Comparing Thermodynamic and Surface Energy models to evaluate and reassess Copper-Nickel bulk and Nano Phase Diagrams

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Abstract. In the present work, Cu-Ni phase diagram is evaluated and assessed using the CALPHAD method for the accurate prediction of liquidus and solidus curves. Phase diagrams were plotted for both bulk and nanoalloys. Phase diagrams for nanoparticles are significantly different from that of the bulk because the melting point of the nanoparticle is a function of particle size. The melting point of the nanoparticle is determined using two different models, Surface Energy model and Enthalpy and Entropy model. Phase diagrams were plotted using both models for Copper-Nickel binary isomorphous system and were compared with the experimental data. It was found that the Enthalpy and Entropy model is in good agreement with the experimental data compared to the Surface Energy model. This is because the Enthalpy and Entropy model considers the thermal interactions at various temperatures whereas the surface energy model only considers the surface free energy of the particle. Also, Enthalpy and Entropy model is a dynamic model because it can predict the melting enthalpy and entropy of the nanoparticles for various particle sizes which result in accurate free energies predictions. Hence, phase diagrams that are predicted using Enthalpy and Entropy model tend to be more accurate than that of the surface energy model.

1. Introduction
Nanomaterials with novel mechanical [1], thermal [2-3], optical [4-6] and electronic properties [7-9] are slowly replacing the conventional materials in almost all fields of engineering and technology. It is hence necessary to understand the behavior of nanomaterials at various temperatures, pressures and compositions. This driving force to understand nanomaterials demand researches to predict phase diagrams for nanomaterials. Phase diagrams for nanomaterials differ from the bulk phase diagrams [10] due to various reasons like surface effects, particle shape, segregation and diverging melting points. Various models are available in the literature [10-17] that predict phase diagrams for nanomaterials considering numerous aspects that affect phase diagrams.

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Wautlet et al [10] calculated the phase diagrams for small materials in a Ge-Si binary system using CALPHAD approach and showed that the phase diagrams of nanoparticles deviate from bulk. In another study by Vallee et al [11], the effect of segregation was included into the model and the phase diagram of the nanoparticles were studied. In yet another similar study by Wautlet et al [12,13], the phase diagrams were studied for the non-spherical nanoparticles. In all of the above papers [10-13], the melting point of the nanoparticles were calculated using direct or indirectly derived formula from the Gibbs-Thompson effect. In the present paper, this model is referred to as “Surface energy model (SE model)”. In another study [14], the melting entropy and melting enthalpy for the nanoparticles of diameter ‘d’ was employed to predict the phase diagrams. The melting points for the nanoparticles were calculated using melting entropy and enthalpy and this method in the present work will be referred to as “Enthalpy and entropy model (E&E model)”.

CALPHAD is one of the most powerful tools in predicting phase diagrams. However, in most of the cases, predictions might not be accurate compared with the experimentation. It is hence required to develop better models that converge with the experimental results. With many better and novel models available in the literature [10-17] to predict the phase diagrams to utmost accuracy, seldom work has been done to compare these models and assess the accuracy of the model. In the present work, two different models have been compared and validated for the accuracy of the liquidus and solidus curves.

2. Thermodynamic Model for the Bulk

CALPHAD method was implemented to predict bulk phase diagram for the Copper-Nickel binary alloy system. An Ideal solution model was employed in which the free energy of a phase can be generally calculated using [18],

\[ \Delta G = X_A G_A + X_B G_B + \Delta G_{mix} \]  

where \( X_A \) and \( X_B \) are the weight fractions of the two elements A and B, \( G_A \) and \( G_B \) are the free energies of the respective elements A and B at a given temperature. The first two terms on the right-hand side of the equation (1) is derived from the rule of mixtures which hold good for mechanical mixtures. However, when the two elements like Copper and Nickel are mixed, they are not just mechanical mixtures but there is an additional free energy due to mixing called as free energy of mixing. The free energy of mixing is given by [18],

\[ \Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} \]  

