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Size-Dependent Variations In Thermodynamic And Mechanical Properties Of Nanosolids

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Nanosolids differ significantly from bulk materials in terms of their size-dependent characteristics, which has piqued a lot of interest in studying these materials. This research examines the mechanical and thermodynamic characteristics of nanosolids as a function of size utilizing theoretical models, mainly the W.H. Qi model. The Qi model, which finds a relationship between the total atomic number and the number of surface atoms, is used to assess the melting temperature fluctuation of nanosolids, such as nanoparticles, nanowires, and nanofilms. The results show that the melting point drops dramatically when the particle size drops because the surface-to-volume ratio increases. In addition, two methods for calculating the Young's modulus of nanosolids are used: Qi's model and Patel's formulation. The results show that the Young's modulus increases as the size of the material increases, which is explained by the stronger interatomic forces present at the nanoscale. Compared to Patil's Lindemann-based criteria, Patel's liquid-drop model is better in line with experimental results. Research like this is essential for fields like nanotechnology and materials science because it sheds light on how nanosolids behave.

Keywords: Nanosolid, Melting point, Young Modulus, Thermodynamic, Size.

I. INTRODUCTION

The characteristics of nanosolids, which are solid-state materials with dimensions on the nanoscale scale, are distinctive and interesting, and they differ greatly from those of bulk materials. A combination of elements, including as an enhanced surface-to-volume ratio, changed atomic bonding, and quantum confinement effects, gives birth to these different features. The study of nanosolids has become incredibly important in the last several decades because of all the different areas where they may be used, including energy storage, biomedical engineering, microelectronics, and catalysis. Nanoscale material property manipulation has paved the way for new fields of study and innovations in technology.

The high surface-to-volume ratio is a defining feature of nanosolids and an important factor in the physical and chemical properties of these materials. The surface atomic number is tiny in comparison to the overall atomic number in bulk materials. On the other hand, nanosolids have changed mechanical behavior, electrical characteristics, and reactivity because a large percentage of their atoms are surface-bound. As a consequence of their high surface energy,

these materials frequently have different optical characteristics, higher catalytic activity, and lower melting temperatures than their bulk equivalents.

The quantum confinement effect is another important factor in how nanosolids behave. As a material's dimensions shrink to the nanoscale, its electrical and optical characteristics alter because electron mobility is limited to discrete energy levels. Bandgap tuning in semiconductor nanostructures is made possible by adjusting the size of nanowires or nanoparticles, and this phenomenon is most noticeable in these contexts. Quantum dots in display technology and photovoltaic cells in solar energy are two examples of optoelectronic systems that can benefit greatly from this kind of tunability.

Because of the higher surface tension and decreased coordination numbers, the atomic bonding in nanosolids is also changed. Stable bonding arrangements are the outcome of the large number of nearby atoms in bulk materials. However, unfulfilled bonding and surface reconstructions result from the lower number of nearby atoms at the surface in nanosolids. Nanosolids operate differently than bulk solids due to these factors, which impact mechanical qualities including hardness, elasticity, and fracture toughness. Surface strain effects can make nanosolids more rigid and strong in some situations, while decreased stability can make them more malleable and pliable in others.

Because nanoparticles improve catalytic effectiveness due to their high surface area and enhanced reactivity, research into nanosolids is of paramount importance in the domain of catalysis. Many chemical processes rely on nano-catalysts, such as those that produce hydrogen, decrease carbon dioxide, or clean up polluted environments. Scientists have developed extremely effective and selective catalysts for a variety of industrial applications by altering the size, shape, and composition of nanoparticles. This allows for the tailoring of surface characteristics. Nanostructured materials have been thoroughly investigated for use in fuel cells, batteries, and supercapacitors; nanosolids, in particular, play an important role in this field.

