Empirical repulsive potential:

An empirical repulsive potential is obtained using the experimental data for noble gases and has the form: $U_{repulsive} = \frac{B}{r^{12}}$, where B is a positive constant.

Lennard-Jones 6-12 potential:

The total potential energy of the two atoms separated by r is the sum of the attractive and repulsive potential and can be expressed as:

$$U(r) = 4\varepsilon[(\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6}],$$

where A and B are defined as $A = 4\varepsilon\sigma^{6}$ and $B = 4\varepsilon\sigma^{12}$. The parameters ε and σ are called the Lennard-Jones parameters and they depend on the polarizability and average dipole moment of an atom in addition to the extent of overlap. These are (ε and σ), in turn, a measure of the strength of the attraction and the radius of the repulsive core, as determined by fitting data in the gaseous state. Table 9 shows the values of these parameters for some noble gases. The values of ε indicates the very weak binding of the solidified noble gases. The plot of Lennard-Jones 6-12 potential is shown in figure 58. Also expressions for ε and σ can be written as: $\varepsilon = \frac{A^{2}}{4B}$ and $\sigma = (\frac{B}{A})^{1/6}$, respectively.

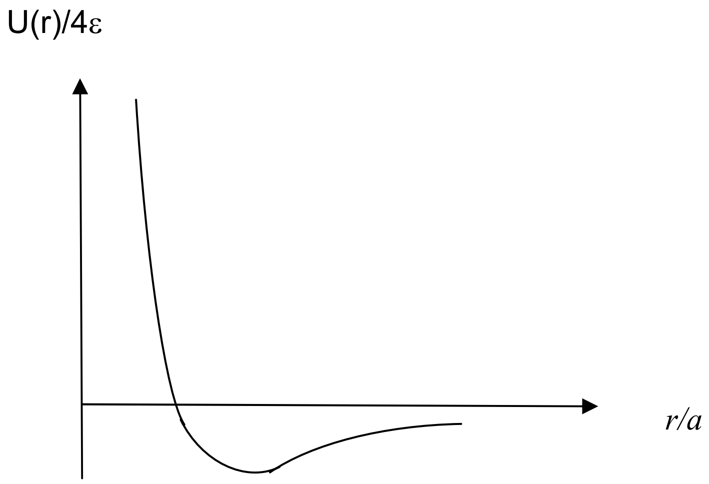

Figure 58: The Lennard-Jones 6-12 potential.

The total potential energy of the crystal:

Considering the atoms in the solid as a set of classical particles, localized with negligible kinetic energy at the points of the observed fcc Bravais lattice, the energy of interaction of the atom at the origin with all the others is $\sum_{\vec{R}\neq 0} U(\vec{R})$. When the total number of atoms in the crystal is N and avoiding to count the energy of a pair of atoms twice we get the total energy of the crystal as $U_{tot} = \frac{N}{2}\sum_{i\neq j} U(\vec{R}_{ij})$, where the sum is over all nonzero vectors in the fcc Bravais lattice. The magnitude of the Bravais lattice vector $\vec{R}_{ij}$ can be defined as the distance between an i^{th} atom and all other atoms j as $\left|\vec{R}_{ij}\right| = M_{ij} r$, where M_{ij} is a dimensionless number and r is considered here as the nearest-neighbor distance.

The total energy per particle may have the expression:

$$u = 2\varepsilon[\sum_{i\neq j}(\frac{1}{M_{ij}})^{12}(\frac{\sigma}{r})^{12} - \sum_{i\neq j}(\frac{1}{M_{ij}})^{6}(\frac{\sigma}{r})^{6}] \quad .$$

This can also be expressed as $u = 2\varepsilon[A_n(\frac{\sigma}{r})^n - A_m(\frac{\sigma}{r})^m]$ for $n > m$.

Notes:

1. $A_n = \sum_j \frac{1}{M_{ij}^n}$ or $A_m = \sum_j \frac{1}{M_{ij}^m}$ is the sum of the inverse n^{th} or m^{th} powers of the distance from a given Bravais lattice point to all others, where the unit of distance is taken to be the nearest neighbor distance. When n=12 , A_n is given to a tenth of a percent by the contributions from the nearest, next-nearest and third-nearest neighbors of the origin. The series $A_{12} = \sum_j \frac{1}{M_{ij}^{12}}$ converges to a value of 12.13 or almost 12. This represents the number of nearest neighbors in the fcc structure. However the second series $A_6 = \sum_j \frac{1}{M_{ij}^{6}}$ may converge to the value 14.45 which departs from 12. The values of A_n for other cubic structures are shown in table 10.
2. Thus it must be recalled that M_{ij} is considered equal one when $\vec{R}_{ij}$ is the Bravais lattice vector joining nearest neighbors and A_n is the number of nearest neighbors when n approaches infinity].

