

STUDY OF THERMOELASTIC PROPERTIES OF NANAMATERIALS UNDER HIGH TEMPERATURE

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ABSTRACT

A theoretical formulation is derived to study the temperature dependence equation of state of nanomaterials under the effect of high temperature. Equation of state is reviewed from the knowledge of thermal expansion of nanomaterials based on the molecular dynamics simulation, assuming the fact that Anderson Gruneisen parameter (δT) is not a temperature independent parameter, but varies with temperature. The formulation is used to study the volume thermal expansion of eight nanomaterials, viz. Ag, Zirconia, ZnO, TiO₂, NiO, Al, 11% AlN/Al, and 39% AlN/Al. The results obtained are compared with the available experimental data. A good agreement between theory and experiment demonstrates the validity of the present approach.

KEYWORDS: high Temperature, equation of state, volume thermal expansion, nanomaterials.

I. INTRODUCTION

Nanomaterials, including nanoparticles, nanowires, nanotubes, and nanoscale thin films with different crystalline sizes (less than 100nm) show different physical and chemical properties compared with their bulk materials by virtue of their small size[1-4]. They are very sensitive to the external parameters like temperature and pressure. The physical properties of these materials depend on structures and interatomic separations. Due to the possibilities of substantially different behaviours compared to the bulk, the study of nanocrystalline materials under high temperature are of current interest.

Hu *et al.* [5] studied the thermal expansion behaviour of silver nanoparticles in ambient air and vacuum in the temperature range 300-1000K by dispersion of partially within pores of mesoporous silica and *in situ* XRD measurements. It has been found that the thermal expansion coefficient of Ag nanoparticles in vacuum is much smaller than the bulk of Ag. However the coefficient in the air is about three times as higher as that in vacuum and close to the value to the bulk. Nanocrystalline Zirconia powder is synthesized with a fairly narrow particle size distribution using amorphous citrate route by Bhagwat and Ramaswamy [6]. The crystalline size determined from XRD has been found 8nm and is close agreement with the particle size determined by TEM. The crystalline size has been found to increase with the increasing temperature. The high pressure behaviour of two samples of ZnO nanorods with different grain sizes have been studied and compared with their corresponding bulk phase by Xiang *et al.* [7]. The pressure induced structural phase transition has been observed experimentally in ZnO (nanorods), ZnS (2.8nm, 5nm, 10nm and 25.5nm), ZnSe (nanoribbons), GaN (2-8nm) and CeO₂ (9-15nm) using *in situ* dispersive X-ray diffraction at room temperature [8-11].

Zhang *et al.* [12] have been fabricated TiO₂ samples with a relative density as high as 95% by means of hot-pressing at temperatures as low as 400 °C and at pressures up to 1.5 GPa. During hot-pressing, the anatase phase transformed to the rutile phase and the amount of the transformation increased with sintering pressure.

The thermal properties have been investigated on newly developed nanocrystalline Al composites supported by Al nanoparticles to explore the potential application of nanocomposites for microelectronic packing [13]. Liu *et al.* [13] examined the thermal conductivity and the coefficient of thermal expansion of the composites at the room and high temperature.

A lot of experimental works have been done to understand the thermal properties of nanomaterials. Equally, there is a lacking of theoretical attempts. The idea of present study is to discuss a simple and straightforward method for evaluation of thermal expansion of nanomaterials. This method is applicable under the assumption that Anderson Gruneisen parameter δ_T is a temperature dependent parameter. Prasad *et al.* [14] studied the Elastic constants and bulk modulus of alkaline earth solids under the effect of high temperature. It has been noted that the results on temperature dependent elastic properties upgrade, if the linear dependence of δ_T with temperature is assumed [14].

Thus assuming the Anderson Gruneisen δ_T as temperature dependent, it is legitimate and may be useful to present a simple theoretical method to investigate the temperature dependent properties of nanomaterials, which is the purpose of present paper. In the present work we have examined the temperature dependence of volume thermal expansion of Ag, Zirconia, ZnO, TiO₂, NiO, Al, 11% AlN/Al, and 39% AlN/Al nanomaterials using the integral equation of state. The theoretical formulation is given in section II, results and discussion in section III.