\( \Delta H_{mix} \) is called as the enthalpy of mixing, \( T \) is the temperature and \( \Delta S_{mix} \) is called as the configurational entropy. In the present work, it has been assumed that the enthalpy of mixing is zero indicating that the model is “Ideal solution model”. Now the free energy of mixing is given by [18]

\[ \Delta G_{mix} = - T \Delta S_{mix} \]  

There is however additional entropy called configurational entropy that plays a major role in deciding the solidus and liquidus. The configurational entropy is independent of the element and arises purely because of the configuration. The configurational entropy for two different elements is given by [18]

\[ \Delta S_{mix} = k \ln W \]  

\( k \) is the Boltzmann constant and \( W \) is the various ways of arranging \( n \) atoms in \( N \) atoms.

On further simplification and by applying Stirling’s approximation, the above equation reduces to [18]

\[ \Delta S_{mix} = - R (X_A \ln X_A + X_B \ln X_B) \]  

Substituting the equation (5) into equation (3) yields

\[ \Delta G_{mix} = R T (X_A \ln X_A + X_B \ln X_B) \]  

Above equation signifies the additional free energy arising due to the configurational entropy. Now the total free energy can be calculated using equations (1,2 & 5) given by

\[ \Delta G = X_A G_A + X_B G_B + R T (X_A \ln X_A + X_B \ln X_B) \]  

Above equation can be used to calculate the free energy plots for various phases. The equations to predict free energy curves for two different phases are given by [18]

\[ \Delta G^u = X_A G_A^u + X_B G_B^u + R T (X_A \ln X_A + X_B \ln X_B) \]  

\[ \Delta G^l = X_A G_A^l + X_B G_B^l + R T (X_A \ln X_A + X_B \ln X_B) \]
According to the equality of chemical potential principle, two equations to predict the solidus and liquidus with varying temperature is given by [19]

$$RT \left( \frac{X_S}{X_l} \right) = H_A \left( 1 - \frac{T}{T_{mA}} \right)$$

(10)

$$RT \left( \frac{1 - X_S}{1 - X_l} \right) = H_B \left( 1 - \frac{T}{T_{mB}} \right)$$

(11)

The solidus and liquidus for various temperatures were calculated for Copper-Nickel binary system. The predicted phase diagram is shown below in Figure 1.

![Cu-Ni phase diagram](image)

**Figure 1.** Predicted phase diagram for the bulk Copper-Nickel binary system

### 3. Thermodynamic Model for Nanomaterials:

The phase diagrams for the nanomaterials are significantly different from that of the bulk [10]. This difference is mainly attributed to the change in the melting point of the nanoparticle with the particle size. Various models are available to predict the melting point of the nanoparticle [10-14]. In the present work, two different models are considered to predict the melting point and the phase diagram of nanoparticles.

#### 3.1. Surface energy model:

This model is equivalent to the Gibb’s Thomson effect which states that the melting point of a particle is function of its size. According to this model, the melting point of the nanoparticle is given by [10-13]

$$T_m(d) = T_m(\infty) \left( 1 - \frac{\alpha}{2R} \right)$$

(12)

Where $T_m(d)$ is the melting point of the nanoparticle of diameter $d$, $T_m(\infty)$ is the melting point of the bulk, $\alpha$ is a constant that varies between 0.4 and 3.3 nm and $R$ is the radius of the nanoparticle.

The melting point of a nanoparticle is plotted as a function of particle radius and is shown in Figure 2.
3.2. Enthalpy and entropy model:

In another model given by [14], the melting enthalpy and entropy of the nanoparticle can be calculated by

\[ H_m(d) = H_m(b) \left( 1 - \left( \frac{d}{d_0} - 1 \right)^{-1} \right) \exp \left( \frac{-2 S_m(b)}{3 R} \right) \left( \frac{d}{d_0} \right)^{-1} \]  \hspace{1cm} (13)

\[ S_m(d) = S_m(b) \left( 1 - \left( \frac{d}{d_0} - 1 \right)^{-1} \right) \]  \hspace{1cm} (14)

Where \( H_m(d) \) is the melting enthalpy of the nanoparticle of diameter \( d \), \( H_m(b) \) is the bulk melting enthalpy, \( d \) is the diameter of the nanoparticle, \( d_0 = 6h \), \( h \) is the bond length, \( S_m(b) \) is the bulk melting entropy, \( S_m(d) \) is the melting entropy of the nanoparticle of diameter \( d \).

