Thermodynamic aspects of nanomaterials

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Thermodynamic properties of nanosized materials



Density is an intensive property of a substance because it does not depend on the amount of that substance; mass and volume, which are measures of the amount of the substance, are extensive properties.

This is not the case in nanoscaled system!

V is a non-extensive variable, Density is a non-intensive variable









Buffat et al.



Available online at www.sciencedirect.com





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Size effect on melting temperature of nanosolids W.H. Qi*

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Model

$$E_{\rm tot} = E_0(n-N) + \frac{1}{2}E_0N, \qquad (1)$$

n = total number of atoms N = number of atoms at the surface E_0 cohesive energy per atom

Then the cohesive energy per mole (E_p) of the nanosolid equals AE_{tot}/n , where A is the Avogadro constant. Eq. (1) can be rewritten as

$$E_{\rm p} = E_{\rm b} \left(1 - \frac{N}{2n} \right) \quad (2) \quad \text{With } E_{\rm b} = AE_0$$

It is known that both the cohesive energy and the melting temperature are parameters to describe the bond strength of materials, and it is reported that the cohesive energy is linear relation to the melting temperature for a material [1,2]. Since the cohesive energy of a nanosolidis the function of N/n, its melting temperature should follow a relation similar to Eq. (2),

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

 T_{mp} = melting temperature of the nanosized crystal T_{mb} melting temperature of the bulk material

[1] J.H. Rose, J. Ferrante, J.R. Smith, Phys. Rev. Lett. 47 (1981) 675.[2] J. Ferrante, J.H. Rose, J.R. Smith, Appl. Phys. Lett. 44 (1984) 53.

Nanosolids	N/n	
Spherical nanosolids	4d/D	
Disk-like nanosolids	(4/3)d[(1/h+2/l])	
Nanowires	(8/3)d/l	
Nanofilms	(4/3)d/h	

The calculated N/n for different nanosolids



Melting temperature of Sn nanoparticles as a function of particle size. The solid line is the calculated results by Eq. (3), where the melting temperature of bulk Sn is 505 K



Melting temperature of In nanowires as a function of wire diameter. The solid line is the calculated results by Eq. (3), where the melting temperature of bulk In is 429.8K

Melting temperature of In nanofilms as a function of film height. Materials Science Forum Vol. 653 (2010) pp 55-75 Online available since 2010/Jun/02 at www.scientific.net © (2010) Trans Tech Publications, Switzerland doi:10.4028/www.scientific.net/MSF.653.55

Prediction of Phase Diagrams in Nano-sized Binary Alloys

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Thermodynamics in Small Particle Systems.

According to Pawlow[P. Pawlow : Z. Phys. Chem. Vol.65 (1909), p 1.] the chemical potentials of pure element X in liquid and solid small particles with radius r,

$$\mu_{X}^{Liquid,Particle} = \mu_{X}^{Liquid,Bulk} + \frac{2\sigma_{X}^{Liquid} \cdot V_{X}^{Liquid}}{r}$$
$$\mu_{X}^{Solid,Particle} = \mu_{X}^{Solid,Bulk} + \frac{2\sigma_{X}^{Solid} \cdot V_{X}^{Solid}}{r}$$

 V_X^{Solid} and V_X^{Liquid} are the molar volumes of pure element X in solid and liquid phases.

Equilibrium:

$$\mu_X^{Liquid, Particle} = \mu_X^{Solid, Particle}$$

$$\mu_X^{\text{Liquid,Bulk}} - \mu_X^{\text{Solid,Bulk}} = \frac{2}{r} (\sigma_X^{\text{Solid}} \cdot V_X^{\text{Solid}} - \sigma_X^{\text{Liquid}} \cdot V_X^{\text{Liquid}})$$

Gibbs energy change of fusion of the element X

 $\mu_X^{Liquid,Bulk} - \mu_X^{Solid,Bulk} = \Delta H_{m,X} \cdot (1 - \frac{T}{T_{m,X}^{Bulk}})$

Approximation: $\Delta S_{m,X} = \frac{\Delta H_{m,X}}{T_{m,X}}$

$$\frac{T}{T_{m,X}^{Bulk}} = 1 - \frac{1}{r} \cdot \frac{2}{\Delta H_{m,X}} \cdot (\sigma_X^{Solid} \cdot V_X^{Solid} - \sigma_X^{Liquid} \cdot V_X^{Liquid})$$



Fig.2. Change in melting point of pure Au with radius of a particle.