Table 10: The lattice sums A_n for the three cubic Bravais lattices.

n	Simple Cubic	Body-centered cubic	Face-centerd cubic
≤ 3	∞	∞	∞
4	16.53	22.64	25.34
5	10.38	14.76	16.97
6	8.40	12.25	14.45
7	7.47	11.05	13.36
8	6.95	10.36	12.80
9	6.63	9.89	12.49
10	6.43	9.56	12.31
11	6.29	9.31	12.20
12	6.2	9.11	12.13

Equilibrium density of the solid noble gases: (Equilibrium lattice constants)

The equilibrium nearest neighbor distance can be obtained when the total energy of the crystal (after neglecting the kinetic energy of noble atoms and considering only the cohesive energy of a noble gas as the Lennard-Jones potential) is minimized. Thus

$$\frac{\partial u}{\partial r} = -2\varepsilon[nA_n(\frac{\sigma^n}{r^{n+1}}) - mA_m(\frac{\sigma^m}{r^{m+1}})]$$

$$\therefore -2\varepsilon[nA_n(\frac{\sigma^n}{r^{n+1}}) - mA_m(\frac{\sigma^m}{r^{m+1}})] = 0$$

Put $n = 12$, $m = 6$ to get the expression for the nearest neighbor distance in equilibrium r$_o$ as: $r_\circ = (\frac{2A_{12}}{A_6})^{1/6}\sigma$

Substitute $A_{12} = 12.13$ and $A_6 = 14.45$ for fcc structure we have $r_o = 1.09\ \sigma$.

Note: This value or $r_o = 1.09\ \sigma$ is almost the same for all elements with fcc structures and is in agreement with the measured value, as seen in table 11. The slight departure of this value for the lighter atoms from the predicted universal value for noble gases may be attributed to an effect of the zero-point kinetic energy which has been neglected in the adopted approach. That is, energy increases when the volume of packing atoms gets smaller. The repulsive force becomes the dominant force which leads to an increase in the lattice constant far from the universal value.

Equilibrium cohesive energy of the solid noble gases:

The cohesive energy of the solid noble gases at absolute zero and at absolute pressure can be obtained when we substitute the equilibrium nearest neighbor distance, r_o, into the expression for the energy per particle: $u_\circ = -\frac{\varepsilon A_6^2}{2A_{12}}$. Again when we substitute $A_{12} = 12.13$ and $A_6 = 14.45$ for fcc structure we get $u_o = -8.6\varepsilon$. This value is the same for all noble gases when the atoms are considered at rest. Quantum-mechanical corrections must be made (because the calculation was conducted using elementary classical theory) to explain the small differences in the values of binding energies.

Table 11: Other information for solid noble gases:

Crystal	Nearest neighbor distance r_o (Experiment) ($\overset{\circ}{A}$)	Nearest neighbor distance r_o (Theory) ($\overset{\circ}{A}$)	Experime-ntal Cohesive energy u_o (eV/atom)	Theoretical Cohesive energy u_o (eV/atom)	Bulk Modulus B_o (Expt.) (10^{10}dyne/ cm^2)	Bulk Modulus B_o (Theory) (10^{10}dyne/ cm^2)
Ne	3.13	2.99	-0.02	-0.027	1.1	1.81
Ar	3.76	3.71	-0.08	-0.089	2.7	3.18
Kr	3.99	3.98	-0.11	-0.12	3.5	3.46
Xe	4.33	4.34	-0.17	-0.172	3.6	3.81

Equilibrium bulk modulus of the solid noble gases:

The bulk modulus is defined by: $B = -V(\frac{\partial P}{\partial V})_T$. We know that the pressure at T=0 may be given by $P = -\frac{dU}{dV}$, where U is the total energy. We can express the bulk modulus using the above relations, as follows: $B = V\frac{\partial}{\partial V}(\frac{\partial U}{\partial V})$

Also from the definition of the energy per particle as $u=\frac{U}{N}$, and the volume per particle $v=\frac{V}{N}$, the bulk modulus is rewritten as:

$$B=v\frac{\partial}{\partial v}(\frac{\partial u}{\partial v})=v\frac{\partial^2 u}{\partial v^2}.$$

Using the chain rule we can show that $B=\frac{v}{(\frac{\partial v}{\partial r})^2}\frac{\partial^2 u}{\partial r^2}$.

Note: The isothermal compressibility κ of solids is defined as the inverse of the bulk modulus and has the units in SI system as m^2N^{-1}.

Example: Show that the bulk modulus at zero temperature for the solid fcc (noble gases) structure can be written in terms of ε and σ as: $B_\circ=\frac{75\varepsilon}{\sigma^3}$.

Solution:

To use the expression $B=\frac{v}{(\frac{\partial v}{\partial r})^2}\frac{\partial^2 u}{\partial r^2}$, we know that $v=\frac{a^3}{4}=\frac{r^3}{\sqrt{2}}$, and $(\frac{\partial v}{\partial r})^2=\frac{9r^4}{2}$. Thus the bulk modulus can be obtained at equilibrium when $r=r_o$ and has the expression: $B_\circ=\frac{\sqrt{2}}{9r_\circ}\left.\frac{\partial^2 u}{\partial r^2}\right|_{r=r_o}$.

Now you need to find $\left.\frac{\partial^2 u}{\partial r^2}\right|_{r=r_o}$. Take the second derivative of $\frac{\partial^2 u}{\partial r^2}=2\varepsilon[n(n+1)A_n(\frac{\sigma^n}{r^{n+2}})-m(m+1)A_m(\frac{\sigma^m}{r^{m+2}})]$ and put n=12. m=6 and $r=r_o$ and r_o=1.09 σ for fcc structure you may find that $\left.\frac{\partial^2 u}{\partial r^2}\right|_{r=r_o} = 523.7\frac{\varepsilon}{\sigma^2}$. Finally this will give us $B_{\circ} = \frac{75\varepsilon}{\sigma^3}$ as requested. (See table 11 for comparing bulk modulus for different solid noble gases).