Drug delivery, imaging, and therapeutic interventions are three areas where nanosolids have made great strides in biomedical applications. Improving treatment effectiveness and lowering adverse effects can be achieved by engineering nanoparticles to transport therapeutic molecules to particular sites within the body. Furthermore, new nanomaterials like quantum dots are being created for use in bioimaging, which will allow for medical diagnostics with high-resolution imaging. Nanosolids' regulated interactions with biological systems and biocompatibility pave the way for novel avenues in individualized healthcare and cutting-edge medical technology.

With the creation of nanoscale transistors, sensors, and memory storage devices, nanosolids are transforming device performance in the realm of electronics and microelectronics. Nanomaterials have allowed electrical components to be miniaturized, resulting in devices with more capacity, efficiency, and speed. Researchers are looking at two-dimensional materials like graphene and carbon nanotubes because they have better electrical and mechanical qualities than standard technologies that rely on silicon.

Nanosolids have many potential benefits, but there are still obstacles to overcome in terms of their stability, integration with current technologies, and large-scale synthesis. Chemical vapor deposition, sol-gel synthesis, molecular self-assembly, and other sophisticated methods are still needed to controllably fabricate nanosolids with exact size, shape, and composition. Also, to make sure nanosolids are safe to utilize in different ways, we need to figure out what effects they may have on people's health and the environment.

Thermodynamic Properties of Nanosolids

The high surface-to-volume ratio and quantum confinement effects of nanomaterials cause them to display unique thermodynamic features when contrasted with bulk materials. Nanoscale dimensions have a major impact on several important thermodynamic parameters, including thermal conductivity, entropy fluctuations, melting point depression, specific heat capacity, and specific heat capacity. Nanosolids' stability, reactivity, and possible uses in areas like thermal management, energy storage, and catalysis are all heavily influenced by these characteristics.

1. Melting Point Depression

Melting point depression, in which a material's melting point drops as its particle size drops, is one of the best-documented size-dependent phenomena in nanosolids. A large number of atoms occupying the nanoparticles' surface is the primary cause of this phenomenon. Due to their lower coordination numbers, surface atoms suffer lesser bonding interactions compared to bulk atoms, which are surrounded by a complete coordination shell. Therefore, less heat is needed to change the phase of these atoms from solid to liquid. The Gibbs-Thomson equation, which quantifies the link between particle size and melting point depression, describes the melting temperature as a function of the nanoparticle radius. This equation emphasizes that the melting point decreases as the particle size decreases, implying that smaller nanoparticles have a more noticeable effect on the melting point.

Due to their unsaturated bonds and enhanced surface energy, surface atoms have a larger Gibbs free energy from an energetic perspective. The melting point of a nanoparticle is reduced because less energy is needed to disturb the atoms on its surface when it is heated. Atomic bonding strength, surface energy, and other material parameters determine the degree to which the melting point is lowered. A good example is the dramatic decrease in melting point observed at the nanoscale for metals such as gold and silver. For example, gold nanoparticles melt at temperatures hundreds of degrees lower than bulk gold. Research into phase transitions, sintering, and nanoparticle production are just a few areas that might benefit from understanding melting point depression.

2. Specific Heat Capacity and Entropy

At the nanoscale, specific heat capacity also varies dramatically, which is a crucial thermodynamic parameter. When compared to bulk solids, nanosolids often have a higher specific heat capacity. The changes in the density of states at smaller dimensions and greater

phonon surface scattering are responsible for this increase. Phonons, which are quantized vibrations of the lattice that transfer heat energy, control the heat capacity of bulk materials. Because of their diminutive size, phonons scatter more readily at surfaces and grain boundaries at the nanoscale, which changes the methods by which heat is transported. The energy distribution across vibrational modes varies when phonons undergo more frequent scattering, which in turn modifies their heat capacity. Materials having strong phonon interactions that rely on size, such ceramics and semiconductors, exhibit this phenomenon to a greater extent.

Furthermore, nanoscale behavior may be understood by applying the Debye model or the Einstein model of heat capacity. Disturbances in heat capacity result from nanoscale fluctuations in the Debye temperature, which describes phonon vibrations. Because they are distinct from vibrations in the bulk, surface phonon modes contribute even more to the specific heat. Quantum confinement effects also play a major role in thermal energy storage and transmission when particle sizes get smaller.

