Solubility of nanoparticles: nonextensive thermodynamics approach

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Abstract

We show in this study that the concepts of *nonextensive thermodynamics*, introduced in a previous work, can be used to express the variations of the solubility of nanoparticles and porous materials according to their mass by power laws, without the need to resort to fractal dimensions. This results in the demonstration of the Ostwald–Freundlich relation. Our approach is based on a thermodynamic description involving the introduction in the internal energy expression of an extensity, χ. χ is an Euler's function of the particle mass with a homogeneity degree, m, which can be other than one; m is the *thermodynamic dimension* of the system. We use this approach to simulate various behaviours, and show that an increase in solubility can be either higher or lower than that envisaged by the Ostwald–Freundlich relation.

1. Introduction

Values of solid solubilities in aqueous and nonaqueous solvents, at various temperatures, are important data for many industrial activities (including some in the pharmaceutical [1], cosmetic [2], and agrochemical [3] sectors) involving homogeneous solutions of active ingredients. Physicochemists mostly use these magnitudes to determine the free energy of transfer of molecular and saline species between various media [4, 5]. However, when the compounds are in the form of porous or particulate material on a nanometric scale, the solubility becomes a magnitude which varies with the size and the shape of the solid. Consequently, the solubility of a compound in a solvent, at a given temperature, cannot be regarded as a thermodynamic characteristic of the system because it depends on its dimensions. This effect was first reported at the beginning of the 20th century by Ostwald [6] and Freundlich [7], who proposed describing the variations of concentration at saturation, $C_{i(\text{sat})}$, of a spherical particle, of radius r, of a molecular solid, i, in a solvent by the relation

$$\ln \frac{C_{i(\text{sat})}}{C_{i(\text{sat})}^*} = \frac{V_i^*}{RT} \frac{2\gamma^{\text{SL}}}{r}. \tag{1}$$

$C_{i(\text{sat})}^*$ is the concentration of i at saturation when the solid i is in unlimited phase [8] (no size effect), V_i^* the molar volume of i, T the temperature, and R the perfect gas constant. This relation is copied from that proposed by Kelvin [9] for liquid–vapour equilibria. The parameter γ^{SL} is the solid–liquid interfacial tension.

This relation is interesting conceptually because it justifies in a simple way obtaining 'supersaturated' solutions of i in metastable equilibrium, since the aggregates formed in the medium have a radius lower than the critical radius r_c, fixed by the supersaturation ratio $\frac{C_{i(\text{sat})}}{C_{i(\text{sat})}^*}$. However, from a practical point of view, the application of this relation poses a number of difficulties. Real solid particles are not, in general, spherical. This is the case, for example, of mineral or organic crystals and their assemblies, of polymer aggregates, and of many other systems. For some materials, including those which are microporous [10–13], it is difficult to describe their spatial structure from the classical geometrical variables of dimension (volume, surface, length). In such conditions, the concept of liquid–solid interfacial tension, γ^{SL}, is inappropriate. This led Mihranyan and Strømme [14] to propose a fractal approach to solubility, based on an approach used by Yin [15] for describing the capillary condensation phenomena. Thus, they predicted the variations of the solubility of solid electrolytes according to the particle size for various values of fractal dimension D.

The principal problem that this type of approach in physicochemistry engenders is that the introduction of a fractal dimension is not straightforward because the mathematical functions underlying the fractality are not naturally included in those of classical thermodynamics. Indeed, classical thermodynamics requires that the variables of dimension (volume, surface, length) used in the expression of internal energy are continuous and continuously derivable functions.

The current trend is to link thermodynamics to fractal dimensions via nonextensive and nonadditive functions of state [16]. Whether or not one accepts these approaches, it is clear that they are internally consistent and constitute a homogeneous theoretical basis. Their common point is that the introduction of fractal dimensions in thermodynamics inevitably involves the loss of the extensivity of the functions of state. Recent works [17, 18] show that the Tsallis approach can be connected to the nanothermodynamics proposed by Hill [19]. This allows introduction of the fractality in the thermodynamics in a correct way.

