# Thermodynamic Scale of Dispersive Capacity of Crystalline Bodies

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**Abstract**

It is assumed that most of the excess free energy of a dispersed system is its excess free surface energy, and the excess free energy of a compact body is the free energy determined by the density of dislocations of $10^{12}$ cm$^{-2}$. A dimensionless thermodynamic criterion for the dispersion of crystalline solids $D_L$ is proposed to be considered as a unit of measurement. A thermodynamic scale of dispersity of crystalline bodies is proposed.

**Keywords**

Scale of measurement; dispersity; particle size; defects; thermodynamic properties; free energy.

## Introduction

The nature and the result of physical-chemical processes are determined by dimensionless criteria composed of dimensional parameters describing the phenomenon under consideration. In hydrodynamics, the Reynolds number, which determines the transition of a laminar flow type to a turbulent flow, plays the most important role. In macrokinetics of isothermal transformation, the key value is the Semenov number, which separates the slow and explosive course of the reaction. The Pilling-Bedward criterion is used to characterize the protective properties of an oxide film.

Disperse systems have a number of characteristic properties that determine their behavior, different from compact bodies, in many chemical and physical processes. Although the particle size is based on this phenomenon, it is convenient to measure the degree of this difference by relative units, normalizing the properties of the disperse system to the properties of a compact one. As a standard comparison state for a compact system, one should choose one in which it has the maximum possible value of the properties being compared under the given conditions. The aim of the paper is to show that dispersive capacity as a property of a system can be measured by numerical values of dimensionless criteria characterizing the degree of difference in specific properties of dispersed and compact bodies.

## Results and discussion

We consider the thermodynamic properties of crystalline bodies. The main components of the excess free energy of these bodies are defects of the crystal lattice and surface energy. In a compact body, the ratio of the surface to the mass is small and the value of the surface energy for it can be neglected. Then the standard state of a crystalline compact body can be take its state with the maximum defectiveness of the crystal lattice, which can be characterized by the maximum dislocation density $\rho = 10^{12}$ cm$^{-2}$. The dislocation density is the total length of the dislocation lines per unit volume of the crystal, i.e. the dislocation density has a dimension of cm/cm$^3$. The energy per unit dislocation length is equal to $0.5Gb^2$, therefore the maximum excess free energy of a compact crystalline body $\Delta G_V$ with a volume $V$ will be equal to:

$$\Delta G_V = 0.5\mu b^2 \rho V \, , \tag{1}$$

where $\mu$ is shear modulus, $b$ is Burgers vector, $V$ is body volume.

If we assume that the maximum distortions of the crystal lattice of dispersed particles and compact bodies are approximately equal, the excess free energy of the dispersed particles is equal to:

$$\Delta G_L = \Delta G_V + \Delta G_S = \Delta G_V + \sigma S , \qquad (2)$$

where $\Delta G_S$ is excess free surface energy, $\sigma$ is specific surface energy, $S$ is the surface of all particles occupying the volume $V$.

If we assume that the dispersed system is a collection of monodisperse spherical particles of diameter $L$, then

$$S = 6V/L .$$

Since it is proposed to normalize the excess free energy of dispersed bodies with respect to the energy of maximally deformed compact bodies, then

$$\frac{\Delta G_L}{\Delta G_V} = \frac{\Delta G_S + \Delta G_V}{\Delta G_V} = \frac{\Delta G_S}{\Delta G_V} + 1 = \frac{12\sigma}{Gb^2 L\rho} + 1 . \qquad (3)$$

The discussion of the excess free energy of dispersed systems becomes meaningful when it is several times greater than the free energy of compact bodies. Therefore

$$\frac{\Delta G_L}{\Delta G_V} \approx \frac{12\sigma}{Gb^2 L\rho} . \qquad (4)$$

In [1–3] The particle size satisfying equality (4) was suggested to be called critical $L_{KP}$, and the relation

$$\frac{12\sigma}{Gb^2 L\rho} = D_L \qquad (5)$$

to be called dimensionless thermodynamic criterion for the dispersion of critical bodies $D_L$.

Values of physical properties required for calculation $\Delta G_S$, $\Delta G_V$ and $L_{KP}$ of certain metals are given in Table 1.

From Table 1 it follows that, although for all metals $D_L = 1$ corresponds to the particle size $(500 \pm 250)$ nm, deviations from the mean value can still be a subject for discussion in determining the difference in the thermodynamic properties of particles of different metals having the same dimensions. These differences can be even greater if we compare the thermodynamic properties of dispersed particles with different types of chemical bonds (metallic, covalent, ionic).

Thus, the thermodynamic properties of dispersed systems are determined not only by the particle size,

but also by other physical properties that determine the value $D_L$. In connection with this, it is advisable to adopt a scale for measuring the thermodynamic properties of dispersed systems, based not on the particle size, but on the value $D_L$, i.e. by normalizing these properties to a state in which they are the same for compact and dispersed systems. With this approach, it is possible to regulate the value of the thermodynamic properties of dispersed systems by choosing the particle size as the only controlled quantity that makes up $D_L$, but it is more appropriate to measure the level of change of these properties and to conduct their comparative analysis using the criterion $D_L$.

It is possible to classify dispersed systems simultaneously by thermodynamic properties, and by the sizes of particles. This is convenient since the boundaries of all four proposed classes roughly coincide, although such a coincidence is not necessary.