3. Thermal Conductivity

One of the most important properties of materials that controls heat transmission is their thermal conductivity, which is much lower in nanosolids than in bulk materials. Restricting heat flow at the nanoscale, phonon-boundary scattering is the primary cause of this decrease. Phonons in bulk materials are able to efficiently transport heat because they travel great distances before they encounter scattering processes. However, the total thermal conductivity is reduced in nanostructures due to the fact that enhanced boundary interactions shorter phonon means free pathways. Nanowires, nanotubes, and thin films are examples of low-dimensional nanostructures where the heat conductivity decreases as a function of size. The efficiency of heat transmission is reduced in these materials because phonons experience increased boundary scattering. One example is the development of silicon nanowires with extremely low heat conductivity, which makes them a promising material for thermoelectric devices.

An electrical voltage may be generated by a temperature gradient—the See-beck effect—and this is the basis for thermoelectric materials. A material's electrical conductivity, thermal conductivity, and See-beck coefficient are the three variables that make up its figure of merit (ZT), which in turn determines the efficiency of thermoelectric materials. Nanostructured materials improve thermoelectric efficiency by lowering heat conductivity while keeping electrical conductivity constant. Thermoelectric generators, systems for recovering heat from waste, and energy-efficient cooling equipment have all benefited greatly from this. In addition, changes in thermal conductivity at the nanoscale affect microchip heat dissipation, thermal insulation coatings, and electrical devices. Minimizing heat accumulation is of the utmost importance in semiconductor technology for preserving the performance and lifetime of devices. To maximize heat dissipation, scientists create high-performance transistors, heat sinks, and nanoscale heat spreaders by manipulating the thermal transport parameters at the nanoscale.

Mechanical Properties of Nanosolids

1. Young's Modulus and Elasticity

A material's stiffness, Young's modulus, changes dramatically at the nanoscale. One reason for size-dependent elasticity is the impact of surface tension and changed interatomic interactions. Surface strain effects cause certain nanosolids to be stiffer than others, whereas atomic bond relaxation causes a decrease in Young's modulus in other nanosolids.

For example, research on silicon nanowires has shown that their stiffness and softness are affected by their diameter and surface passivation. The development of nanoscale mechanical systems and flexible electronics relies on an understanding of these variances.

2 Hardness and Plasticity

As grain size decreases in nanocrystalline materials, the hardness of the material, which is defined as the resistance of the material to deformation, typically advances. On the other hand, hardness diminishes owing to grain boundary sliding and dislocation annihilation when grain sizes are exceedingly tiny (below a critical limit). This phenomenon is known as an inverse Hall-Petch effect. Wear-resistant coatings and nanostructured metals, which are utilized in high-strength applications, are applications that are impacted by this phenomenon.

3. Fracture Toughness and Deformation Mechanisms

In comparison to bulk materials, nanosolids exhibit deformation tendencies that are exclusive to themselves. Conventional fracture processes, such as crack propagation by dislocation motion, are effectively prevented at the nanoscale. In its place, phenomena such as surface diffusion and dislocation starvation establish themselves as the dominating ones.

Through the use of restricted dislocation motion, it has been discovered that some nanostructured materials exhibit increased fracture toughness. The exhaustion of dislocation sources, on the other hand, causes others to become more fragile, which ultimately results in catastrophic collapse. For the purpose of producing nanostructured materials that are durable for use in aerospace, biomedical implants, and microelectromechanical systems (MEMS), it is essential to have a solid understanding of these deformation processes.