We have developed a *nonextensive thermodynamics* approach [20] which does not involve fractality. Its basis is the same as that of classical thermodynamics with the same functions of state, but supposes that they can be nonextensive. This property is introduced by means of integer or fractional *thermodynamic dimensions*. This approach is particularly adapted to the description of the complex systems (porous, interpenetrated phases, dispersed solutions, nanoparticles, etc) and can be used to describe a number of physicochemical behaviours by power laws [21, 22]. Here, we use this approach to tackle the issue of the solubility of nanoparticles and porous systems.

To facilitate understanding of our approach, we will describe some of the bases of nonextensive thermodynamics (NET) [20].

2. Theory

2.1. Conceptual bases of nonextensive thermodynamics

In a system defined by its content (n_1, n_2, n_i moles), the description of its behaviour requires the usual variables, S, V, and n_i, and a variable of extensity χ. The internal energy can then be

written

$$dU = T\,dS - P\,dV + \sum \mu_i\,dn_i + \tau\,d\chi \tag{2}$$

τ is an intensive tension extent, associated with χ. It can be positive or negative. This shape is classical, and in the case of interfacial systems χ is associated with an area and τ with a surface tension. Classically, in thermodynamics, the variables of extensity associated with tension extents are assumed to be extensive variables, i.e. Euler's functions of the system mass of order $m = 1$. We considered the possibility that they are not extensive ($m \neq 1$). In the light of this assumption, we will specify the properties of χ. Consider a system consisting of n_1 moles of 1, n_2 moles of 2, n_i moles of i; the extensity χ is a function of the system mass

$$\chi = \chi(n_1, n_2, \ldots, n_i). \tag{3}$$

By convention, this extent has the property of an Euler's function of order m. If the system content is multiplied by λ, then

$$\chi_\lambda = \chi(\lambda n_1, \lambda n_2, \ldots, \lambda n_i) = \lambda^m \chi. \tag{4}$$

The parameter m is the homogeneity degree of the Euler's function. This is, by convention, *the thermodynamic dimension of the system*. Its value can be equal to one, in which case classical thermodynamics applies. The introduction of the nonextensive thermodynamics in the extensity magnitudes implies that the functions of state of the thermodynamics (U, S, etc) are no longer extensive. Consequently, the tension extents associated with the extensities may not be intensive. We chose, by convention, to conserve this property for the temperature[1] T and for τ. For consistency, the chemical potentials and the pressures become nonintensive extents; this means that they vary with the system mass. Kelvin's relation [9], showing that the vapour pressure above a water drop depends on the sphere radius, is thus an illustration of this phenomenon.

We show that for a nonextensive system constituted of n moles of compound, of volume V, of extensity χ and of dimension m, there is a relationship between the pressure of the nonextensive system $^{\mathrm{NE}}P$ and the pressure of the environment P,

$$(^{\mathrm{NE}}P - P) = \tau\frac{d\chi}{dV} = m\frac{\tau\chi}{V}. \tag{5}$$

This relation generalizes Laplace's relationship for nonextensive systems. It does not involve a radius of curvature or precise geometrical borders of the nonextensive system but it is defined from its physicochemical variables alone. It obviously allows finding the results known for situations with simple geometry. In the case of a liquid drop of interfacial tension γ^{LV} and radius r, the pressure difference between the inside of the drop ($^{\mathrm{NE}}P = P_d$) and the external pressure of the gaseous atmosphere is obtained by introducing the interfacial parameters in equation (5), $\tau = \gamma^{\mathrm{LV}}$, $\chi = A^{\mathrm{LV}}$. Note that when the drop volume is multiplied by λ, the area A^{LV} is multiplied by $\lambda^{2/3}$. The area is then an extensity of dimension $m = 2/3$ towards the mass or the drop volume. *The drop liquid is thus a nonextensive phase of thermodynamic dimension equal to* $2/3$. We can write

$$(P_d - P) = m\frac{\tau\chi}{V} = \frac{2}{3}\frac{\gamma^{\mathrm{LV}}A^{\mathrm{LV}}}{V} = 2\frac{\gamma^{\mathrm{LV}}}{r} \tag{6}$$

which corresponds to Laplace's relationship.