II. METHOD OF ANALYSIS

The Anderson Gruneisen parameter [15] is given by

$$\delta_T = -\frac{1}{\alpha B_T} \left(\frac{\partial B_T}{\partial T} \right)_P = \frac{V}{\alpha} \left(\frac{\partial \alpha}{\partial V} \right)_P \quad (1)$$

Where thermal expansion coefficient is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (2)$$

And Bulk modulus reads as

$$B_T = -V \left(\frac{\partial P}{\partial V} \right)_T \quad (3)$$

Using the Maxwell thermodynamics relation given by Wallace [16] we have

$$B_T = \left(\frac{\partial \alpha}{\partial P} \right)_T = \frac{1}{B_T} \left(\frac{\partial B_T}{\partial T} \right)_P \quad (4)$$

In sight of Equations (2) to (4), Anderson parameter can also be defined as

$$\delta_T = \frac{V}{\alpha} \left(\frac{\partial \alpha}{\partial V} \right)_P \quad (5)$$

On integration Equation (5), we get

$$\frac{\alpha}{\alpha_0} = \left(\frac{V}{V_0} \right)^{\delta_T} \quad (6)$$

α_0 And V_0 are thermal expansion coefficient and volume at room temperature and atmospheric pressure respectively. Equation (6) reads as [17]

$$\frac{\alpha}{\alpha_0} = \left(\frac{r}{r_0} \right)^{3\delta_T} \quad (7)$$

Kumar [18] derived the relation for $r(T)$ as a function of temperature by considering the definition of thermal expansion coefficients as:

$\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)$, on solving we get

$$\frac{dr}{dT} = \frac{\alpha r}{3} \quad (8)$$

As $V \propto r^3$, now from Equation (7) and Equation (8), we get

$$\frac{dr}{dT} = \frac{\alpha_0}{3} \left(\frac{r^{3\delta_T+1}}{r_0^{3\delta_T}} \right) \quad (9)$$

Integration of Equation (9) gives

$$r(T) = r_0 \left(\frac{1}{1 - \delta_T \alpha_0 (T - T_0)} \right)^{\frac{1}{3\delta_T}} \quad (10)$$

Now from Equation (10) and Equation (7) we get the expression for thermal expansion coefficient as

$$\alpha(T) = \alpha_0 \left(\frac{1}{1 - \delta_T \alpha_0 (T - T_0)} \right) \quad (11)$$

From Equation (6) and Equation (11), one can develop

$$V = V_0 \left(\frac{1}{1 - \delta_T \alpha_0 (T - T_0)} \right)^{\frac{1}{\delta_T}} \quad (12)$$

Eq. (12) is developed taking the definition of Anderson Gruneisen parameter, where δ_T is temperature independent. But this Eq. (12) only works above the Debye temperature θ_D [23]. Inspired with this condition, model should be applicable for the entire range of temperature starting from the room temperature to melting temperature; we have made an effort to modify Eq. (12) assuming that δ_T is not the temperature independent parameter. It has been noted [14] that the value of δ_T changes with temperature. The empirical temperature dependence of δ_T is deliberated as

$$\frac{\delta_T}{\delta_T^0} = \left(\frac{T}{T_0} \right)^k \quad (13)$$

δ_T^0 is the value of Anderson Gruneisen parameter at reference $T = T_0$. The new dimensionless parameter k can be calculated from the slope of the graph plotted between $\log \delta_T$ and $\log(T/T_0)$.

Under the effect of temperature the product of thermal expansion coefficient and bulk modulus remains constant [19] that is

$$\alpha B_T = \text{Constant} \quad (14)$$

On differentiating Equation (14) with respect to temperature and at constant pressure, we get

$$\left(\frac{dB_T}{dT} \right)_p = -\frac{B_T}{\alpha} \left(\frac{d\alpha}{dT} \right)_p \quad (15)$$

From Equation (15) and Equation (1)

$$\delta_T = \frac{1}{\alpha^2} \left(\frac{d\alpha}{dT} \right)_p \quad (16)$$

Equation (13) and equation (16) give

$$\delta_T^0 \left(\frac{T}{T_0} \right)^k = \frac{1}{\alpha^2} \left(\frac{d\alpha}{dT} \right)_p \quad (17)$$