II. REVIEW OF LITERATURE

Chattopadhyay, Pratyay et al., (2021) When it comes to nanoscience and other scientific disciplines, germanium, a semiconductor, has several uses. Based on what is known about germanium's bulk properties, researchers have tried to learn more about its nanoscale qualities. Research into the nanoscale thermo-elastic characteristics of germanium and its compounds is essential for their efficient use in nanotechnology and related areas. Researchers have examined the relationship between the bulk modulus, thermal expansivity, melting point, and form of pure nano germanium. The calculation of Young's modulus has been attempted using two distinct formalizations. This article presents a comparative examination of the two formalisms using experimental values. In order to determine the optimal formalism for

calculating Young's modulus in germanium micro crystals, comparison research was conducted.

Goyal, Monika et al., (2019) The effect of size, shape, and temperature on the elastic characteristics of nanomaterials is investigated in this study. In order to derive the expressions of nanomaterials' elastic moduli and thermal expansivity, we expanded Guisbiers et al.'s formulation of the melting temperature expression used for nanostructures. The combined isobaric Tait equation of state and Guisbiers model are used to study the impact of nanomaterials' size, shape, and temperature on their Young's modulus and thermal expansivity. You may compare the current calculated findings with the simulated outcomes and the experimental data that is accessible. With decreasing nanomaterial size, thermal expansivity rises and Young's modulus falls. The Young's modulus decreases as the temperature increases; the highest decline is seen in spherical nanomaterials, while the least occurs in nanofilms (NFs). If the particle size is decreased, the rate of modulus decrease will be faster. We find that the current forecasts are quite congruent with the existing theoretical and experimental datasets. As a consequence, the current computed findings are in agreement with the overall characteristic of variation.

Kholiya, Kuldeep et al., (2014) The size dependency of thermodynamic variables (melting and Debye temperatures) and elastic properties (bulk modulus, young modulus, thermal expansion coefficient) may be investigated using a simple theoretical model. Next, the model is used on a spherical nanosolid of lead, a nanowire of gold, and a nanosphere of iron. Results from this investigation show that the approach suggested in this work is legitimate since they are in good accord with existing experimental data.

Sharma, Geeta et al., (2014) Thermoelastic characteristics of nanoparticles that rely on their size and shape are investigated using a basic theoretical model. Nanomaterials show extreme sensitivity to changes in temperature and pressure in addition to their size and form. The availability of certain experimental data allows us to compare the model predictions, thus we have chosen Ni, Cu, Fe, and SnO2 nanomaterials. Under varying dimensions, pressures, and temperatures, we have investigated the changes in volume and bulk modulus. Available experimental data has been compared with the findings. The reliability of the theory is bolstered by the fact that its predictions align well with those of the model. On top of that, we have used our approach to foretell outcomes in areas lacking experimental data. The scientists studying the nanomaterials in different experimental settings may find this useful.

Kumar, R. et al., (2013) Nanomaterials' size-and shape-dependent vibrational and thermodynamic characteristics are investigated using a basic theoretical model. Various forms of -Fe, Sn, Ag, and in nanoparticles were examined in terms of their Debye temperatures, Debye frequencies, melting entropies, and enthalpy. The experimental data is compared with the acquired findings. The theory put forward in this study is supported by the experimental findings, which accord well with the model predictions.

Kumar, R. et al., (2010) A straightforward theoretical approach is devised for the purpose of investigating the size dependency of nanomaterials' bulk modulus, Young modulus, and

coefficient of volume thermal expansion. Various nanomaterials have been taken into account, including spherical α-Fe, Cu nanowires, and spherical Ni nanofilms. Results are evaluated in comparison to the experimental data that is currently accessible. The model proposed in this study is supported by a good agreement between theory and experiment.

Bhatt, Jeewan et al., (2009) Based on the thermo-elastic characteristics of some nanomaterials as a function of temperature, this research is conducted. Based on the proposal of Singh and Gupta, the thermal expansivity (αT), volume thermal expansion (V/V0), and bulk modulus (KT) are the thermo-elastic parameters that have been computed using the integral form of the equation of state (IFEOS). The foundation of IFEOS is the observation that the temperature has a considerable impact on the Anderson Grüneisen parameter (δT). Many nanomaterials, including fullerene, nanocrystalline nickel Ni, and n-(Ni+Fe) alloy, have been subjected to this equation of state. The fullerene thermal expansivity (αT) and volume thermal expansion (V/V0) results were compared to molecular simulation data. The thermal expansivity (αT) results for n-Ni and n-(Ni+Fe) were compared to experimental data, which was discovered to be closely aligned with the results. That is why the results of this research prove that IFEOS is a viable method for nanomaterials.

