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REGULAR ARTICLE

Theoretical consideration of the anomalous temperature dependence of the surface tension of pure liquid gallium

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Abstract The surface tension of pure liquid gallium in the temperature range 303–503 K (303 K is the melting point) was previously measured using the noninvasive method of capillary wave spectroscopy (CWS). The result of this experiment showed that the value of surface tension increases from 303 to 345 K indicating a negative surface excess entropy (S^{σ}), and decreases linearly from $\sim$345 to 503 K confirming a negative slope, and thus a positive S^{σ}. This unusual behavior of Ga is not known for other liquid metals such as Bi, Pb, Hg, Sn and Al. The reported experimental behavior is modeled here. A theoretical equation for calculating the surface tension of liquid Ga, based upon formulating a proper partition function that includes the rotational part, is derived and described. The theory predicted no maximum in the temperature-dependence of the surface tension, as seen in the experiment, where the analysis was done over a large temperature range (325–503 K). The value obtained from this mathematical expression indicates that the temperature variation of surface tension has no positive slope within the temperature range 303–345 K. At $T > 345$ K, the surface tension shows the usual linear temperature-dependence with a negative slope. Therefore, the equation is only applicable for the latter temperature range. A comparison between the theoretical and experimental values of surface tension of liquid Ga is discussed.

Keywords Surface chemistry · Surface tension · Gallium

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1 Introduction

This manuscript describes the use of the Eyring statistical thermodynamical theory for modeling the surface tension of gallium, and relies on model statistical mechanics calculations that do not naturally incorporate structural predictions or consideration of the metallic state of the liquid. A surface is defined as the termination of the bulk state (as solid or liquid), where the equations based on three-dimensionality are not sufficient to describe the complete physical state of the system [1]. At the surface region, bulk symmetry is perturbed and gives rise to altered interaction forces. This broken symmetry is responsible for the peculiar behavior of surfaces and interfaces, which lead to different types of phenomena such as surface tension and the existence of capillary waves at liquid surfaces. In addition, a surface of a solid is considered to be a point of defects, which induces, for example, surface melting of certain pure metals at temperatures below the bulk melting points [2].

Interfacial and surface properties of condensed matter phases are important from both fundamental and technological points of view [3]. These properties are related to wettability of a liquid surface by the other liquid that has lower surface tension or of solid substrates by liquids of different intermolecular and interatomic interactions. Studies on surface properties and their relation to macro and microscopic phenomena have been done [4–10].

Recently, wetting phenomena in Ga–Bi and Ga–Pb liquid alloys, by capillary wave spectroscopy (CWS) [11–13] was investigated. They have determined the temperature-dependence of the surface tension of pure liquid Ga in the temperature range of $T_m = 303$ K up to 503 K, using the noninvasive method of CWS [11], which displayed an anomalous dependence in the range of 303–345 K (Fig. 1).

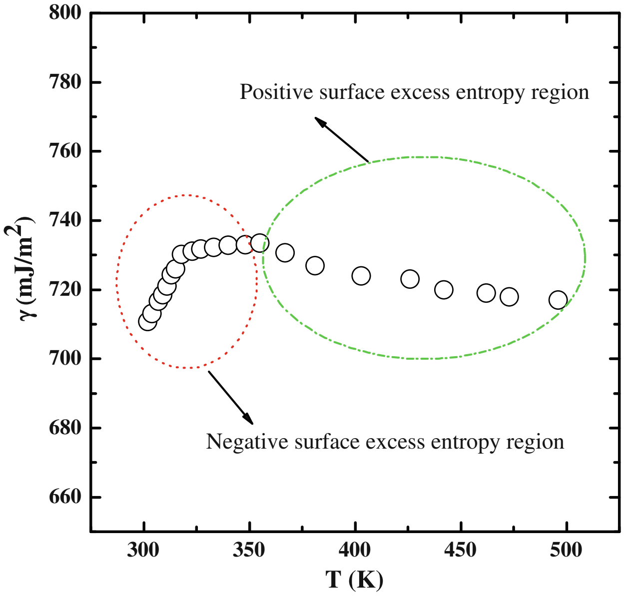

Fig. 1 Measured temperature-dependence of the surface tension of liquid Ga (Ref. [11])

A similar anomalous behavior has also been reported [14, 15]. In all these studies, there was no attempt to consider this behavior theoretically, and therefore, it was of interest to investigate, theoretically, the abnormal and unique behavior of Ga by the classical statistical thermodynamic formulation of Eyring [16]. This paper illustrates a derivation of an equation for calculating surface tension of liquid gallium, assuming that there are some molecular species (Ga_2 dimers) [17, 18] at the surface of the liquid, and these species possess rotational motion. Therefore, the main interesting idea is to take into account the rotational part in the total partition function assuming formation of dimer Ga_2 molecules at low temperatures.