Experimental Value:

- [32] C.J. Coombes : J. Phys. F Vol.2 (1972), p.441.
- [33] J.R. Sambles : Proc. Roy. Soc. Lond. A. Vol.324 (1971), p.339.

Binary Alloy Phase Diagrams of Small Particle Systems consisting of Pure Solid Phases and Liquid Phase.

The phase diagrams can be evaluated by only the information on the Gibbs energy in the bulk and the surface tension of liquid phase, which can be obtained as functions of temperature. Example : Cu-Bi Au-Si $\Delta G^{Total} = \Delta G^{Bulk} + \Delta G^{Surface}$

$$\Delta G^{Bulk} = N_A \Delta G_A^{LS} + N_B \Delta G_B^{LS} + G^{Excess,L} + RT \left(N_A \ln N_A + N_B \ln N_B \right)$$

$$G^{Excess\,,L} = N_A N_B \left\{ L_0 + L_1 \left(N_A - N_B \right) + L_2 \left(N_A - N_B \right)^2 + L_3 \left(N_A - N_B \right)^3 \right\}$$

where ΔG_A^{LS} and ΔG_B^{LS} are Gibbs energies of pure liquid phases relative to those of pure solid

L = interaction parameter

Example

Cu

$$G_{Cu}{}^{L} = -48.7 - (-142.53101) \cdot T + 31.380005 \cdot T \cdot (1.0 - \ln T)$$

$$G_{Cu}{}^{S} = -8044.1 - (-110.40401) \cdot T + 24.852997 \cdot T \cdot (1.0 - \ln T)$$

$$-0.0037865 \cdot T^{2}/2 - (-138909)/2/T$$

$$\Delta G_{Cu}{}^{LS} = G_{Cu}{}^{L} - G_{Cu}{}^{S}$$

Pb

$$G_{Pb}{}^{L} = -7347.8 - (-133.83501) \cdot T + 36.112106 \cdot T \cdot (1.0 - ln T) -(-0.0097362) \cdot T^{2}/2 - (-279073)/2/T - 3.2384 \times 10^{-6} \cdot T^{3}/6 G_{Pb}{}^{S} = -7608.7 - (-75.81465) \cdot T + 24.221176 \cdot T \cdot (1.0 - ln T) -0.0087111 \cdot T^{2}/2 \Delta G_{Pb}{}^{LS} = G_{Pb}{}^{L} - G_{Pb}{}^{S}$$

 $G^{\text{Excess},\text{L}} = N_{\text{A}}N_{\text{B}}\{L_{0} + L_{1}(N_{\text{A}} - N_{\text{B}}) + L_{2}(N_{\text{A}} - N_{\text{B}})^{2} + L_{3}(N_{\text{A}} - N_{\text{B}})^{3}\} / \text{J} \cdot \text{mol}^{-1}$

Cu-Pb [43]

$$L_0 = 27190.2 - 4.21329 \cdot T$$

 $L_1 = 2229.2 - 0.53584 \cdot T$
 $L_2 = -7029.2 + 6.48832 \cdot T$
 $L_3 = -7397.6 + 5.07992 \cdot T$

$$\Delta G^{Total} = \Delta G^{Bulk} + \Delta G^{Surface}$$

$$\Delta G^{\text{Surface}} = \frac{2\sigma^L V^L}{r} - \frac{2\left(N_A \sigma^S_A V^S_A + N_B \sigma^S_B V^S_B\right)}{r}$$

R.A. Swalin : Thermodynamics of Solids, John Wiley, New York (1962).

$$\sigma_X^S = 1.25\sigma_{X,mp}^L + \frac{\partial \sigma_X^L}{\partial T} \left(T - T_{X,mp} \right) \qquad \left(X = A \text{ or } B \right)$$

Correction factor because surface tension of solid at T_m is 25 larger than surface tension of liquid