III. RESEARCH METHODOLOGY

Using the W.H.Qi model, one may understand how the melting point varies with the size of nano-solids. The model has successfully predicted the melting point of nanoparticles, nanowires, and nanofilms, which varies with their size. The following is the nanosolid's melting point as calculated using the Qi model:

$$T_{mp} = T_{mb}\left(1 - \frac{N}{2n}\right) \tag{1}$$

where n is the overall atomic number in a nanosolid and N is the total atomic number on its surface. The nanosolid's melting point (Tmp) and the bulk material's melting point (Tmb) are used here. Nanosolids come in several shapes and sizes, and Table 1 shows the N/n equations for spherical nanosolids, nanowires, and nanofilms.

Table 1: N/n for three different types of nanosolids

Nanosolid	$\boldsymbol{N/n}$
Nanosphere	$4d/D$
Nanowire (h>>1)	$(8/3)(d/l)$
Nanofilm (l>>h)	$(4/3)(d/h)$

The atomic diameter (d) and the nanoparticle diameter (D) are used here. In the case of the

disk-shaped nanosolid, l represents the nanowire diameter and h the nanofilm width.

According to the model proposed by R. Kumar et al., the following is the volume thermal expansion coefficient for nanosolids.

$$\alpha_{nm} = \alpha_b \left(1 - \frac{N}{2n}\right)^{(-1)} \tag{2}$$

The volume thermal expansion coefficients of the nanosolid and the equivalent bulk material are denoted by α_{nm} and α_b, respectively.

The following is the equation of the isothermal bulk modulus that was established by Pandya et al.:

$$B = B_0\left(\frac{V}{V_0}\right)\left(1 + (B_0' + 1)\left(1 - \frac{V}{V_0}\right)\right) + B_0\left(\frac{V}{V_0}\right)\left(\frac{(B_0'+1)}{2}\left(1 - \frac{V}{V_0}\right)^2\right) \tag{3}$$

where B'_0 is the pressure derivative of the isothermal bulk modulus at zero pressure, and B_0 is the isothermal bulk modulus at room temperature. At a pressure of zero, the volume is V_0, and at a pressure of one, it is V.

The ratio of the nano-crystal to bulk crystal Young modulus has been calculated using two separate formalisms. S. Patil et al. suggested the following formula for the Young modulus of nanosolids, using the Qi model:

$$\frac{Y_{nm}}{Y_{bm}} = exp\left(\pm\frac{S_{vib}-1}{\frac{r}{r_0}-1}\right) \tag{4}$$

Here, Ynm is the nanosolid's youthful modulus and Ybm is its corresponding bulk value; r0 is the critical radius at which the surface concentration of nanocrystal atoms is maximized. You may find the value of "r0" by

$$r_0 = (3\text{-}d)h \tag{5}$$

where d=0 for spherical nanosolids, d=1 for nanowires, and d=2 for nanofilms, with h being the atomic diameter. The ratio of the surface-to-interior mean square displacement of atoms in a nanosolid, as expressed by the vibrational entropy, is

$$S_{vib} = \left(\frac{2S_{nm}}{3R}\right) + 1 \tag{6}$$

Here R is the ideal gas constant and Snm is nano melting entropy given by

$$S_{nm} = S_{mb} + \left(\frac{3R}{2} ln\left(1 - \frac{N}{2n}\right)\right) \tag{7}$$

A material's melting enthalpy (Hmb) and bulk melting temperature (Tmb) are defined as Smb=Hmb/Tmb. Looking at Table 1, we may find the N/n value.