We will apply these definitions of NET relations to the solubility of a solid compound, i, in a solvent S, at temperature T. We will suppose that i constitutes a nonextensive phase

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[1] In physics, there are several developments of nonextensive thermodynamics using conventions in which the temperature is considered as a nonintensive variable [23].
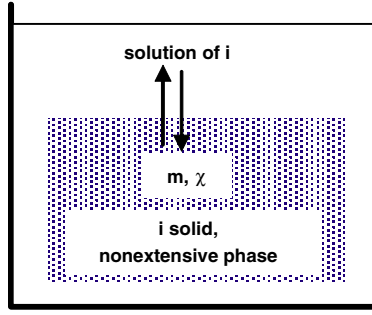
Figure 1. Scheme of the system considered. The solid i constitutes a nonextensive phase of dimension m and of extensity χ. This solid is placed in a solvent, at temperature T, in which it is partially soluble.

(figure 1). One can note that, in many aspects, our approach is very close to the Hill's nanothermodynamics (NT) [24–26]. Indeed, our approach could be regarded as a specific case of NT. Instead of opposing these two approaches (NET and NT), they should be considered as complementary and giving two different visions of the same reality.

2.2. Solubility; equilibrium conditions

The equilibrium between solid i and i in solution at saturation in S is expressed by writing the equality of the chemical potentials of i in its two forms. Consider the solid as a nonextensive phase without any residue of unlimited phase [27, 28]. The solid, $i(s)$, is at pressure $^{\mathrm{NE}}P$ of the nonextensive phase. The solution (b) is at the external pressure P

$$\mu_{i(s)}^{^{\mathrm{NE}}P} = \mu_{i(b)}^{P}. \tag{7}$$

The chemical potential of i solid varies with the pressure P as follows:

$$\left(\frac{\partial \mu_{i(s)}}{\partial P}\right)_{T,n_k} = V_i^*. \tag{8}$$

V_i^* is the molar volume of solid i. If its value varies slightly with the pressure, then

$$\mu_{i(s)}^{^{\mathrm{NE}}P} = \mu_{i(s)}^{P} + V_i^*(^{\mathrm{NE}}P - P). \tag{9}$$

Combining equations (5) and (9), one obtains

$$\mu_{i(s)}^{^{\mathrm{NE}}P} = \mu_{i(s)}^{P} + V_i^* m\tau \frac{\chi}{V}. \tag{10}$$

The general equilibrium condition between the solid i constituting a nonextensive phase of volume V and a saturated solution of i at pressure P can then be written as

$$\mu_{i(b)} = \mu_{i(b)}^{\infty} + RT \ln a_{i(\mathrm{sat})} = \mu_{i(s)} + V_i^* m\tau \frac{\chi}{V}. \tag{11}$$

$\mu_{i(b)}^{\infty}$ is the standard chemical potential of i at infinite dilution in solvent S and $a_{i(\mathrm{sat})}$ is the activity of i at saturation in the concentration scale.

Consider the equilibrium between the pure solid, in unlimited phase, and its saturated solution at the same temperature,

$$\mu_{i(b)}^{\infty} + RT \ln a_{i(\mathrm{sat})}^* = \mu_{i(s)}. \tag{12}$$

By combining equations (11) and (12),

$$\ln \frac{a_{i(\mathrm{sat})}}{a_{i(\mathrm{sat})}^*} = \frac{V_i^*}{RT} m\tau \frac{\chi}{V}. \tag{13}$$

A general relation is thus established between the activities at saturation of a single species under its nonextensive and unlimited forms, and the thermodynamic parameters of the system. When the concentrations of saturated solutions are low, the values of activity coefficients of species in solution can be considered to be equal to one. If i is a molecular species, the values of activities are equal to the values of concentrations of i at saturation.

$$\ln \frac{\{C_{i(\text{sat})}\}}{\{C_{i(\text{sat})}^*\}} = \frac{V_i^*}{RT} m \tau \frac{\chi}{V}. \tag{14}$$