On integrating Equation (18), we get

$$\delta_T = \frac{1}{\alpha^2} \left(\frac{d\alpha}{dT} \right)_p$$

$$\delta_T^0 \frac{T^{k+1}}{T_0^k (k+1)} = -\frac{1}{\alpha_T} + c$$

Where C is the constant of integration. From preliminary condition $T = T_0$ and $\alpha = \alpha_0$,

$$\delta_T^0 \frac{(T^{k+1} - T_0^{k+1})}{T_0^k (k+1)} = -\frac{1}{\alpha_0} - \frac{1}{\alpha}$$

$$\text{Or, } \alpha / \alpha_T = \left(1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k+1)} (T^{k+1} - T_0^{k+1}) \right)^{-1} \quad (18)$$

From Equation (13) and Equation (1) we get

$$\delta_T^0 \left(\frac{T}{T_0} \right)^k = -\frac{1}{\alpha_0 B_0} \left(\frac{\partial B_T}{\partial T} \right)_p \quad (19)$$

On integrating eq. (19), one can get

$$\int_{B_0}^{B_T} dB_T = -\alpha_0 B_0 \delta_T^0 \int_{T_0}^T \left(\frac{T}{T_0} \right)^k dT$$

$$\text{Or, } B_T / B_0 = \left(1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k+1)} (T^{k+1} - T_0^{k+1}) \right) \quad (20)$$

This is the expression for the bulk modulus as a function of temperature.

The expression for volume expansion can be obtained by Equation (1), Equation (2) and Equation (20) as:

$$dB_T = -B_T \delta_T \frac{dV}{V} \quad (21)$$

Differentiating Equation (20) with respect to temperature, we get

$$dB_T = -\left(\alpha_0 B_0 \delta_T^0 / T_0^k \right) T^k dT \quad (22)$$

From Equation (21) and Equation (22)

$$dV / V = \alpha_0 / \left(1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k+1)} (T^{k+1} - T_0^{k+1}) \right) \quad (23)$$

On integration Equation (23), we get

$$V / V_0 = \exp \int_{T_0}^T \alpha_0 dT / \left(1 - \frac{\alpha_0 \delta_T^0}{T_0^k (k+1)} (T^{k+1} - T_0^{k+1}) \right) \quad (24)$$

Equation (24) is well known Singh and Gupta [20] equation of state for the volume thermal expansion. The value of volume thermal expansion as a function of temperature has been calculated for given nanomaterials using Equation (24). Dimensionless parameter k for the agreed nanomaterials can be calculated from Equation (13).

Table 1. Values of input parameter

Nanomaterials	$\alpha \times 10^{-5}/K$	references
Ag	1.8	[5]
Zirconia	3.46	[6]
ZnO	1.04	[7]
TiO ₂	1.52	[12]
NiO	3.77	[21]
Al	7.8	[13]
AlN/Al (39%)	4.2	[13]
AlN/Al (11%)	5.88	[13]