The following is how the Young modulus ratio may be calculated according to the method used by G. Patel et al.:

$$\frac{Y_{nm}}{Y_{bm}} = 1 + \left(1 - \left(1 - \frac{(\beta)(S)A}{6}\right)\right) \tag{8}$$

the material constant is denoted by β while the form factor of the material is represented by S. A is the ratio of surface area to volume.

IV. RESULTS AND DISCUSSION

Figure 1 displays the projected findings for spherical nanosolids, nanowires, and nanofilms, as determined by evaluating the melting temperatures for nano-germanium using eq. (1). The relationship between the size of the nanosolid and the melting point is seen in Figure 1. Figure 1 shows our anticipated outcomes for nanosolids less than 13 nm. This is due to the fact that our outcomes for larger nanosolids are similar to those of their bulk equivalent.

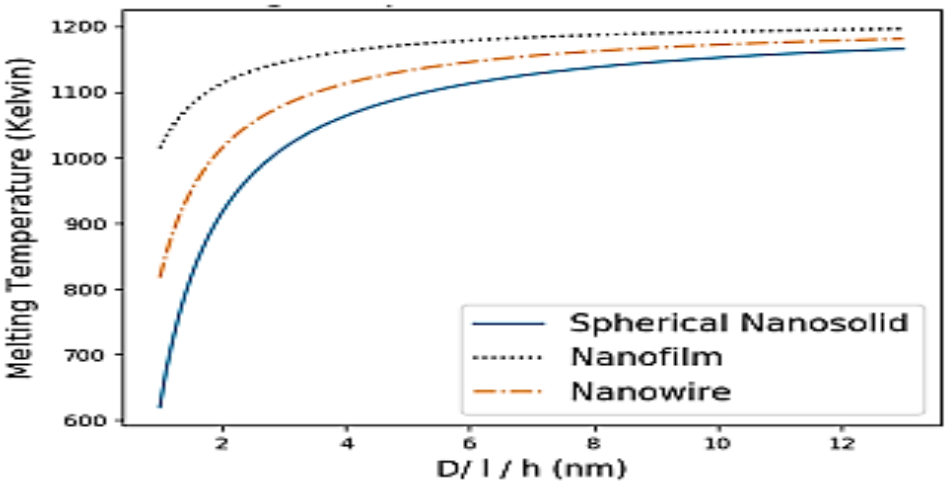

Figure 1: Nanogermanium melting points for spherical nanosolid (D nm), nanowire (l

nm), and nanofilm (h nm) geometries as a function of size

The melting point drops as the nanosolid's size drops, and the trend of melting point fluctuation is almost the same for all geometries. When considering spherical nanosolids, it is discovered that form has a substantial impact on melting point. For tiny particles, there is a noticeable variation in the melting point. Thermodynamic and thermal characteristics are changed at the nano-level due to the enormous rise in the surface-to-volume ratio. In the nanoscale region, the melting point drops as particle size falls. This is because, at the nanoscale, the surface-to-volume ratio is much improved. The surface-to-volume ratio grows dramatically, leading to a rise in the number of atoms on the surface, at sizes less than 20 nm. The melting point drops much below 20 nanometers because half of the bonds on the surface are dangling bonds.