If i is an electrolyte, for example $A_x B_y$, the activities are linked to the mean concentration $C_\pm$ and the mean activity $\gamma_\pm$ of the salt in solution by

$$a_{A_x B_y} = a_A^x a_B^y = a_\pm^{(x+y)} = \gamma_\pm^{(x+y)} C_\pm^{(x+y)}. \tag{15}$$

In a sufficiently diluted salt solution, we can suppose that $\gamma_\pm \approx 1$, which leads to

$$\ln \frac{\{C_{\pm(\text{sat})}\}}{\{C_{\pm(\text{sat})}^*\}} = \frac{1}{(x+y)} \frac{V_{A_x B_y}^*}{RT} m \tau \frac{\chi}{V}. \tag{16}$$

If a medium of given ionic strength is considered, the ratio of activity coefficients can be considered to be constant, leading to a similar relation with a different value of τ.

Here, we consider the consequences of these relations by analysis of various different situations. To simplify the demonstrations, we will use the situation in which i is a molecular species and the saturated solution is diluted (equation (14)).

3. Application to solubility

First, we will consider the case in which the geometry of the nonextensive phase is sufficiently well defined to allow the extensity χ to be identified as an area.

3.1. The extensity is an area

3.1.1. Ostwald–Freundlich law.   Consider a solid particle, i, that is a sphere of radius r at equilibrium in its saturated solution. In this case, the dimension m is equal to two-thirds. If the extensity is identical to the liquid–solid area, A^{SL}, the tension τ is equal to the surface tension γ^{SL}, and the volume of the nonextensive phase is equal to the particle volume, then the Ostwald–Freundlich relation is found,

$$\ln \frac{\{C_{i(\text{sat})}\}}{\{C_{i(\text{sat})}^*\}} = \frac{V_i^*}{RT} \frac{2}{3} \gamma^{\text{SL}} \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{V_i^*}{RT} \frac{2\gamma^{\text{SL}}}{r}. \tag{17}$$

In this situation, a decrease of the particle radius involves an increase in the concentration of i at saturation equilibrium, which consequently becomes higher than that of the pure solid in unlimited phase. There is an interesting discussion of this relation in *Surface Tension and Adsorption* by Defay and Prigogine [29].

This relation is also interesting from a theoretical point of view because it supposes that a value of γ^{SL} may be determined experimentally because the solubility of a material can be measured for spherical particles whose size is known. This calculation was carried out by Defay and Prigogine from measurements made on barium sulfate in water. In this way, they determined the surface tension: $\gamma^{\text{SL}} = 1.350 \text{ N m}^{-1}$ at 298 K. It is thus surprisingly simple to determine a quantity which is generally calculated by semi-empirical approaches and wettability studies [30–32].

However, in addition to the experimental difficulties of determining the particle size (and the particles must be spherical), the introduction of a solid–liquid interfacial tension supposes

that the interface is at equilibrium and of constant curvature: this can only be an assumption in the case of a solid. The result is that no one can be certain of the validity of the measurement of γ^{SL} by this method.

In our approach, this problem does not explicitly appear because equation (14) is based on a property of the system response to the variations of its mass (extensity); neither the interfacial area nor the use of Laplace's relation is required. Thus, it seems appropriate to express the equilibrium without identifying the tension τ as the interfacial tension γ^{SL} and to write the Ostwald–Freundlich law in a more general form

$$\ln \frac{\{C_{i(\text{sat})}\}}{\{C_{i(\text{sat})}^*\}} = \frac{V_i^*}{RT} \frac{2\tau}{r}. \tag{18}$$

We will proceed on this basis for the following cases.

3.1.2. The particle is not spherical. Equation (18) can be used to address the case of particles of classical crystalline forms, for example that corresponding to a cube of edge a and of volume a^3. Initially, the thermodynamic dimension of the system is determined by multiplying its mass by a number λ as leaving its form unchanged. In this operation, the volume will be also multiplied by λ (at constant density), whereas the surface area of the cube, $6a^2$, will be multiplied by $\lambda^{2/3}$. The thermodynamic dimension of the system is $m = 2/3$. Then

$$\ln \frac{\{C_{i(\text{sat})}\}}{\{C_{i(\text{sat})}^*\}} = \frac{V_i^*}{RT} \frac{2}{3} \tau \frac{6a^2}{a^3} = \frac{V_i^*}{RT} \frac{4\tau}{a}. \tag{19}$$

The solubility of i in this crystalline structure is thus related to the length of the cube edge: it increases as the edge length decreases.