2 Theoretical formulation and discussion

The theoretical consideration here is based on classical statistical thermodynamics formulation of Eyring et al. [16]. Their theory is focused on the assumption that the metal upon melting acquires vacancies that are moving freely through the melt, and there is short-range order in the liquid [16]. These freely moving vacancies, called fluidized vacancies, have a volume fraction that corresponds to the volume change of the metal upon melting, or about 3–4% for transition and non-transition metals. Using statistical mechanics, partition functions account for the gas-like behavior of the fluidized vacancies and for the solid-like behavior of the liquid metal. In light of advances in statistical mechanics and quantum mechanics, since the development of the Eyring theory, the fluidized vacancy model seems a bit artificial, and so the addition of rotating dimers is ad hoc but necessary to account for the behavior. The thermodynamic properties of the liquid metal may be calculated from the relationship between the Helmholtz free energy and the partition functions. Eyring has shown that this approach can predict the thermodynamic properties of a large number of liquids and pure liquid metals. The Eyring approach in calculating the surface tension of a liquid metal was made by Schoutens [19], who calculated the surface tension of pure liquid Al. He assumed that the probability of diatomic modules is extremely small, and as a consequence, the partition function for rotation is unity. Here, we follow up with this formulation, by taking into account the rotation partition function in the overall formulation.

The Helmholtz free energy and the partition function are related via the thermodynamic equation:

$$F = -k_B T \ln f^{\sigma} \tag{1}$$

where k_B is the Boltzmann constant, T the absolute temperature and f^{σ} the partition function which is defined as:

$$f^{\sigma} = f_B f_{mL} \tag{2}$$

where f_{mL} is the partition function for the surface atoms and f_B for the bulk liquid atoms. Note that the Helmholtz free energy and the partition function are usually specified by A and Q, respectively, by others. The product form of the partition functions in Eq. 2 implies independent probabilities, which is a good approximation when dealing with the liquid and surface states. The surface tension is calculated from:

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{N,V,T} \tag{3}$$

where N is Avogadro's number and V the molar volume which is given by

$$V = \frac{M}{\rho(T)} \tag{4}$$

where M is the atomic weight and $\rho(T)$ the density as a function of temperature of the liquid in question.

The surface area occupied by a monolayer of atoms on the liquid surface (A) is given by:

$$A = \varphi N_c \tag{5}$$

where φ is the area occupied by one atom and N_c the total number of sites available for atoms on the liquid surface.

The Eyring model appears to constrain the surface to be monolayer. The X-ray scattering experiments [18] and theory, instead, indicate that the surface extends for many layers, and is stratified. The significant liquid structure theory assumes that the transition from liquid to gas is restricted to one layer, but the liquid surface of Ga exhibits a strong surface layering with many layers. These observations are not incorporated into the present calculation.

Any partition function can be written as the product of partition functions describing each process involved [15, 19].

$$f_{\mathrm{B}} = (f_{\mathrm{s}})^{N_{\mathrm{B}} V_{\mathrm{s}}/V} \left(f_{\mathrm{g}}\right)^{N_{\mathrm{B}}(1-V_{\mathrm{s}}/V)} \tag{6}$$

where V_{s} is the molar volume of the solid at the triple point. Both f_{s} and f_{g} the partition functions for the solid and gas-like behavior of the bulk liquid, respectively. These can be further separated into the product partition functions [19] as shown in Eqs. 7 and 8.

$$f_{\mathrm{s}} = f_{\mathrm{Einstein}} f_{\mathrm{rot}} f_{\mathrm{vib}} \vartheta(T) \tag{7}$$

$$f_{\mathrm{g}} = f_{\mathrm{trans}} f_{\mathrm{rot}} f_{\mathrm{vib}} \tag{8}$$

In this case, rotation, vibration, and translation motions have been accounted. The term $\vartheta(T)$ is the partition function for the internal degrees of freedom [15].

