

A semi-infinite solid

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Abstract

The static relaxation of a semi-infinite solid is shown to imply a dilation, or an oscillatory behaviour, of the lattice parameter, on approaching the surface.

We consider a simple model of semi-infinite solid, extending over a half-space and consisting of parallel planes labeled by $n = 1, 2, \dots$. The distance between the planes n and $n + 1$ is denoted by $a + \xi_n$, and each plane is assumed to interact with its nearest and next-nearest neighbours by a potential Φ , which depends only on the distance between the planes. The potential Φ is a typical inter-atomic potential, like the Lennard-Jones potential for instance, consisting of a strongly repulsive short-range part and an attractive long-range tail. The energy of this solid can be written as

$$E = \sum_{n=1}^{\infty} [\Phi(a + \xi_n) + \Phi(2a + \xi_n + \xi_{n+1})] \quad , \quad (1)$$

and we ask how the lattice parameter varies with the depth from the surface, *i.e.* what is ξ_n as a function of n .

We assume that ξ_n is much smaller than a and expand the energy given by (1) in powers of ξ_n up to the second order; we obtain

$$\begin{aligned} E = & \sum_{n=1}^{\infty} [\Phi(a) + \Phi(2a)] + \xi_1 [\Phi'(a) + \Phi'(2a)] + \\ & \frac{1}{2} \xi_1^2 [\Phi''(a) + \Phi''(2a)] + \sum_{n=2}^{\infty} \xi_n [\Phi'(a) + 2\Phi'(2a)] + \\ & \sum_{n=1}^{\infty} \xi_n \xi_{n+1} \Phi''(2a) + \frac{1}{2} \sum_{n=2}^{\infty} \xi_n^2 [\Phi''(a) + 2\Phi''(2a)] \quad . \end{aligned} \quad (2)$$

The equilibrium conditions $\partial E / \partial \xi_n = 0$ give

$$\Phi'(a) + \Phi'(2a) + [\Phi''(a) + \Phi''(2a)] \xi_1 + \Phi''(2a) \xi_2 = 0 \quad , \quad (3)$$

and

$$\Phi'(a) + 2\Phi'(2a) + \Phi''(2a) \xi_{n-1} + [\Phi''(a) + 2\Phi''(2a)] \xi_n + \quad (4)$$

$$\Phi''(2a) \xi_{n+1} = 0, \quad n = 2, 3, \dots$$

For $n \rightarrow \infty$ the lattice parameter approaches that corresponding to an infinite solid, *i.e.* $\xi_n \rightarrow 0$; we get from (4)

$$\Phi'(a) + 2\Phi'(2a) = 0 \quad , \quad (5)$$

an equation which gives the parameter a . Introducing the notations $R = -\Phi''(a)/\Phi''(2a)$ and $A = -\Phi'(2a)/\Phi''(2a)$ equation (4) can be transcribed as

$$\xi_{n+1} - (R - 2)\xi_n + \xi_{n-1} = 0 \quad (6)$$

and the boundary condition (3) becomes

$$(R - 1)\xi_1 - \xi_2 = A \quad . \quad (7)$$

The solution to these equations is

$$\xi_n = \frac{A}{t + 1} t^n \quad , \quad (8)$$

where

$$t = \frac{1}{2} \left[R - 2 - \sqrt{R(R - 4)} \right] \in (0, 1) \quad (9)$$

for $R > 4$, and

$$t = \frac{1}{2} \left[R - 2 + \sqrt{R(R - 4)} \right] \in (-1, 0) \quad (10)$$

for $R < 0$.

The parameters R and A have always the same sign; indeed, $R/A = \Phi''(a)/\Phi'(2a)$, and from (5) we can see that a is always to the left of the minimum of the potential Φ , while $2a$ is on the right; hence, both $\Phi''(a)$ and $\Phi'(2a)$ have positive values, and $R/A > 0$. The solution (8) corresponding to (9) represents therefore a dilation of the solid near its surface, while ξ_n corresponding to the second case given by (10) represents a vanishing oscillation with $\xi_1 > 0$. As expected, there is no contraction of the solid near its surface.

The above solutions correspond indeed to a minimum of energy. Introducing ξ_n given by (5) into (2) we obtain, after some algebra,

$$E = \sum_{n=1}^{\infty} [\Phi(a) + \Phi(2a)] - \frac{1}{2} \Phi'(2a) \xi_1 \quad , \quad (11)$$

and one can see that this energy is indeed smaller than the energy corresponding to the undistorted solid ($\xi_1 = 0$); from (11) we can also define the bulk energy

$$E_b = N \cdot [\Phi(a) + \Phi(2a)] \quad , \quad (12)$$

where N is the number of planes, and the surface (or relaxation) energy

$$E_s = -\frac{1}{2} \Phi'(2a) \xi_1 \quad , \quad (13)$$

such that $E = E_b + E_s$. From (11) we can also estimate the energy needed to break an infinite solid into two halves; it is given by

$$\Delta = -[\Phi(a) + 2\Phi(2a)] + 2E_s \quad . \quad (14)$$

For convenience, we give here the parameters involved in this theory for the Lennard-Jones potential $\Phi(r) = r^{-12} - r^{-6}$. This potential has a minimum at $r = 1.122$ and a change of curvature at $r = 1.24$; from (5) we obtain the bulk lattice parameter $a = 1.120$. In addition $\Phi''(a) = 15$, $\Phi''(2a) = -0.06$, $\Phi'(2a) = 0.02$, such that $R = 233$ and $A = 0.33$; one can see that t is extremely small in this case ($t \sim 10^{-5}$), and ξ_n given by (8) vanishes extremely fast with increasing n ; therefore, a continuum approximation to the discrete equations (6) is not appropriate.

It is interesting perhaps to see what would the relaxation effect be, if observable, on the X-ray scattering by such a semi-infinite lattice. The intensity of the scattered X-ray can be written as

$$I \sim \left| \sum_{n=1}^{\infty} \int dx \delta(x - na - \xi_n) e^{iqx} \right|^2, \quad (15)$$

where q is the wavevector perpendicular to the surface of the lattice. Leaving aside the surface effects we can write approximately $\exp(iq\xi_n) = 1 + iq\xi_n$, since ξ_n is sufficiently small, and get, in the neighbourhood of any reciprocal vector $G = (2\pi/a) \cdot \text{integer}$,

$$I \sim N \cdot \delta(q - G) + q^2 \frac{f^2 t^2}{1 + t^2 - 2t \cos aq}, \quad (16)$$

where $f = A/(t + 1)$. It is easy to see that the shape of the Bragg peaks is distorted in an asymmetric way (except for the central peak $G = 0$), as if the lattice would undergo an apparent "contraction": indeed, the intensity is larger for $q^2 \geq G^2$ than for $q^2 \leq G^2$, in virtue of the fact that (16) is an increasing function of q^2 . Provided the effect is observable, this would create the illusion that G is slightly displaced toward larger values, *i.e.* the lattice parameter appears to diminish.

Finally, it is noteworthy to discuss the relaxation of a slab of finite thickness, *i.e.* consisting of a finite number of parallel planes. In this case ξ_n is a superposition of the n -th powers of the two solutions $t_{1,2}$ of equation (6), with $t_1 \cdot t_2 = 1$; the constants of this superposition are determined by the two boundary conditions, similar to (7), corresponding to the two surfaces of the slab. Apart from these computational details, the above results are qualitatively valid in the case of a slab, too.