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INVESTIGATION OF SOLID ARGON CRYSTAL BY MEANS OF ISOBARIC-ISOENTHALPIC MOLECULAR DYNAMICS METHOD

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ABSTRACT

Structural properties of solid argon crystal containing 256 atoms have been investigated using a molecular dynamics calculation method which allows for both changes of the molecular dynamics cell size and shape. The Lennard-Jones potential energy function has been chosen as interatomic interactions potential and equations of motion of the system have been solved by computer using the Verlet algorithm. It has been found that the lattice parameter is ~5.3 Å, the volume coefficient of thermal expansion is $b = 1.38 \times 10^{-3}\ K^{-1}$ at zero pressure, the bulk modulus is 3.53 GPa at 10 K and the total configurational energy is -0.082 eV/atom at zero pressure and 10 K. The results are consistent with literature values.

ÖZET

Moleküler dinamik hücresinin hacim ve şekil değişimine izin veren bir moleküler dinamik hesaplama yöntemi kullanılarak 256 atomlu katı argon kristalinin yapısal özellikleri incelenmiştir. Atomlararası etkileşme potansiyeli olarak Lennard-Jones potansiyel enerji fonksiyonu seçilmiş ve sistemin hareket denklemleri Verlet algoritması kullanılarak bilgisayarla çözülmüştür. Hesaplamalar sonucunda örgü parametresi ~5.3 Å, sıfır basınçta hacimsel termal genleşme katsayısı b =1.38x$10^{-3}K^{-1}$, 10 K sıcaklıkta hacim modülü 3.53 GPa ve potansiyel enerji -0.082 eV/atom olarak bulunmuştur. Sonuçlar literatür ile uyumludur.

INTRODUCTION

Molecular dynamics simulation is powerful tool which has been used for many years to study the structural and dynamical properties of condensed matter systems [1-3]. In the study of solids, applications have been made in elastic constants for a crystalline system in equilibrium [4], epitaxial crystal growth from the melt [5], quenched liquids [6], and polymorphic transitions in single crystals [7]. Another area where Molecular Dynamics (MD) and Monte Carlo simulations have made significant contributions is thermodynamics properties of materials. The basic input to the MD simulation technique is knowledge about the interatomic potential energy function among particles in the system under study.

Andersen has introduced a method of carrying out molecular dynamics calculations allowing the volume of a cubic MD cell to vary [8]. The statistical ensemble associated with Andersen's treatment, is the isoenthalpic-isobaric or (NPH) ensemble (H system's enthalpy, P pressure, and N number of particles). Parrinello and Rahman (PR) subsequently extended the method to allow for changes of the MD cell shape [9]. Therefore, PR theory allows the anisotropic volume changes as well as isotropic volume changes but in isotropic case the theory does not give the same results of Andersen theory because of a used arbitrary parameter (W) which has dimension of mass. Although this problem has been solved by Ray [10], but in anisotropic case the physical interpretation of Ray's equation does not appear to be easy. The values of W have no influence on the evaluation of static properties, since in a classical system the equilibrium properties do not depend on the mass of the constituents.

An important feature of the PR theory is that it may be used to study solid-solid structural transformations as a function of temperature, external pressure, and potential energy function of the system. A number of recent papers apply the PR theory to such studies [11-13]. In the present study, the PR theory has been used to investigate the structural properties of solid argon crystal of 256 atoms at the 0-231 MPa pressure and 5-75 K temperature.

METHOD

Classical MD calculation method consists of numerical solutions of Newton's equations of motion obtained from Lagrangian or Hamiltonian functions written for a statistical mechanical system. Coordinates, velocities and masses of particles are represented by $\mathbf{r}_i$, $\dot{\mathbf{r}}_i$, and m_i, respectively, in a statistical ensemble which has N particles, i = 1, 2,...,N. If interatomic interaction is defined by a PEF like $f(r_{ij})$, total configurational energy of the system will be

$$V_N = \frac{1}{2}\sum_{i\neq j}\phi(r_{ij}) \qquad (1)$$

where $r_{ij} = |\mathbf{r}_{ij}| = |\mathbf{r}_i - \mathbf{r}_j|$. The equation of motion of the system is also obtained from (1);

$$m_i\ddot{\mathbf{r}}_i = \sum_{j\neq i}\frac{d\phi(r_{ij})}{dr_{ij}}\hat{\mathbf{r}}_{ij} \qquad (2)$$

This equation of motion is solved using any of the algorithms that have been successfully applied to second-order differential equations [14-19].