The partition function for the oscillation of atoms in the solid may be calculated from Einstein's theory, by using Eq. 9.

$$f_{\mathrm{Einstein}} = \frac{\exp\left(\frac{E_{\mathrm{S}}}{RT}\right)}{\left[1 - \exp\left(-\frac{\theta}{T}\right)\right]^3} \tag{9}$$

where θ is the Einstein temperature [18], E_{s} the sublimation energy and R the universal gas constant.

According to the transient state theory (TS), the rotational motion of the solid-like molecules in the liquid state is considered as a rigid rotor or as a harmonic oscillator [20–23]. Therefore, the rotational energy, according to this theory, is given by:

$$E_{\mathrm{rot}} = \frac{1}{2l}\left(P_{\theta}^2 + \frac{P_{\beta}^2}{\sin\theta}\right) + U \tag{10}$$

where I is the moment of inertia. The P_{θ} and P_{β} the angular momentum. This form has a wide variety of applications [24]. For a rigid diatomic molecule, the potential energy is given by:

$$U = -B\cos\phi \tag{11}$$

where B is the potential energy barrier and Φ the angle between the molecular axis and the direction of the field. The rotational partition function can be obtained by integrating the Boltzmann factor as follows:

$$\begin{aligned} f_{\mathrm{rot}} &= \frac{1}{\alpha h^2}\int \int\limits_{-\infty}^{+\infty} \int\limits_{0}^{2\pi} \int\limits_{0}^{\pi} e^{-E_{\mathrm{rot}/kT}}\, \mathrm{d}\Phi \mathrm{d}\beta \mathrm{d}P_{\Phi} \mathrm{d}P\beta \\ &= \frac{8\pi^2 I k_{\mathrm{B}} k_{\mathrm{B}} T}{\alpha h^2 \quad B} \sinh\frac{B}{k_{\mathrm{B}}T} \end{aligned} \tag{12}$$

where α is the symmetry number. In TS theory, it is assumed that the potential energy barrier, B proportional to the neighboring molecules. Also, the neighboring probability of the molecule is proportional to V_{s}/V, and so the potential energy barrier can be expressed by:

$$B = \xi(V_{\mathrm{s}}/V) \tag{13}$$

where ξ is a proportionality factor. In addition, the liquid molecules are partitioned by three kinds of degrees of freedom that are the solid-like, the transient and the gas-like. The full partition function, including the rotational part, is given by:

$$\begin{aligned} f_{\mathrm{B}} &= \left\{\frac{\mathrm{e}^{E_{\mathrm{s}}/RT}}{\left(1-\mathrm{e}^{-\theta_s/T}\right)^3}\left[1 + n\left(\frac{1-\mathrm{e}^{-\theta_s/T}}{1-\mathrm{e}^{-\theta_t/T}}\right)^3 \frac{V-V_{\mathrm{s}}}{V_{\mathrm{s}}} \times \mathrm{e}^{\left(-\frac{aE_{\mathrm{S}}}{n\left(\frac{V-V_{\mathrm{S}}}{V_{\mathrm{S}}}\right)RT}\right)}\right]\right\}^{\frac{V_{\mathrm{S}}}{V}N} \left[\frac{(2\pi mkT)^{3/2}}{h^3}\frac{\mathrm{e}V}{N}\right]^{\frac{V-V_{\mathrm{S}}}{V}N} \left[\frac{8\pi^2 IkTkT}{2h^2 \quad B}\sinh\frac{B}{kT}\right]^N \\ f_{\mathrm{mL}}^{N'} &= \left\{\frac{\mathrm{e}^{E'_{\mathrm{s}}/RT}}{\left(1-\mathrm{e}^{-\theta'_{\mathrm{s}}/T}\right)^3}\left[1 + n'\left(\frac{1-\mathrm{e}^{-\theta'_s/T}}{1-\mathrm{e}^{-\theta'_t/T}}\right)^3 \frac{V-V_{\mathrm{s}}}{V_{\mathrm{s}}} \times \mathrm{e}^{\left(\frac{a'E'_{\mathrm{S}}}{n'\left(\frac{V-V_{\mathrm{S}}}{V_{\mathrm{S}}}\right)RT}\right)}\right]\right\}^{\frac{V_{\mathrm{S}}}{V}N'} \left[\frac{(2\pi mkT)^{3/2}}{h^3}\frac{\mathrm{e}V}{N}\right]^{\frac{V-V_{\mathrm{S}}}{V}N'} \left[\frac{8\pi^2 IkTkT}{2h^2 \quad B'}\sinh\frac{B'}{kT}\right]^{N'} \end{aligned} \tag{14}$$