III. RESULTS AND DISCUSSION

In the existing work, we have computed the volume thermal expansion V/V_0 under the effect of high temperature and atmospheric pressure using Equation (24) of Ag, Zirconia, ZnO, TiO₂, NiO, Al, 11% AlN/Al, and 39% AlN/Al nanomaterials. It has been observed that the volume expansion increases linearly with temperature. The Input data used in our calculation are given Table 1 and results are narrated in Figures 1-8. During these studies δ_T^0 has been taken four, which is supported by Birch Murnaghan EOS [22-23] and Kumar *et al.* [24]. The new dimensionless parameter k can be calculated from the slope of the graph plotted between $\log \delta_T$ and $\log(T/T_0)$. The values of k for given nanomaterials are found -0.56, -3.5, -1.57, -1.78, -1.34, -1.24, -0.85, -0.67 respectively. Volume expansion is calculated by Equation (24) as a function of temperature in the range of 300-1000K for Ag nanomaterial. The results obtained are reported in Figure 1 along with the experimental data for comparison as reported by Y. Hu *et al.* [5]. There is a good agreement with the experiment. They [5] also discussed the relation of volume dependence of thermal expansion, so the philosophy developed in the current work is supported by the Y. Hu *et al.* [5]. The result obtained for the Zirconium nanomaterial by Equation (24) are reported in Figure 2 sideways with the experimental data as given by M. Bhagwat and V. Ramaswamy [6] for judgment reason. This shows the agreement with our theory. For ZnO nanomaterials, results are reported in Figure 3 by using Equation (24) laterally with the experimental data as performed by Wu X *et al.* [7]. It is found to be a sound promise with the experiment [7]. In case of TiO₂, results are presented in Figure 4 using Equation (24). Experimental data reported by W.F. Zhang *et al.* [12] by Raman scattering study on anatase TiO₂ nanocrystals have been included for comparison. It is realized that the results are very much close to the experiment [12], which strongly support the theory. Figure 5 displays the findings of the NiO nanomaterial as reported by Equation (24) along with the experimental results [21]. This shows the good accord between our theory and experiment [21]. Liu *et al.* [13] have been investigated the thermal properties for newly developed nanocrystalline Al composites strengthened by AlN nanoparticles. We have included these materials Al, AlN/Al 11%, and AlN/Al 39% in our work. Results obtained by Equation (24) are reported in Figures 5-8, along with the experimental values [13]. Figures show that as temperature increases volume thermal expansion increases linearly and matching perfectly with the experimental findings. It is realized that there is a very good agreement among theory and experiment throughout the temperature range for all nanocrystalline Al composites.

In this present work we have discussed a simple model free from potential, which may be used for any class of nanomaterials. The model used in the existing work needs less input parameters, which are readily available and includes the effect of temperature.