Our approach has its limitations because not all structures have the properties of Euler's functions. This can be proven by considering a cylindrical particle of height h whose base is of diameter d (figure 2). Suppose that the particle grows with increasing mass without any change in base area but with increasing height h. The cylinder volume is $V = \frac{\pi d^2}{4} h$ and the area $A = 2\frac{\pi d^2}{4} + \pi dh$. If the cylinder mass is multiplied by λ, only h will be multiplied by λ and consequently the surface area of the cylinder will become $A_\lambda = 2\frac{\pi d^2}{4} + \lambda \pi dh$. In this case, the area is not an Euler's function of the mass and the relations of NET do not apply. For this reason, it must be systematically verified that the extensity is an Euler's function of the mass before equation (14) can be applied. However, for cylindrical particles that are sufficiently long for the surface area of the base to be negligible relative to the surface areas of the sides ($h \gg \frac{d}{4}$), the total surface area approximates to an Euler's function of order one of the mass. The dimension of the system is unity. Then,

$$\ln \frac{\{C_{i(\text{sat})}\}}{\{C_{i(\text{sat})}^*\}} = \frac{V_i^*}{RT} \tau \frac{4\pi dh}{\pi d^2 h} = \frac{V_i^*}{RT} \frac{4\tau}{d}. \tag{20}$$

In this case, the particle solubility is dependent on the length of the cylinder but is independent of its diameter.

There are many examples which can be used to illustrate the value of applying equation (14) to objects of various sizes and forms. We will consider the case of nanoparticles whose spatial structure cannot be simply described from classical dimensions (volumes, areas, lengths).

3.2. General case. Power laws: consequence of the NET

Consider a given mass, M, of solid i presumed to constitute a nonextensive phase. The volume V of the system is a homogeneous function of order one of the mass whereas the extensity χ
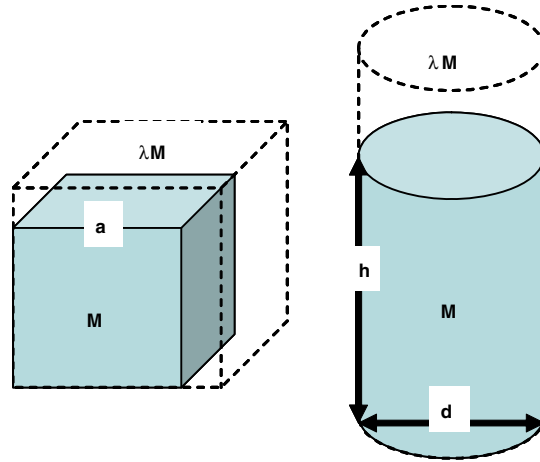
Figure 2. Two kinds of geometrically defined particles are considered. Their mass is multiplied by λ. The cube increases in size with no change in shape. The cylinder increases in size with no change in base area.

is a homogeneous function of order m. The ratio between χ and V is therefore a homogeneous function of order $(m - 1)$ of the solid mass. This corresponds to

$$\frac{\chi}{V} = kM^{m-1}, \tag{21}$$

where k is a characteristic constant of the nonextensive phase considered. This condition combined with equation (14) leads to

$$\ln\frac{\{C_{i\,(\text{sat})}\}}{\{C^*_{i\,(\text{sat})}\}} = \frac{V_i^*}{RT}m\tau kM^{m-1} = \frac{V_i^*}{RT}mYM^{m-1}. \tag{22}$$

To simplify the notations, the product τk is replaced by Y. Y is a characteristic extent of the solid. Its unit, u, depends on the value of m, $u = \text{N m}^{1-3m}$.

Thus, we show that in the general case the solubility of i depends on the mass of the solid in the system according to a power law.

This implies that the solubility determined experimentally will depend on the method of measurement used. This behaviour is particularly interesting for the solubility of porous materials. Despite rigorous searches in the literature, we did not find any experimental evidence either supporting or contradicting this analysis.