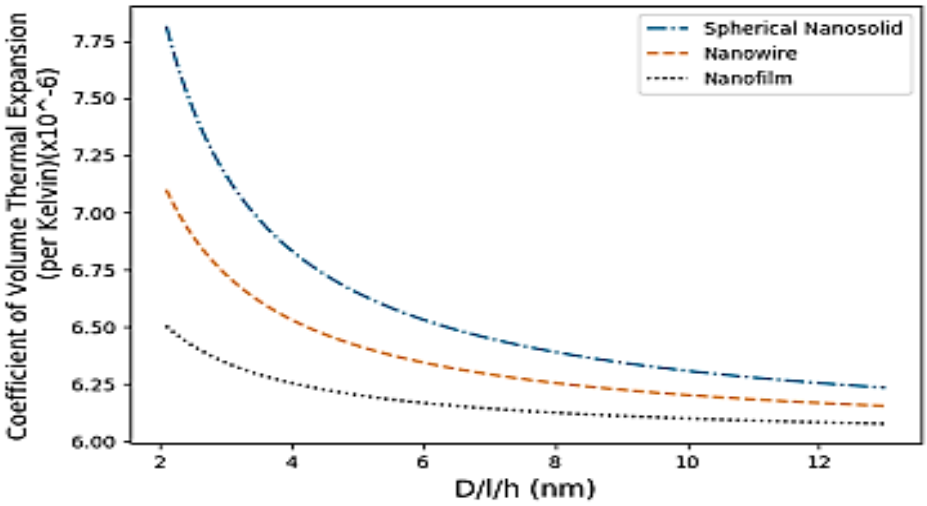

Figure 2. The size-dependent variation of the nanogermanium coefficient of volume thermal expansion for spherical nanosolid (D nm), nanowire (l nm), and nanofilm (h nm) geometries

An equation for nano-germanium's coefficient of volume thermal expansion has been calculated. Figure 2 displays the anticipated outcomes for nanowires, nanofilms, and spherical nanoparticles. at all forms, there is a noticeable fluctuation in the nanosolids' coefficient of volume thermal expansion (α) at sizes below 10 nm. It is seen in this range that, as the nanosolids' size lowers, (α) rises. Coefficient of volume thermal expansion (α) values for nanosolids larger than 10 nm are comparable to those of their equivalent bulk counterparts in every instance.

As illustrated in Figure 3, the isothermal bulk modulus varies with compression according to the values computed from equation (3). The parameters that were fed into the isothermal bulk modulus calculation are listed in Table 2.

Table 2. Input parameters used for the computation of bulk modulus

B'_0	B'_0 (GPa)	Particle Size
4	112	13 nm
4	92	49 nm
3	74.9	Bulk Germanium

The Hall-Patch effect is supported by our findings from the research of the compressibility of nano germanium, which show that nano size samples are less compressible than bulk materials. It is possible that the higher surface area between grains in nanosized particles gives energy, increasing hardness, since our data show that bulk modulus increases with decreasing particle size. Therefore, when the pressure increases, nano-germanium hardens.

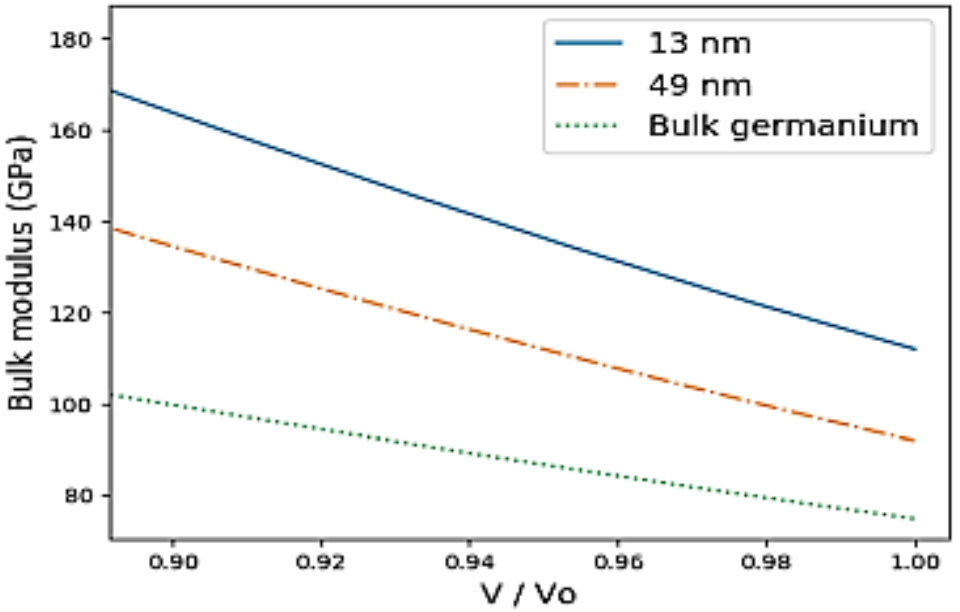

Figure 3. Germanium and nano-germanium with a spherical shape: bulk modulus vs volume compression