Molar volume of the liquid alloy: $V^{L} = N_{A}V_{A}^{L} + N_{B}V_{B}^{L}$

Molar volume of the solid
$$V_X^S = \frac{V_X^L}{(1 + \alpha_X)}$$

where $\alpha_{\rm X} = (V_{{\rm X},{\rm m}}^{\rm L} - V_{{\rm X},{\rm m}}^{\rm S})/V_{{\rm X},{\rm m}}^{\rm S}$, which is the ratio of the volume change of solid due to the fusion Tanaka

	Surface tension σ_{x}^{L} / N	m ⁻¹ of pure liquid con	ponents [47] $\frac{\partial \sigma}{\partial T} / \operatorname{Nm}^{-1} \mathrm{T}^{-1}$	
Cu	$\sigma_{\rm Cu}^{\rm L} = 1.303 - 0.00023 \cdot (T - 1356.15) - 0.00023$			
Pb	$\sigma_{\rm Pb}^{\rm L} = 0.458 - 0.00013 \cdot (T - 600.55)$		-0.00013	
Bi	$\sigma_{\rm Bi}^{\rm L} = 0.378 - 0.00007 \cdot (T - 544.1)$ -0.00007			
Au	$\sigma_{Au}^{L} = 1.169 - 0.00025 \cdot (T - 1336.15) - 0.00025$			
Si	$\sigma_{\rm Si}^{\rm L} = 0.865 - 0.00013 \cdot (T - 1687.15) - 0.00013$			
	Molar volume / m ³ mol ⁻¹ of pure liquid components [47]			
Cu	$V_{\rm Cu}^{\rm L} = 7.94 \times 10^{-6} \cdot \{1.0 + 0.0001 \cdot (T - 1356.15)\}$			
Pb	$V_{\rm Pb}{}^{\rm L} = 19.42 \times 10^{-6} \cdot \{1.0 + 0.000124 \cdot (T - 600.5)\}$			
Bi	$V_{\rm Bi}^{\rm L} = 20.80 \times 10^{-6} \cdot \{1.0 + 0.000117 \cdot (T - 544.1)\}$			
Au	$V_{\rm Au}^{\rm L} = 11.3 \times 10^{-6} \cdot \{1.0 + 0.000069 \cdot (T - 1336.15)\}$			
Si	$V_{\rm Si}^{\rm L} = 11.1 \times 10^{-6} \cdot \{1.0 + 0.00014 \cdot (T - 1687.15)\}$			
	$\sigma_{\rm X,m.p.}$ ^L / Nm ⁻¹ [47]	$T_{\rm X,m.p.} / {\rm K} [47]$	$\alpha_{\rm X} = (V_{{\rm X},{\rm m}}^{\rm L} - V_{{\rm X},{\rm m}}^{\rm S})/V_{{\rm X},{\rm m}}^{\rm S}$ [48]	
Cu	1.303	1356.15	0.0396	
Pb	0.458	600.55	0.0381	
Bi	0.378	544.1	-0.0387	
Au	1.169	1336.15	0.055	
Si	0.865	1687.15	-0.095	



Fig.4. Activities of components in bulk and surface tension of liquid alloys.



Fig.5. Change in melting points of Pb, Cu, Bi and Si with radius of a particle.





Start with Gibbs free energy: G = U - TS + PV = F + PV

Note that PV is usually much less than U for condensed matter:

 $G \cong F$

We can write the Gibbs free energy of mixing for two phases with the same structure:

 $G = x_{\rm A}G_{\rm A} + x_{\rm B}G_{\rm B} + I_{\rm AB}x_{\rm A}x_{\rm B} - T\Delta S_{\rm mixing}$

Here I_{AB} denotes the Interaction energy between the two components (this is the same form as the non-regular solution model)

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Solid solubility limit in alloying nanoparticles

G Ouyang, X Tan, C X Wang and G W Yang¹

Accordingly, we obtain the Gibbs free energies of α and β phase solid solutions of components A and B with two different structures in the system as follows:

$$G^{\alpha} = x_{A}G_{A} + x_{B}(G_{B} + \Delta G_{B}) + I^{\alpha}_{AB}x_{A}x_{B} - T\Delta S_{\text{mixing}}$$

$$G^{\beta} = x_{A}(G_{A} + \Delta G_{A}) + x_{B}G_{B} + I^{\beta}_{AB}x_{A}x_{B} - T\Delta S_{\text{mixing}}$$
(5)
(6)

where ΔG_i (*i* = A, B) and I_{AB}^i (*i* = α , β) denote the Gibbs free energy of the structural transformation of the single component (e.g. from the α to the β phase) and the interaction energy between two phases.