In the PR theory the position vectors of the particles in the MD cell, $\mathbf{r}_i$ (i = 1,...,N), are described in terms of scaled coordinates,

$$\mathbf{s}_i = (x, h, z) \quad \text{with} \quad 0 \pounds x, h, z \pounds 1 \quad ,$$

$$\mathbf{r}_i = \mathbf{a}x + \mathbf{b}h + \mathbf{c}z \tag{3}$$

where **a**, **b**, and **c** are three time-dependent vectors which span the MD cell. Defining the matrix **h** (**a**, **b**, **c**), whose columns are given by the components of the vectors **a**, **b**, and **c**. Hence, the position of the particle i is rewritten as

$$\mathbf{h} = \begin{pmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{pmatrix} ,$$

$$\mathbf{r}_i = \mathbf{h}\mathbf{s}_{i.} \; . \tag{4}$$

Square of distance between particles i and j is found as follows depending on the $\mathbf{G} = \mathbf{h}\text{¢}\mathbf{h}$ metric tensor;

$$r_{ij}^2 = \mathbf{s}_{ij}\text{¢}\, \mathbf{G}\, \mathbf{s}_{ij} \tag{5}$$

where prime mark means transpose of a vector or tensor. Therefore, Lagrangian function of a MD cell (NPH) is obtained as follows [9];

$$L = \frac{1}{2}\sum_i m_i \dot{s}_i' \,\mathbf{G}\, \dot{\mathbf{s}}_i - \sum_i \sum_{j>i} \phi(r_{ij}) + \frac{1}{2} W \mathrm{Tr}(\dot{\mathbf{h}}'\dot{\mathbf{h}}) - P_{ext} V \tag{6}$$

where W is an arbitrary constant which has the dimension of mass, P_{ext} denotes the externally applied hydrostatic pressure, and V is the volume of the MD cell, V = det**h**. Equations of motion of the particles and the MD cell is obtained as follows from the Lagrangian of the system;

$$\ddot{\mathbf{s}}_i = -\sum_{j\neq i} m_i^{-1} \frac{d\phi(r_{ij})}{r_{ij}\, dr_{ij}}(\mathbf{s}_i - \mathbf{s}_j) - \mathbf{G}^{-1}\dot{\mathbf{G}}\dot{\mathbf{s}}_i \ , \qquad i = 1, \ldots, N \tag{7}$$

$$\ddot{\mathbf{h}} = W^{-1}(\pi - P_{ext})\mathbf{A} \tag{8}$$

where $\mathbf{A} \equiv V\mathbf{h}'^{-1}$ and **p** is microscopic stress tensor which is a dyadic given as follows;

$$\pi = V^{-1}\left[\sum_i m_i \mathbf{v}_i \mathbf{v}_i - \sum_i \sum_{j>i} \frac{d\phi(r_{ij})}{r_{ij}\, dr_{ij}} \mathbf{r}_{ij}\mathbf{r}_{ij}\right] \tag{9}$$

The forces on the particles were derived from Lennard-Jones interaction potential,

$$f(r_{ij}) = 4\, e\, [(s/r_{ij})^{12} - (s/r_{ij})^{6}]\ . \tag{10}$$

The parameters used for argon in the present study are as follows; unit length s = 3.405 Å, unit energy e = 165.3×10^{-16} erg , unit mass m_{Ar} = 6.63382×10^{-23} g , and the time unit t = $s(m/e)^{1/2}$ = 2.16 ps. Arbitrary mass parameter of the system was chosen as W = $2m_{Ar}$. For computer programming, reduced parameters without dimension were used and these parameters carrying asterisks (*) are different from others. In this case, reduced parameters are as follows; length **r*** = **r**/s, temperature T* = Tk_B/e

and pressure $P^* = Ps^3/e$ (~ 41.88 MPa). Numerical integration of the equations of motion given at equations (7) and (8) were carried out using the Verlet algorithm [14], and to ensure a reasonable numerical stability the integration time step is taken to be $Dt = 0.01t$ or 21.6 fs. In order to reduce the computer time, a cutoff radius of $r_c = 8.5$ Å was applied to the potential energy function.