The findings for the ratio of the Young's modulus of nanosolids to that of the bulk solid, as predicted by equations (4) and (8), are juxtaposed in Figure 4. An rise in the young modulus is caused by an increase in the tangential force, which is enhanced when the size of the nanowire lowers and the surface-to-volume ratio increases, as well as the number of atoms on the surface.

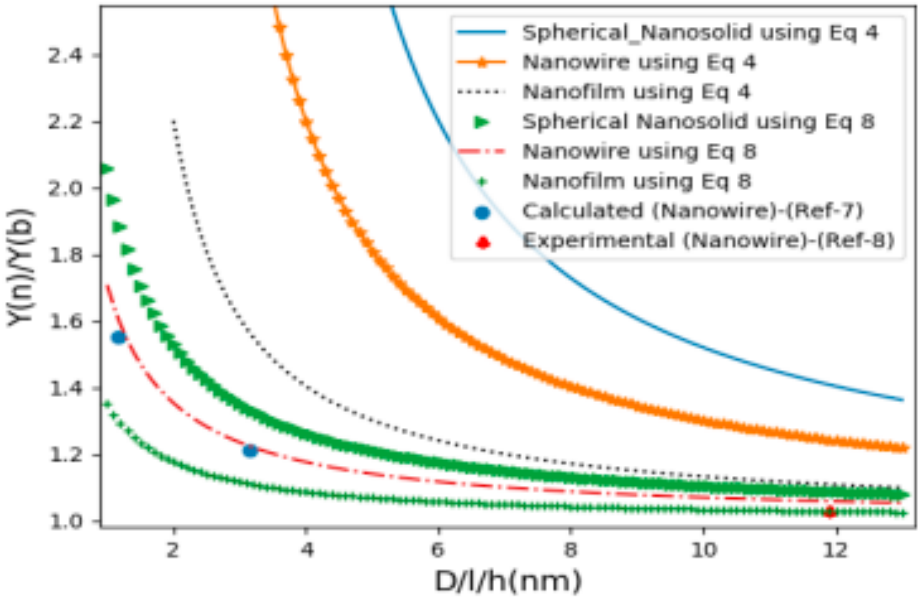

Figure 4. A size-dependent ratio Quantifying the nanosolid-to-bulk Ge Young modulus by use of equations (4) and (8)

In the case of nanowires, the obtained experimental data and other calculated findings show a high degree of agreement with the expected Young modulus ratio using eq. (8). When compared to the work of G. Patel et al., the findings produced by Patil et al., formulation differ significantly. On Lindemann's melting criteria is Patil's formulation based. The empirical link between the Young modulus and the size of nano solids has been derived by Patel and colleagues using a liquid drop model. The binding energy increases as the size decreases, leading to an increase in the Young modulus as a result. Because these two formalisms rely on distinct sets of assumptions, we find that they produce quite different outcomes.

V. CONCLUSION

As the surface-to-volume ratio increases, more surface atoms will have dangling bonds, and the melting point of nanosolids will drop as their size lowers, according to the data. Nanosolids smaller than 10 nm also show substantial fluctuation in the coefficient of volume thermal expansion, indicating greater thermal effects at the nanoscale. Nanosized germanium has a higher hardness and is less compressible than bulk germanium, according to the bulk modulus study. Mechanical strength is size and form dependent for nanosolids, as has been shown in studies of Young's modulus that use various theoretical techniques. In terms of agreement with experimental results, Patel's liquid-drop model outperforms Patil's formulation, according to a comparison of the two.

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