For the single components the Gibbs free energy for melting can be written as:

$$G_{\rm A} = H_{\rm mA} \left(d_{\rm A} \right) - T S_{\rm mA} \left(d_{\rm A} \right)$$

$$G_{\rm B} = H_{\rm mB} \left(d_{\rm B} \right) - T S_{\rm mB} \left(d_{\rm B} \right)$$

Here the melting enthalpy and entropy are considered to be functions of diameter!

$$H_{\rm m}(d) = H_{\rm mb} \left(1 - 1/\left(d/d_0 - 1\right)\right) \\ \times \exp\left(-\frac{2S_{\rm mb}}{3R} \times \frac{1}{d/d_0 - 1}\right)$$
(9)
$$S_{\rm m}(d) = S_{\rm mb} \left(1 - 1/\left(d/d_0 - 1\right)\right)$$
(10)

where $H_{\rm mb}$ and $S_{\rm mb}$ are the bulk melting enthalpy and entropy, *R* is the ideal gas constant and d_0 is the critical diameter of nanoparticles. Note that there is an assumption that almost all atoms are situated on the surface of nanoparticles, and the surface of the solid is the same as that of the liquid,

Size-dependent interaction energy and values for the structural transformation are also discussed. This can be inserted into the Gibbs free energy for the α and β phases, and the phase diagram determined from the common tangent.

From this it is determined that the solid solubility increases with decreasing diameter, with a threshold around 20 nm.





Large Melting-Point Hysteresis of Ge Nanocrystals Embedded in SiO2 Q. Xu, I. D. Sharp, C.W. Yuan, D. O. Yi, C.Y. Liao, A. M. Glaeser, A. M. Minor, J.W. Beeman, M. C. Ridgway, P. Kluth, J.W. Ager III, D. C. Chrzan, and E. E. Haller PHYSICAL REVIEW LETTERS, 97, 155701, Oct. 2006





Transient liquid phase sintering of CeO_2 with Co



Fig. 1. Dependence of the relative density on sintering temperature of pure 2 mol-% MO doped nanosized $Ce_{0.8}Gd_{0.2}O_{1.9}$ powder compacts. (Cons heating rate of 5 °C/min to 1200 °C.)

Gauckler et al. Adv. Mat. 2001,13 1081







Fig. 7. Size-dependent melting of CoO layers on CGO with a = 470 °C nm. Z delineates the thickest part of the CoO lens between two spherical powder particles.



Fig. 6. a) Dark field TEM and b) bright field TEM of an amorphous grain boundary phase in Ce_{0.8}Gd_{0.2}O_{1.9} doped with 1 mol-% CoO sintered at 900 °C for 10 min. c) HRTEM image of 5 mol-% CoO doped CGO equilibrated at $T_{\text{sinter}} = 1400 \text{ °C}$ for 2 h. The grain boundary thickness is less than 0.5 nm.

Gauckler et al. Adv. Mat. 2001,13 1081

Nanoparticles are often polymorphs of bulk material with different physical and chemical properties

Lattice Constant for Pt as a function

of cluster size Klimenkow et al, Surf. Sci. 391 (1997) 27-36 4,0 2,80 attice Constant [Å] Pt Bulk 3,9 2.75 2,70 3,8 2,65 atomic dista 3,7 2,60 2,55 3,6 2,50 3,5 -2,45 3,4 25 30 35 40 15 20 10 Particle Size [Å]





Inhomogeneous State of Nanoparticles

Crystal lattice _____ Segregation $\Delta a / a = \theta_2 \kappa \frac{\gamma}{l'} \qquad r_s^* = \theta_5 . \Delta_s$ $\theta_5 = 5; \theta_2 \approx 1; \theta_6 \approx 3.5; \Delta s \approx 3nm$