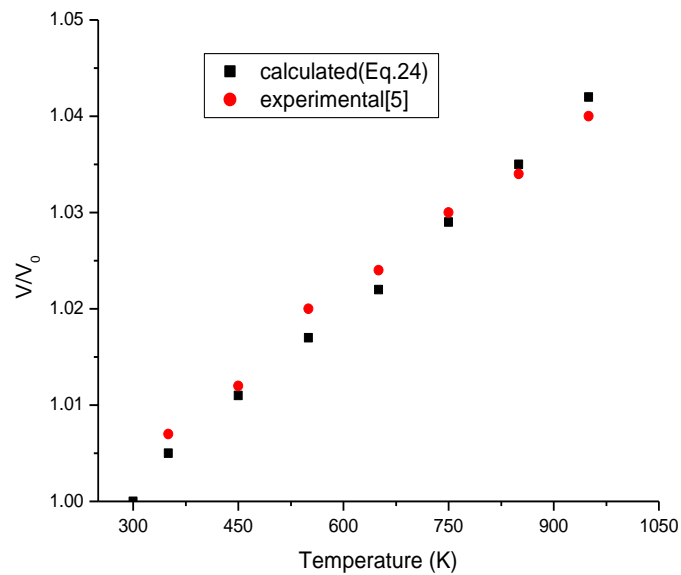


Fig.1. Temperature dependence of V/V_0 of Ag nanomaterial

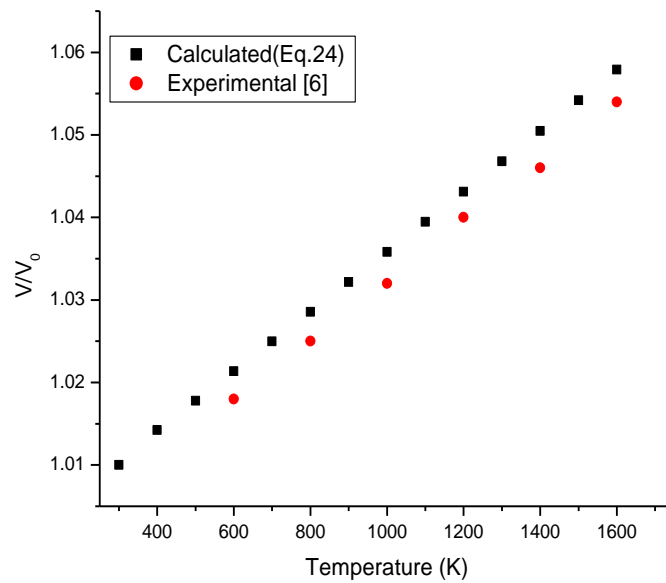


Fig.2. Temperature dependence of V/V_0 of Zirconia nanomaterial

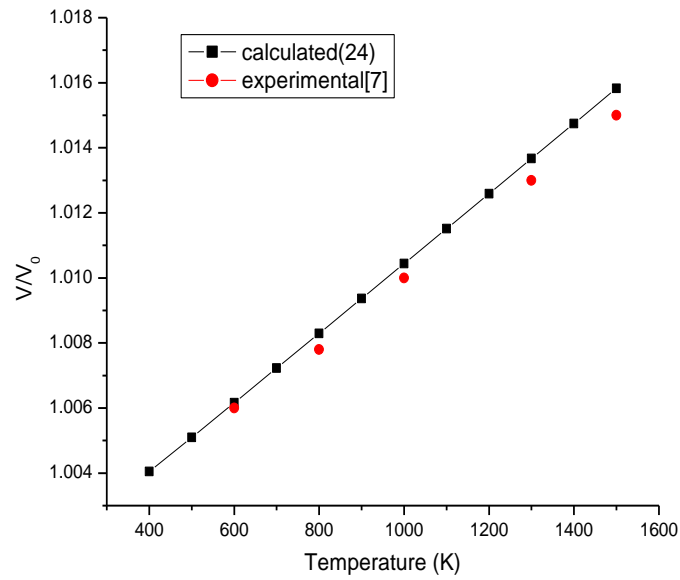


Fig.3. Temperature dependence of V/V_0 of ZnO nanomaterial

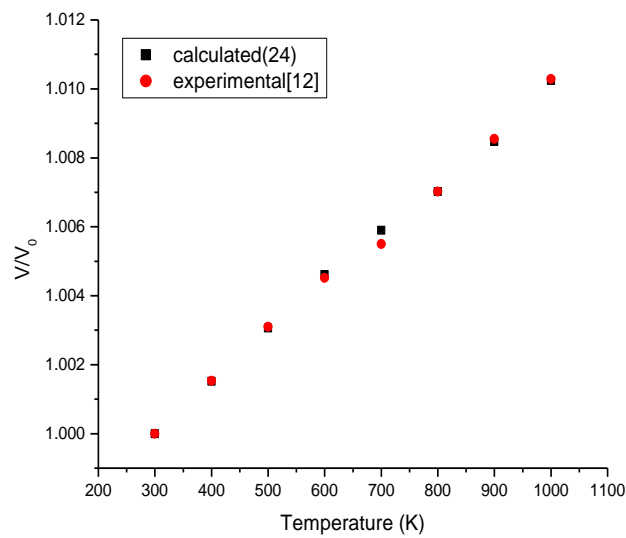


Fig.4. Temperature dependence of V/V_0 of TiO_2 nanomaterial

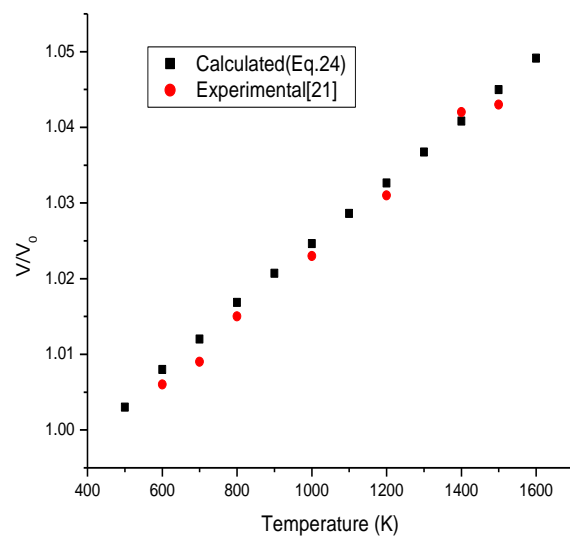


Fig.5. Temperature dependence of V/V_0 of NiO nanomaterial

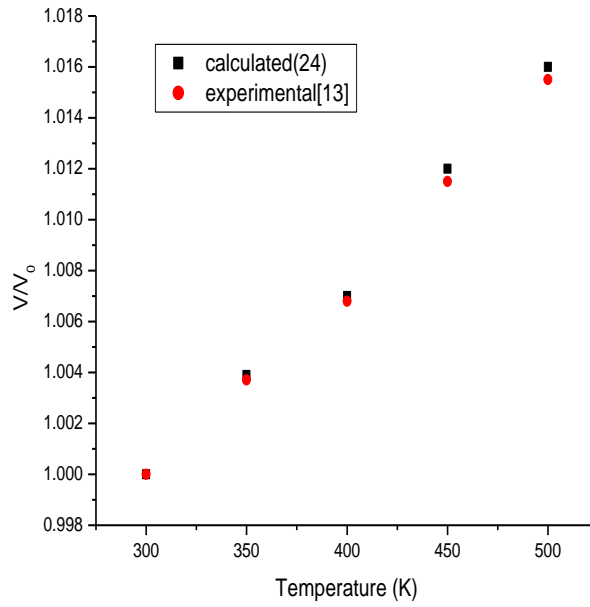


Fig.6. Temperature dependence of V/V_0 of Al nanomaterial

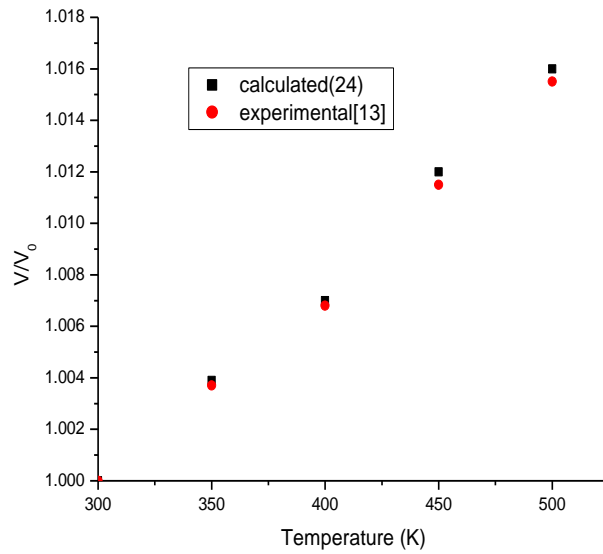
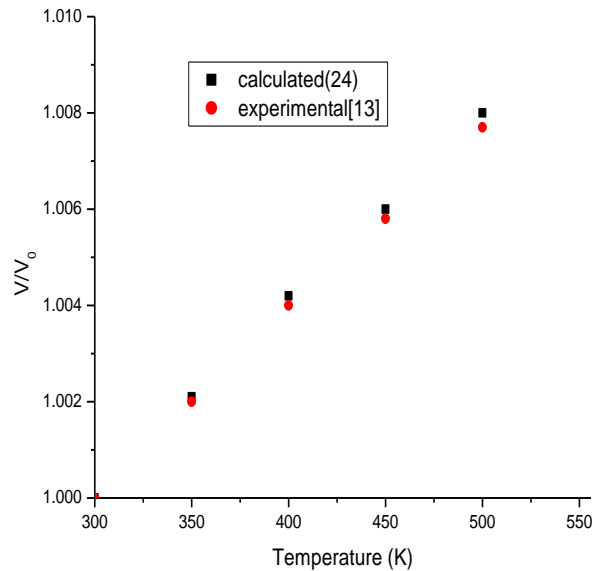


Fig.7. Temperature dependence of V/V_0 of AlN/Al 11% nanomaterial

Fig.8. Temperature dependence of V/V_0 of AlN/Al 39% nanomaterial

IV. CONCLUSION AND FUTURE WORK

The integral form of equation of state (Equation 24) has been examined on the assumption that Anderson Gruneisen δ_T is dependent upon temperature. The formulation gets verifications from the thermodynamic analysis. The good agreement between calculated and the experimental values of volume thermal expansion at higher temperature for the nanomaterials under study reveals the validity of the relationship used in the present work. It has been used to predict the values of thermal expansion at temperature range of measurement where experimental data not found so far. Due to the simplicity and applicability it may be of current interest to the scholars engaged in this area. This study may be tremendous impact in high pressure and high temperature research [24-25] where the results at high temperatures are required. By using the same integral equation of state one can calculate the elastic constants of nanomaterials at high temperature. Also we can estimate the bulk modulus and size dependence of thermoelastic properties of nanomaterials under varying temperatures.

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