frequencies $\omega(k)$ are calculated to order k^2 rather than k , one obtains the second term of order c^{-3} in the expansions (27) and (28). That term gave¹ a correction of only 3%, even at the first layer under the surface. One can therefore expect the results (27) and (28) to be good within a few percent everywhere one or more layers below the surface.

We understand that some of our results have recently been derived in a different way.⁵

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