κ volume compressibility coefficient
1 radiusof the particle
γ surface energy

Inhomogeneous State of Nanoparticles

$$r_{sI}^* = \theta_6 a. \left(\frac{\delta_s^2 a^3 (G - \overline{G})}{kT}\right)^{1/3}$$

 κ volume compressibility coefficient 1 radius of the particle γ surface energy $\delta_s = (a_f / a - 1) a_f$ is the effective radius of a foreign atom. G shear modulus





Free energy of two-component nanoparticles



Fig. 2. Schematic transformation of two-element nanoparticle with initially hamogeneous structure into the heterogeneous phase.

 f_1 and $f_2 = 1 - f_1$ are the concentrations of component A in nanoparticles



Example: Alumina







Phase stability



 $F_{v_2,f_2} + \frac{\gamma_2 S_2}{V_2} < F_{v_1,f_1} + \frac{\overline{\gamma_1} S_1}{V_2}$

Example: m – t Zirconia; TiO2: Anatase - Rutil

$$\Delta T_{t^{-}} \frac{T_{t}}{\lambda} \cdot \left(\frac{\overline{\gamma}_{2} S_{2}}{V_{2}} - \frac{\overline{\gamma}_{1} S_{1}}{V_{1}} \right)$$

 λ is the heat of phase transition per unit volume T_{t} phase transition temperature

With decreasing nanoparticle size the phase with lower surface energy (packed more tightly) become energetically favoured. For example, in the case of the common body-centered cubic (BCC) and face-centered cubic (FCC) crystal lattice the latter may become energetically more favourable

Stable structures of TiO₂ as a function of cluster size

Ranade et al Proc. Nat. Acad. Sci. 99 (2002) 6476





Phase diagramme I







Phase diagramme II





W.A.Jesser, Mat Res Innovat (1999) 2; 211-216.

Materials properties are not constant

Calorimetric measurements show that the energy dependence of supported Pb particles vary much more quickly than predicted by the Gibbs-Thompson relationship."This shows that the surface energy increases substantially as the radius decreases below 3 nm." C.T Campbell et. al. Science 298 (2002) 811-814



Equilibrium Thermodynamics

A Different Approach to Nanothermodynamics

Terrell L. Hill, Nano Letters Vol 1 (2001) 273-275

"In contrast to macrothermodynamics, the thermodynamics of a small system will usually be different in different environments."

Motivation

- We have so far considered size effects arising from surface curvature
- This treatment is a first approximation more rigorous treatments also exist
- Other types of size effects have not been considered
- Here we will survey current studies (theoretical and experimental) of nanoscale thermodynamics
- Note that this field is fairly new still many different theories and unclear effects!

Nanothermodynamics - Hill

- The study of small systems at equilibrium requires modification of ordinary thermodynamics
- This was first studied in 1961-64 by T.L. Hill
- Definitions of state functions must be modified by correction terms, accounting for surface effects, edge effects, translation, rotation, etc.
- This leads to some surprising results, in particular that thermodynamic properties depend on the environment – that is, which variables are allowed to be independent
- Entropy, for example, depends on how "open" a small system is

Ensembles of Small Systems

- Nanothermodynamics is developed for ensembles of small systems – that is, macroscopic samples containing very many identical small components
- This allows for the connection of macroscopic variables and functions to small systems.
- In other words, measurements made on larger samples can be connected to the properties of individual small systems
- The equations of nanothermodynamics connect the macroscopic properties of an ensemble to the individual small systems that it contains.

A Different Approach to Nanothermodynamics

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NANOLETTERS 2001 Vol. 1, No. 5 273-275

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> Thermodynamics for macroscopic systems: dU = TdS - pdV

$$dU = TdS - pdV + \sum \mu_i dN_i$$
 Gibbs

For example, if the system is a small one-component spherical aggregate that has a nonnegligible surface free energy term proportional to $N^{2/3}$, above equation is no longer applicable.