The structural behavior of the system for 5-75 K temperature interval was examined at the following order; (i) The argon crystal of 256 atoms was prepared in an fcc structure. The MD cell was a cube of edge length 23.83 Å and as usual, the periodic boundary condition was adopted. (ii) Initial velocities of particles were obtained by means of Maxwell's velocity distribution which is consistent with T = 5 K, initial rate of the shape changes (**h**/ t) was taken as zero, and the system was equilibrated for a period of 500 time steps (or MD steps) at zero pressure. The system was then followed for a further 2000 time steps in order to accumulate statistical information. (iii) Starting from the final configuration of the each run the temperature was increased up to 75 K in 10° increments, while holding the pressure constant. 2500 time steps were accrued between temperature changes and the physical quantities (i.e., volume of the unit cell, lattice parameter, configurational energy per atom, the mean displacement of an atoms group near the MD cell center, and the internal pressure) were calculated at the each time step. Then, time averages of these quantities over the last 2000 time steps were found at each temperature.

The structural behavior of the system at 0-231 MPa pressure interval was examined at the following order; (a) the above mentioned items (i) and (ii) was repeated taking T = 10 K . (b) The pressure was increased up to 231 MPa in 21 MPa increments, under constant temperature. 2500 time steps were accrued between pressure changes and the physical quantities were calculated at the each step in last 2000 time steps. Then, time averages of the calculated quantities over the last 2000 time steps were found at each pressure.

RESULTS AND DISCUSSION

Time evolution of the volume, the lattice parameter, the configurational energy, the mean displacement of the atom group, and the internal pressure calculated from the virial theorem can be seen from Figure 1(a-d), for zero external pressure. As seen from Figure 1(a and b), fluctuations on the volume and the lattice parameter are increased at high temperatures. The abnormal fluctuations in the lattice parameter must be taken into account together with variation of angles among lattice axes because of the changes of the MD cell shape. Therefore, the lattice deformation occurring at high temperatures can be examined in detail. The changes of configurational energy with time at each run of different temperatures are shown in Figure 1(c). Due to the increases of the atomic displacements at higher temperatures the amplitude of the fluctuations on the energy is increases (Figure 1d). Real-space atomic locations and time evolution of the atomic coordinates on the (100) plane of the MD cell can be seen in Figure 2(a-d) for various temperatures. The increases of atomic displacements at high temperatures were also seen from this figure. The values of the internal pressure at every ten time step have been given in Figure 1(e). It is observed from this figure that time average of the pressure over the full scale of time is nearly zero. The instantaneous pressure increases on the time evolution of the internal pressure are due to the rapid temperature increments. Then, a quick relaxation to nearly zero are seen, so that mechanical equilibrium is conserved.

The time averages over the last 2000 time steps at each run of different temperature and literature values of the above mentioned quantities were tabulated in Table I. The volume coefficient of thermal expansion calculated for 25 and 55 K temperatures, $b = V^{-1} (\ V/\ T)$, was about 1.38×10^{-3} K^{-1} for the zero pressure MD results in Table I, which was 33 percent larger than the value of 1.04×10^{-3} K^{-1} calculated from the literature values in Table I. The discrepancy between the calculated and literature values is large. This discrepancy is because the Lennard-Jones potential parameters were estimated and widely used for argon in liquid phase or near the melting point (T £ 83.3 K), secondly because the calculations in here are predicting zero pressure value in contrast to experimental value at atmospheric pressure, and thirdly because the potential energy function was vanished at the used cutoff radius r_c.

As seen from Figure 2(a) for 5 K, atoms are rather at constant sites and show very small displacements. When temperature reaches at 35 K, atomic displacements are smaller than $r_o/10$, where r_o is the distance between the nearest atoms, and it is observed that stable structure is conserved (see Figure 2(b)). It is also observed that atomic displacements are around $r_o/10$ at 65 K and bigger than $r_o/10$ value at 75 K as seen from Figures 2(c) and (d), respectively. This also can be seen at the places indicated by arrows in Figure 1(d). These results indicate that lattice softening and unstable behaviour begins. After this temperature the anharmonic phenomena are play an important role on the lattice stability [20].