where n, n', a and a' are parameters that should be, theoretically, determined. In the development of the theoretical formulation, these parameters will drop out. Both θ_{s} and θ_{t} are the Einstein temperatures for the solid-like and for the transient, respectively. The prime quantities refer to surface atoms corresponding to the unprimed quantities. Also, N is given by:

$$N = N_{\mathrm{B}} + N' \tag{15}$$

where N_{B} is the number of atoms in the bulk and N' the number of atoms on the surface.

Now we can write:

$$\ln f^{\sigma} = \ln(f_{\mathrm{B}} f_{\mathrm{mL}}) = \ln f_{\mathrm{B}} + \ln f_{\mathrm{mL}} \tag{16}$$

By using Eqs. 14–16, the following equation is obtained:

$$\ln f^{\sigma} = N'\frac{V_{\mathrm{s}}}{V}\left\{\ln\frac{\Xi^{\sigma}1 + n'\left[\frac{\left(1-\exp\left(-\theta'_{\mathrm{s}}/T\right)\right)}{\left(1-\exp\left(-\theta'_{\mathrm{t}}/T\right)\right)}\right]^{3}\left[(V/V_{\mathrm{s}}) - 1\exp\left[-a'E'_{\mathrm{s}}V_{\mathrm{s}}/(V - V_{\mathrm{s}}\right]RT\right]}{\Xi\left[1 + n\left[\frac{(1-\exp(-\theta_{S}/T)}{(1-\exp(-\theta/T)}\right]^{3}[(V/V_{\mathrm{s}}) - 1]\exp[-aE_{\mathrm{s}}V_{\mathrm{s}}/(V - V_{\mathrm{s}})RT]\right]}\right\} + \ln\Psi - N'\ln\frac{B'\sinh\frac{B'}{kT}}{B\ \sinh\frac{B}{kT}} \tag{17}$$

where $\Xi^{\sigma} = \frac{\exp\left(\frac{E'_{S}}{RT}\right)}{\left[1-\exp\left(-\theta'_{S}/T\right)\right]^{3}}$ $\Xi = \frac{\exp\left(\frac{E_{S}}{RT}\right)}{[1-\exp(-\theta_{S}/T)]^{3}}$ and the function Ψ contains all terms that do not include N'. From Eq. 3, one gets γ for close packing [25] as follows:

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{N,V,T} = \varphi^{-1}\cdot\left(\frac{\partial F}{\partial N_{c}}\right)_{N,V,Y}$$
$$= \varphi^{-1}\left(\frac{V_{s}}{V}\right)\left(\frac{\partial F}{\partial N'}\right)_{N,V,T} \tag{18}$$

where $\varphi = \frac{\sqrt{3}}{2}\left(\frac{\sqrt{2V_{\mathrm{s}}}}{N}\right)^{2/3}$. Upon taking the derivative in Eq. 18, the function Ψ disappears because it does not contain terms that include N'. In addition, Eyring et al. [26] used the approximations that $n \approx n'$, $a' = a$, $\ln(\vartheta'(t)/\vartheta(t)) = 0$, and showed that:

$$E'_{\mathrm{s}} \cong \frac{3}{4}E_{\mathrm{s}}(1+f) \quad \text{and} \quad \theta'_{\mathrm{s}} = \theta_{\mathrm{s}}\left(\frac{3}{4}+\frac{3}{4}f\right)^{1/2} \tag{19}$$

where f is a dimensionless constant parameter. Combining Eqs 17–19 gives,

$$\gamma = \varphi^{-1}\left(\frac{V_{\mathrm{s}}}{V}\right)kT\left[\frac{E_{\mathrm{s}}}{RT}(1-3f)+\frac{3}{2}\ln\frac{3}{4}(1+f)-\ln\frac{B\prime\sin h\frac{B\prime}{kT}}{B\sin h\frac{B}{kT}}\right] \tag{20}$$

Now, ξ in the bulk liquid has been set to 12 and that of the surface has been set to 9.