Using the above equations, the melting point of the nanoparticle can be determined by the thermodynamics given by

\[ T_m = \frac{H_m}{S_m} \]  \hspace{1cm} (15)

The plot of melting point of the nanoparticle versus the particle size is shown below in Figure 3.
3.3. Comparison between the two models:
The melting point of a nanoparticle as a function of particle size were plotted for two different models and compared as shown in the Figure 4.
It can be seen that the two models diverge in predicting the melting points of the nanoparticle. The divergence between the two models increases as the particle size decreases up to about 10 nm. The melting points differ between the two models significantly below 100 nm diameter. This can be attributed to the two different approaches. The SE model derived basically from the Gibbs-Thompson effect, takes into consideration the surface and vapour pressures to predict the melting point of the small particles. However, the E&E models consider the thermodynamic aspects of melting and hence differs from the former model. The phase diagram for Copper-Nickel system was generated considering these two different models.

3.4. Phase diagram prediction using two models:
The two simultaneous equations (10) and (11) were used to predict Copper-Nickel phase diagrams. The only change in the equation is using different melting point for the nanoparticle according to the prediction of the model. The phase diagram is predicted for the Cu-Ni system using the SE model and is compared with the bulk as shown in Figure 5.

![Figure 5. Phase diagrams for bulk and nanoparticle of size 25 nm plotted with SE model](image)

The melting point of the nanoparticle determined by the E&E model is used and the phase diagrams are plotted for both bulk and the nanoparticle and compared as shown in Figure 6.
4. Experimental Validation and Discussions:
The predicted phase diagrams were validated with the experimental results carried out by Jiri Sopousek [20]. The phase diagrams were plotted for two models and compared with the bulk and is shown in Figure 7.
Table 1 shows the experimental results compared with the SE model and E&E model.

| Spacing | Nanoparticle Calculated | Enthalpy and Entropy model | Surface energy model |
|---------|-------------------------|---------------------------|---------------------|
|         | 1093                    | 1060.18                   | 1003.2              |
|         | Experimental            |                           |                     |
|         | 1068                    | -                         | -                   |
| Error   | 2.34 %                  | 0.73 %                    | 6.46 %              |

It can be seen from the above table that the E&E model better predicts the experimental results carried out by [20]. The SE model [10-13] deviates by 6%. This is mainly attributed to the idea that the SE model only deals with the surface free energy and calculates the free energy curves. However, the E&E model [14] considers the principal thermodynamic aspects like enthalpy and entropy. The melting enthalpy of the nanoparticle is significantly different from that of the bulk. Similarly, the melting entropy of the nanoparticle also differs. These aspects are not considered in SE model and hence the melting point predictions are not very accurate. Reasonably accurate predictions are possible in E&E model because the melting point is the function of melting enthalpy and entropy unlike surface energy model. The error is significantly reduced in the E&E model and does seem to work better in predicting the solidus and liquidus curves for nanoparticles. The major drawback in the SE model is that it does not contemplate any aspect of thermodynamics except for the surface free energy. Although surface free energy is the major contributor in predicting the melting point, there are also other features like additional enthalpy and entropy that are equally important. The present works thus proves to be significantly better in predicting the phase diagrams for binary systems.

5. Conclusion:
The two models, SE model and enthalpy and entropy model were utilized to predict the melting point of the nanoparticle and also to plot phase diagrams. The SE model underestimates the solidus curve for a 25nm particle size whereas the E&E model estimates with reasonable accuracy. This is due to the fact that the E&E model considers the thermodynamic parameters to predict the melting point of the nanoparticle whereas the SE model only consider the surface free energy.