Time evolution of the volume, the lattice parameter, the configurational energy, the mean displacement, the temperature of the system calculated from equipartition theorem, and the pressure which is externally applied on the system are shown in Figure 3(a-f). It should be noted that the volume of the unit cell and the lattice parameter responds very rapidly to the change in external pressure. The configurational energy per atom decreases initially up to its minimum value, and then increases, as seen from Figure 3(d), because the repulsive interactions between the atoms are dominated.

Table I. Time averages of the lattice parameter, volume of the unit cell and configurational energy per atom for each run of different temperature and zero pressure, and literature values which are obtained from the plot of the lattice parameter versus temperature at nearly atmospheric pressure (Fig. 13 in Ref. 21, p.143).

	Lattice Parameter (Å)		Volume (Å^3)		Energy (eV/atom)	
T (K)	Calc.	Literature	Calc.	Literature	Calc.	Literature
0						-0.080 [21]
5	5.287	5.300 [21]	147.7	148.8 [21]	-0.0828	--
15	5.311	5.305 "	149.5	149.3 "	-0.0811	--
25	5.338	5.315 "	151.9	150.1 "	-0.0794	--
35	5.364	5.328 "	154.3	151.2 "	-0.0776	--
45	5.394	5.345 "	156.8	152.7 "	-0.0758	--
55	5.427	5.368 "	158.2	154.8 "	-0.0739	--
65	5.465	5.390 "	163.1	156.6 "	-0.0718	--
75	5.512	5.430 "	167.2	160.1 "	-0.0695	--