The discrepancy in the determination of the dispersive capacity in these two approaches can be demonstrated by the example of dispersed copper and silver particles of the same size. For copper particles with a size of 50 nm, the dispersive capacity $D_L = 7.9$, and for silver particles $D_L = 9.0$ (see Table 1). That is, when the particle sizes are equal in this scale, the silver dispersion is 12 % higher than the copper dispersion, and this discrepancy is independent of the particle size.

This approach can be extended to a comparison of the dispersion of compact bodies with nanoscale elements of the structure. In this case, in formulas (2) – (5), the value of the surface energy at the solid-vacuum interface should be replaced by the surface energy of the boundaries of the elements of the structure.

The proposed classification seems to be relevant and useful, especially if we take into account the intensive development of nanotechnology and nanomaterials in recent times. In the same connection, it is noteworthy that it is expedient to extend the proposed approach to normalizing the properties of nanomaterials to the properties of compact bodies without nanostructural components to a wider range of materials. In particular, the properties of optical, acoustic, semiconductor nanomaterials should be normalized to the properties of materials determined by the wavelengths of the de Broglie wavelengths of characteristic processes; magnetic nanomaterials – to the properties of materials with a certain value of domains or domain walls, etc.

Table 1

**Properties of metals and calculated values $\Delta G_S$, $\Delta G_V$ and $L_{KP}$ [1, 4, 5]**

| Metal | Shear modulus, $G \cdot 10^4$, MPa | Burgers vector $b$, nm | Surface energy, MJ/m$^2$ | Molar volume $V$, cm$^3$/mol | $\Delta G_V$, J/mol ($\rho = 10^{12}$ cm$^{-2}$) | $\Delta G_S$, J/mol ($L = 500$ nm) | $L_{KP}$, nm ($\rho = 10^{12}$ cm$^{-2}$) |
|---|---|---|---|---|---|---|---|
| Cu | 4.85 | 0.256 | 1115 | 7.11 | 120 | 95 | 420 |
| Ag | 3.00 | 0.289 | 945 | 10.27 | 128 | 116 | 712 |
| Au | 2.78 | 0.288 | 1230 | 10.20 | 118 | 150 | 640 |
| Mg | 1.75 | 0.321 | 728 | 14.00 | 252 | 122 | 484 |
| Ca | 0.76 | 0.394 | 386 | 26.20 | 117 | 121 | 392 |
| Al | 2.70 | 0.286 | 1040 | 10.00 | 110 | 168 | 564 |
| Ti | 3.96 | 0.295 | 1744 | 10.63 | 183 | 184 | 514 |
| Zr | 3.60 | 0.323 | 1498 | 13.97 | 268 | 251 | 478 |
| Hf | 5.10 | 0.321 | 1553 | 13.47 | 353 | 251 | 354 |
| V | 4.66 | 0.263 | 1627 | 8.36 | 135 | 163 | 604 |
| Nb | 3.75 | 0.286 | 1927 | 10.76 | 165 | 249 | 753 |
| Ta | 6.85 | 0.286 | 2388 | 10.90 | 305 | 312 | 506 |
| Cr | 7.40 | 0.250 | 1591 | 7.23 | 167 | 138 | 412 |
| Mo | 12.8 | 0.272 | 2240 | 9.39 | 444 | 252 | 282 |
| W | 16.0 | 0.274 | 2790 | 9.54 | 573 | 319 | 277 |
| Fe | 8.30 | 0.248 | 1624 | 7.09 | 181 | 138 | 379 |
| Co | 8.15 | 0.251 | 1445 | 6.70 | 172 | 116 | 340 |
| Ni | 7.45 | 0.249 | 1440 | 6.60 | 152 | 114 | 374 |

## Conclusions

It has been shown that dispersive capacity as a property of a system can be measured by numerical values of dimensionless criteria characterizing the degree of difference of specific properties of dispersed and compact bodies.

A new scale for measuring the dispersive capacity of crystalline bodies is proposed. The scale is based on the normalization of thermodynamic properties determined by the excess free energy, dispersed system to the properties of a compact system that does not contain nanoscale structural elements. As the standard state of the latter, the state of maximum saturation with defects in the crystal lattice has been chosen.

## References

1. Levinsly Yu.V. Odin iz bezrazmernyh kriteriev sovmestimosti pokrytij s metallicheskoj osnovoj [One of the dimensionless compatibility criteria for coatings with a metal substrate]. *Pis'ma v ZhTF*, 2003, vol. 29, issue 5, pp. 49-53. (Rus)

2. Levinsly Yu.V. Eshche raz o termodinamicheskom kriterii dispersnosti [Once again on the thermodynamic criterion of dispersive capacity]. *Materialovedenie,* 2004, issue 3, pp. 55-56. (Rus)

3. Levinsly Yu.V. O termodinamicheski obosnovannom kriterii dispersnosti metallicheskih poroshkov [On the thermo-dynamically valid criteria for the dispersion of metallic powders]. *Materialovedenie*, 2003, no. 7, pp. 15-17. (Rus)

4. Fridel' Zh. *Dislokacii* [Dislocations]. Moscow: Mir, 1967, 623 p. (Rus)

5. Ragulya A.V., Skorohod V.V. *Konsolidirovannye nano-strukturnye materialy* [Consolidated nanostructured materials]. Kiev. Naukova Dumka, 2007, 374 p. (Rus)

6. Levinsly Yu.V., Lebedev M.P. *Teoreticheskie osnovy processov spekaniya metallicheskih poroshkov*. Moscow, Nauchnyj mir, 2014, 372 p. (Rus)