Generalization of Thermodynamics

Consider first the internal energy of a macroscopic system. For a multicomponent system without external fields, an arbitrary change can be written as:

$$dU = TdS - PdV + \sum_{k=1}^{c} \mu_k dn_k$$

For an ensemble of small systems, the change in internal energy for the entire system is the sum of the small systems.

$$dU_{t} = TdS_{t} - PdV_{t} + \sum_{k=1}^{c} \mu_{k} dn_{k,t}$$
$$U_{t} = NU$$
$$S_{t} = NS$$
$$V_{t} = NV$$
$$n_{k,t} = Nn_{k}$$

where t indicates "total for the system" and N is the number of systems in the ensemble.

Generalization of Thermodynamics

However when these systems are sufficiently small, correction terms must be introduced.

To account for the correction terms in the internal energy (and other state functions), a new term is introduced:

$$dU_{t} = TdS_{t} - PdV_{t} + \sum_{k=1}^{c} \mu_{k}n_{k,t} + EdN$$
$$E \equiv \left(\frac{\partial U_{t}}{\partial N}\right)_{S_{t}, V_{t}, n_{k,t}}$$

This accounts for the fact that, if V_t , S_t and $n_{k,t}$ are held constant, there is a change in U_t when the change in V and n_k of *individual* systems becomes important (in other words, as N becomes large).

Generalization of Thermodynamics

This new parameter **E** is called the *subdivision potential*, and gives a measure of how the energy of the ensemble changes as the component systems are divided.

In other words, it measures how the internal energy changes as the *average system size* (within an ensemble) changes (for constant *total* volume and number of moles) E is a kind of system (rather than molecule) chemical potential, called the "sub-division potential."

If the systems of the ensemble are macroscopic and are subdivided in order to increase N in eq 4 (e.g., in an extreme case, each system is cut in half to double N), this will not have a noticeable effect on E_t if S_t , V_t , and Ni_t are all held constant. That is, surface effects, edge effects, system rotation and translation, etc., are all negligible for macroscopic systems, and hence *E* is essentially zero: the term E d N does not contribute appreciably to the equation. But the effects just mentioned are *not* negligible if an ensemble of small systems is subdivided to increase N in eq 4. This is because such an increase in N implies a decrease in V and N_i (V_t , and N_{it} are held constant): unlike macroscopic systems, size effects are significant in small systems.

Effect of Environment

In contrast to macrothermodynamics, the thermodynamic properties of a nanoscale system will depend on the *environment* – that is, which variables are chosen as independent

As an example: Consider an incompressible aggregate of N spherical molecules in a temperature bath at T. The aggregate will have a certain entropy S associated with translation, rotation and vibration of molecules within it.

In contrast, consider that the bath contains molecules at a certain potential μ which can go on and off of the aggregate (adsorb/desorb). Here μ and T are environmental variables (while N is not). At equilibrium there will be a mean value of N. If μ is chosen to give the same N as the above case, the entropy will be *larger in this case* because of fluctuations in N.

In other words, entropy depends on which variables are independently controlled. S= f(translation, rotation, vibration)



if μ so that $\overline{N} = N$ in the T,N case,

S in the μ ,T case is larger (additional fluctuation)



Variables:N,P,T Variables:µ,P,T N: 100 – 1000 P can be ignored (incompressibility.

Variables n, P, T

This is a one-component system at T and P where the number of moles in each system is independently fixed. An example would be a colloidal particle of n moles in an inert solvent.

Here the chemical potential of each system (particle) is determined by the number of moles n. The extra term then accounts for the way the chemical potential changes with size (e.g. curvature) for a small system.

$$dU_t = TdS_t - PdV_t + \sum_{k=1}^{c} \mu_k n_{k,t} + EdN$$
$$E = (\mu - \hat{\mu})n$$

Variables µ, P, T

This is an example of a completely "open" one-component system (all environmental variables are intensive). An example would be a colloidal particle in a solvent (at P and T) where the solvent contains molecules at μ which can add to the particle.

It should be noted that in a macroscopic system these three variables *cannot be independent*. However small systems have an extra "degree of freedom" introduced by the extra term in the energy equation.

Variables µ, P, T

In this case the extra term has a more complex form determined by size effects on both pressure and chemical potential.

$$dU_t = TdS_t - PdV_t + \sum_{k=1}^{c} \mu_k n_{k,t} + EdN$$
$$E = U - TS + PV - \mu n$$

It is important to note that entropy will also depend on size for a small system, because fluctuations in variables can be significant.