On this basis, we provided enough details for checking the main result Eq. 20. However, according to our calculations with the parameters and functions provided, the resulting theoretical function does not have a maximum: it is only a decreasing function in the temperature range 303–503 K (Fig. 2). In fact, the first term in the square brackets of Eq 20, $E_{\mathrm{s}}(1-3f)/RT$, is the dominating one. The calculations show that it is of the order of 50, whereas the second term is equal to −0.3 and the third term in the brackets is of the order of 0.5–4.5, depending on the definition of the ξ units. In the multiplying term, $\varphi^{-1}(V_{\mathrm{s}}/V)^{2}kT$, the temperature-dependent part is $1/V^{2}$ that is $(\rho/\mathrm{m})^{2}$, where m is constant, ρ the density of liquid gallium which was measured by Masanori et al. [27]. This reference shows the resulting function as the lowest one in Fig. 3. It is clear that ρ is monotonically decreasing and almost a linear function with temperature between 0 and 900 °C or 273 and 1,173 K. By definition, ρ positive, and therefore, ρ^{2} (and the leading term in Eq. 20: $\varphi^{-1}(V_{\mathrm{s}}/V)^{2}kT[E_{\mathrm{s}}(1-3f)/RT]$) will never have a maximum. In order to validate the approach/model used, the surface tension data of liquid gallium reported by others [28–30] have been tested, and showed the same results as shown in Fig. 2.

The sublimation energy, molar volume and other parameters needed to calculate the surface tension of Ga using Eq. 20 were taken from literature [26]. Equation 20 has been used to calculate the surface tension of Ga as a function of temperature with the following data [25]: $E_{\mathrm{s}}(Ga) = 64$ kcal/mol, $V_{\mathrm{s}}(\mathrm{solid}) = 11.4\ \mathrm{cm}^{3}/\mathrm{mol}$ and $f = 0.091$. The molar volume of liquid Ga is the only temperature-dependent parameter since its density changes with temperature. A comparison between the experimental values of the surface tension of liquid Ga and the theoretical ones obtained from Eq. 20 is demonstrated in Fig. 2.

The experimental values are ~20% higher than the theoretical ones. This is due to the simplicity of the model and the assumptions made. Nevertheless, the model predicts the same order of magnitude values for the temperature-dependence of the surface tension of pure liquid Ga. The outcome of the model shows, clearly, surface tension with no maximum. An increase in entropy is correlated with disordering of the surface at high temperature. Moreover, it should be mentioned that Ga expands upon freezing, and this, in turn, might seem a contradiction to the assumption, that the fluidized vacancies have a volume fraction that corresponds to the volume change of the metal upon melting. Since the model yields, relatively, good results, this effect has a little influence on the temperature behavior of the surface tension of liquid Ga. In addition, it proves that the classical thermodynamic formulation is valid even for materials that have anomalous characteristics.

Figure 2 is a plot that shows the gallium surface tension behavior observed theoretically and experimentally for a wide temperature interval, and predicts how well the qualitative functional behavior of the theory and experiment agrees. It may be mentioned that the surface tension of liquid Ga is ten times higher than that of water. Although there is a difference of about 20% between the experimental and theoretical values, the derived equation looks acceptable since the model is simple and the difference is expected. This observation is explained by the fact that gallium metal as a solid has an unusual crystal structure and it exists as discrete diatomic molecules rather than