References
[1] George R, Kashyap K T, Rahul R, Yamdagni S, Strengthening in carbon nanotube/aluminium (CNT/Al) composites, *Scripta Materialia* 53 (2005) 1159–1163.
[2] Jianwei Che, Tahir Cagın and William A Goddard III, Thermal conductivity of carbon Nanotubes, *Nanotechnology* 11 (2000) 65–69.
[3] Motoo Fujii, Xing Zhang, Huaqing Xie, Hiroki Ago, Koji Takahashi, Tatsuya Ikuta, Hidekazu Abe and Tetsuo Shimizu, Measuring the Thermal Conductivity of a Single Carbon Nanotube, *PRL* 95, 065502 (2005).
[4] Guo G Y, Chu K C, Linear and nonlinear optical properties of carbon nanotubes from first-principles calculations, *Physical Review B* 69, 205416 (2004).
[5] Misewich J A, Electrically Induced Optical Emission from a Carbon Nanotube FET", *Science* 300 (5620): 783–786.
[6] J. Chen; et al. (2005). "Bright Infrared Emission from Electrically Induced Excitons in Carbon Nanotubes", *Science* 310 (5751): 1171–1174.
[7] Philip Collins G, Keith Bradley, Masa Ishigami, Zettl A, Extreme Oxygen Sensitivity of Electronic Properties of Carbon Nanotubes, *Science*, 10 Mar 2000:Vol. 287, Issue 5459, pp. 1801-1804.

[8] Teri Wang Odom, Jin-Lin Huang, Philip Kim, Charles Lieber M, Atomic structure and electronic properties of single-walled carbon nanotubes, *Nature* 391, 62-64 (1 January 1998).

[9] Min Ouyang, Jin-Lin Huang, Charles Lieber M, Fundamental Electronic Properties and Applications of Single-Walled Carbon Nanotubes, *Acc. Chem. Res.*, 2002, 35 (12), pp 1018–1025.

[10] Wautelet M, Dauchot J P, Hecq M, Phase diagrams of small particles of binary systems: a theoretical approach, *Nanotechnology* 11 (2000) 6–9.

[11] Vallée R, Wautelet M, Dauchot J P, Hecq M, Size and segregation effects on the phase diagrams of nanoparticles of binary systems, *Nanotechnology* 12 (2001) 68–74.

[12] Wautelet M, Dauchot J P, Hecq M, On the phase diagram of non-spherical nanoparticles, *J. Phys.: Condens. Matter* 15 (2003) 3651–3655.

[13] Wautelet M, Dauchot J P, Hecq M, Size effects on the phase diagrams of nanoparticles of various shapes, *Materials Science and Engineering C* 23 (2003) 187–190.

[14] Ouyang G, Tan X, Wang C X, Yang G W, Solid solubility limit in alloying Nanoparticles, *Nanotechnology* 17 (2006) 4257–4262.

[15] Joongchul Park, Joonho Lee, Phase diagram reassessment of Ag–Au system including size effect, *Computer Coupling of Phase Diagrams and Thermochemistry* 32 (2008) 135–141.

[16] Joonho Lee, Joongchul Park, Toshihiro Tanaka, Effects of interaction parameters and melting points of pure metals on the phase diagrams of the binary alloy nanoparticle systems: A classical approach based on the regular solution model, *CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry* 33 (2009) 377-381.

[17] Shirinyan A S, Gusak A M, Wautelet M, Phase diagram versus diagram of solubility: What is the difference for nanosystems?, *Acta Materialia* 53 (2005) 5025–5032.

[18] Porter D A, Easterling K E, Phase Transformations in Metals and Alloys, second edition, Chapman and Hall, 1996.

[19] Jacques Steininger, Thermodynamics and Calculation of the Liquidus-Solidus Gap in Homogeneous, Monotonic Alloy Systems, *Journal of Applied Physics*, volume 41, 6 May 1970.

[20] Jiri Sopousek, JanVrestal, Jiri Pinkas, Pavel Broz, Jiri Bursik, Ales Styskalik, David Skoda, Ondrej Zobac, Joonho Lee, Cu–Ni nanoalloy phase diagram – Prediction and experiment, *CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry Volume 45*, June 2014, 33-39.

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