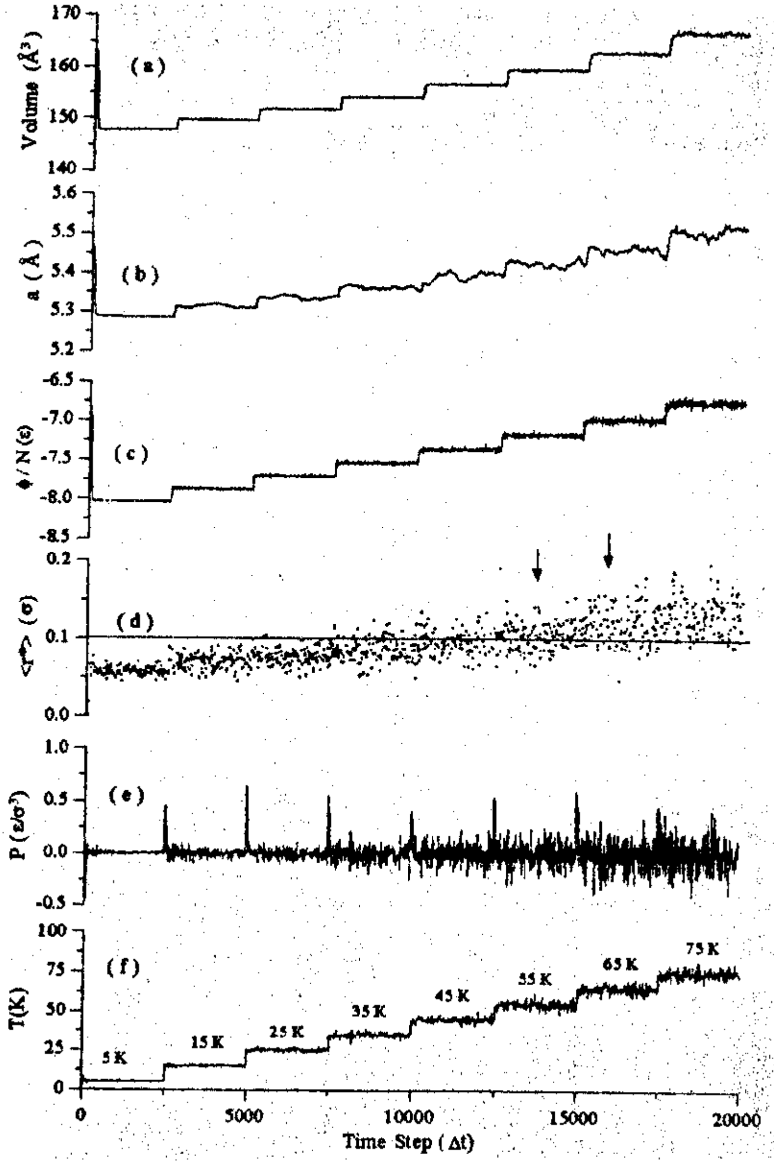
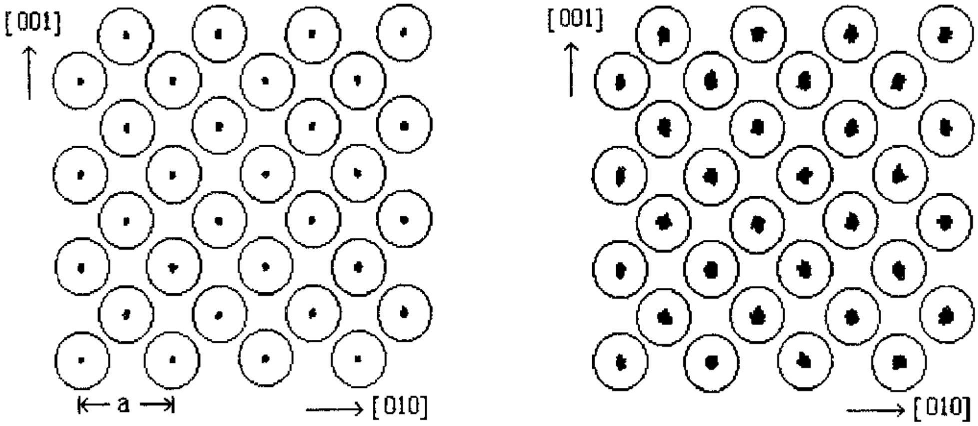
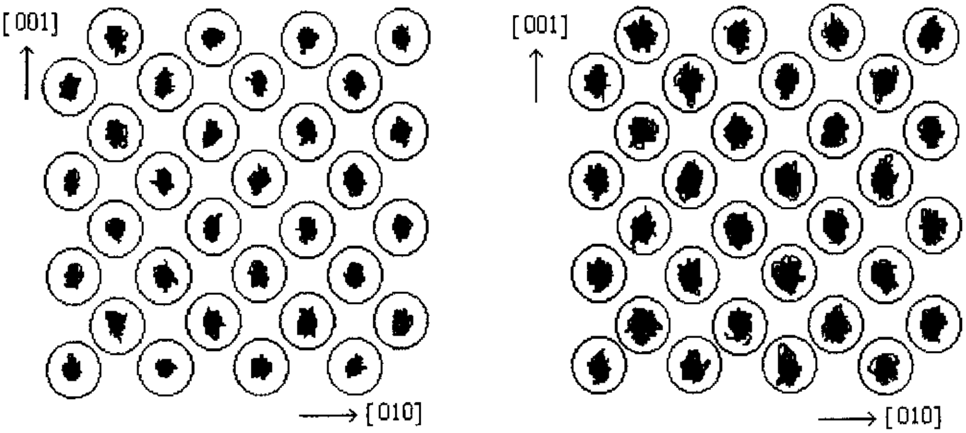


Figure 1. Time evolution of (a) the unit cell volume, (b) lattice parameter, (c) configurational energy per atom, (d) the mean displacement of atoms, (e) the reduced internal pressure calculated from Eq. (9) and (f) the temperature of the system which was increased in 10° increments at every 2500 time step. The arrows on the plots of the mean displacement indicate the regions of the strongly anharmonic behaviour begin.



(a) 5 K (b) 25 K



(c) 55 K (d) 75 K

Figure 2. Real-space atomic locations and time evolution of the atomic coordinates on the (100) plane at zero external pressure and four different temperatures. a is the lattice parameter.

Time averages of the quantities changed depending on pressure are given in Table II. However, the literature values of this work have not found. Using the pressure and the volume given in Table II, the isothermal bulk modulus, $B_m = -V(\partial P/\partial V)$, and compressibility, $k = 1/B_m$, of argon at 10 K were found to be 3.53 GPa and 0.28 GPa^{-1}, respectively. Experimental values of these parameters for 77 K are also as follow; Bm = 1.6 GPa and k = 0.94 GPa^{-1} [21], and Bm = 1.66 GPa and k = 0.6 GPa^{-1} [20]. If the temperature difference between the calculations and the literature taken into account, the bulk modulus and compressibility were calculated with an error as in the calculation of the thermal expansion coefficient, because the bulk modulus of a solid decreases with increasing temperature.