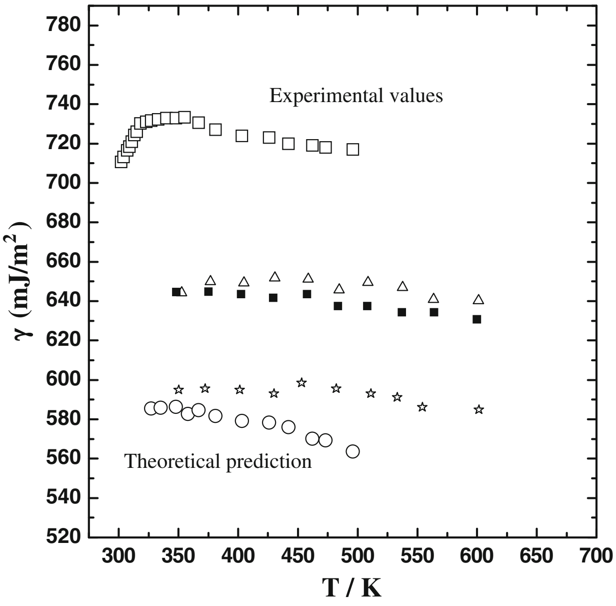

Fig. 2 Comparison between the theoretical (*open circles*) and the experimental (*open squares*) surface tension values of pure liquid gallium. $S\sigma$ means surface excess entropy. A maximum is not seen in the theoretical surface tension. *Open triangles*, *open stars* and *solid squares* represent the results of the surface tension data of liquid Ga taken from Refs. 15, 28, 29 and 30

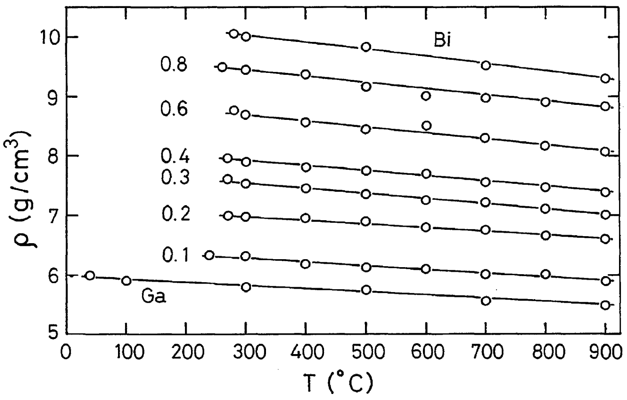

Fig. 3 Temperature-dependence of density of liquid Bi–Ga (taken from Ref. [27] as Fig. 5)

as a metallic structure. The coexistence of monoatomic and diatomic molecular fluid characteristics in liquid gallium was determined by Gong et al. [17]. The liquid gallium–solid diamond studies of Van der Veen [18] do rely upon the presence of Ga dimers at the interface. Although this hypothesis can be right, the approximation used, the significant liquid structure theory of Eyring, is too simplistic to study the present problem because it includes many free or tune parameters for which reason it lacks prediction power. However, Ga has low melting point and has the longer liquid range of any known substance. The boiling point for Ga is very high indicating that the dimer structure no longer exists in the liquid. Since the experimental surface tension of Ga increases at low temperature, it may be suggested that some of the dimer molecules exist at the surface of liquid Ga, and above 345 K they are destroyed.

3 Conclusion

We adapted the Eyring theory to calculate liquid gallium surface tension. The theory introduces the presence of gallium dimers at the surface and is able to account for the anomalous temperature-dependence of the surface tension. The paper convincingly demonstrates the ability of a simple approach like Eyring theory to provide a semi-quantitative understanding of complex liquid behavior. This paper gives a derivation that describes the temperature-dependence of the surface tension of gallium. Experimentally, it is observed that, in the temperature range of 303–345 K, the surface tension of this element increases upon heating. This behavior is described using the theory of significant structures of Eyring. The new feature introduced in this framework is the presence of gallium dimers at the surface. It may be said that the positive slope of the surface tension of liquid Ga is ambiguous that differs from other liquid metals and has no simple explanation. Gallium has an unusual structure (orthorhombic) in which each metal atom has one close neighbor, and six more distant neighbors. This remarkable structure tends towards discrete diatomic molecules. Gallium is also unusual because the liquid expands by 3.1% when it forms the solid like water, i.e., the solid is less dense than the liquid. This property is unique to Ga, although there are several other pure substances, such as Si, Ge and P that also display this phenomenology. The very low melting point is due to the unusual structure and is also related to the strength of the bonding, but the structure no longer exists in the liquid. The obtained theoretical equation for calculating surface tension of the liquid Ga, based on these facts, is interesting and seems scientific. Therefore, in this manuscript, an attempt was made to describe the anomalous temperature-dependence of the liquid gallium surface tension by using a classical thermodynamics theory approach. The result is very important and can provide additional insight for the understanding of the physical and chemical properties of gallium.

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