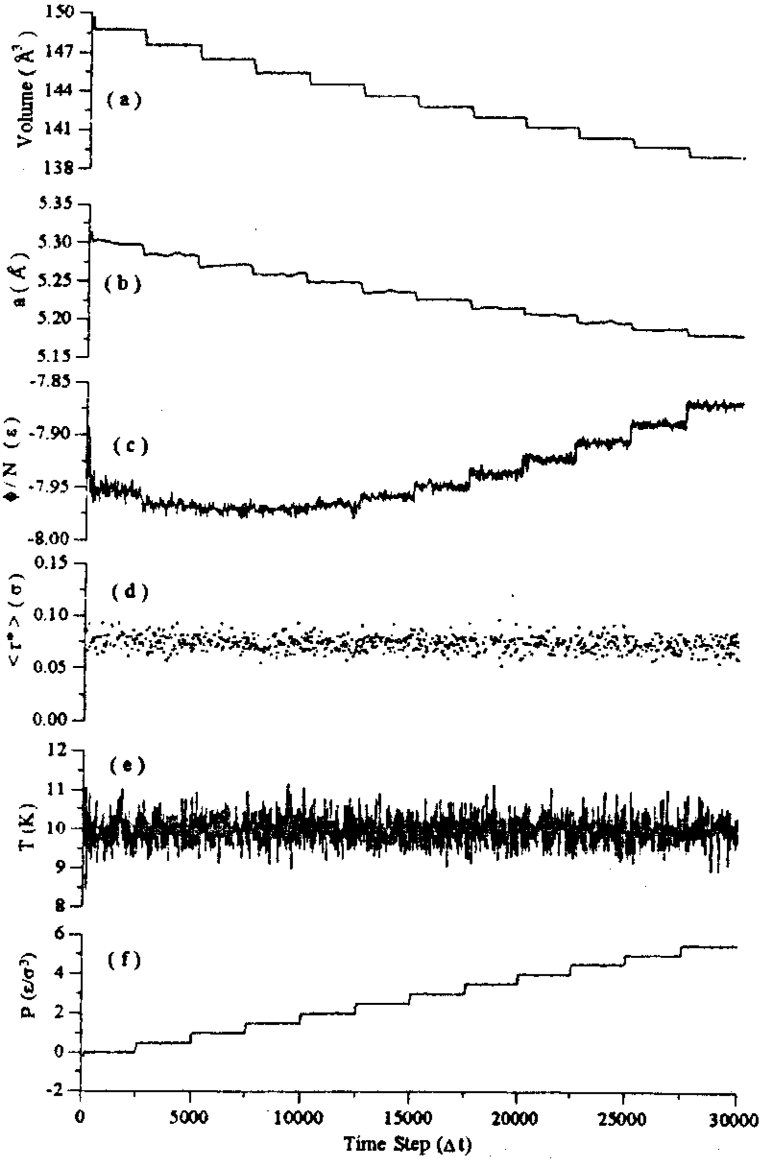


Figure 3. Time evolution of (a) the volume, (b) the lattice parameter, (c) the reduced configurational energy per atom, (d) the mean displacement of atoms, (e) fluctuations of temperature of the system and (f) the externally applied pressure on the system which was increased in 0.5P* (or 21 MPa) increments at every 2500 time step (f).

Table II. Time averages of the lattice parameter, volume of the unit cell, and configurational energy per atom for each run of different pressure at 10 K constant temperature. The literature values of this work have not been found.

Pressure, P (MPa)	Lattice Par., a (Å)	Unit Cell Volume, V (Å^3)	Potential Energy, f/N (eV/atom)
0	5.299	148.8	-0.0820
21	5.284	147.6	-0.0822
42	5.271	146.5	-0.0823
63	5.259	145.5	-0.0822
84	5.249	144.6	-0.0821
105	5.237	143.7	-0.0821
126	5.227	142.8	-0.0820
147	5.216	142.0	-0.0818
168	5.207	141.3	-0.0817
189	5.198	140.5	-0.0815
210	5.189	139.8	-0.0814
231	5.182	139.2	-0.0812

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