The solubility of nanoparticles corresponds to a particular case of equation (21).

3.2.1. Case of nanoparticles of dimension m and of mass M_p. Consider a solid i in the form of identical nanoparticles, all having the same properties of nonextensive phases of dimension m. The mass of a particle is M_p, its volume V_p, and its extensity χ_p. We will consider a system in which any addition of i solid will increase the number, N, of identical nanoparticles. This situation is described by the following relations:

$$V = NV_p \qquad \chi = N\chi_p \qquad \frac{\chi}{V} = \frac{\chi_p}{V_p} = kM_p^{m-1}. \tag{23}$$

The solubility of i depends on the nanoparticle mass according to a power law which can be written in logarithmic form.

$$\log\left(\ln\frac{\{C_{i\,(\text{sat})}\}}{\{C^*_{i\,(\text{sat})}\}}\right) = \log\left(\frac{V_i^*}{RT}mY\right) + (m-1)\log\left(M_p\right). \tag{24}$$
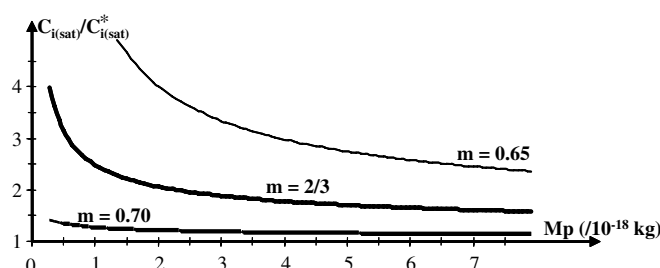
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Figure 3. Variations of supersaturation ratio $\frac{C_{i(sat)}}{C_{i(sat)}^*}$ for a solid i against the thermodynamic dimension, m.

Various simulated behaviours for this system with several values of m are given in figure 3. To facilitate comparisons, we will use the numerical data reported by Mihranyan and Strømme in their paper [14]: molecular weight of i equal to 0.7 kg mol^{-1} and $\gamma^{SL} = 0.1$ N m^{-1}. The value of Y (equal to 4.835 975 862 u) chosen for the simulations corresponds to an Ostwald–Freundlich behaviour ($m = 2/3$) for a spherical particle with the reported characteristics, the masses being expressed in kilograms.

In the range of particle masses chosen, the shapes of the curves are similar to those suggested by Mihranyan and Strømme calculated by the fractal approach. This is logical since both approaches involve power laws. For $m = 2/3$ and for spherical particles, the behaviour corresponding to the Oswald–Freundlich law is clearly described. For $m < 2/3$, the mass effect strongly amplifies the solubilization of i, even for values of m very close to this value. The result is that there must be systems for which the nanoparticle solutions will be able to reach very high values of supersaturation ratio. For $2/3 < m < 1$, the mass effect of the nanoparticle on solubilization is, in contrast, lower than that corresponding to a spherical particle. The results of these simulations lead to several observations.

The first concerns the diversity of the expected behaviours and in particular that creating a nanoparticle of i does not necessarily result in a large increase in its solubility. This is the case of the nonextensive phases of dimension $m > 2/3$. So, breaking a solid into more pieces is insufficient to increase its solubility.

The second observation relates to the case where the solubility is substantially increased ($m < 2/3$). These results can be misleading as concerns to their possible applications and we do not completely share the conclusions of Mihranyan and Strømme: although the solubility of a compound i can be increased if the solid has a nanoparticle structure with $m < 2/3$, the supersaturated solution will be in metastable equilibrium and it will thus tend to return to its stable state in all situations. The system will spontaneously evolve with the appearance in the medium of a crystal that is larger than the nanoparticle.

The crystal size will increase at the nanoparticles' expense: the nanoparticles will dissolve and the solubility will decrease. Accordingly, industrial application of this property seems to us to be problematic.

4. Conclusion

The nonextensive thermodynamics (NET) constitutes a consistent set of relations which allow description of the physicochemical behaviours of complex systems, and in particular nanoparticles and porous systems, but also geometrically well defined systems including crystals.

Like fractal approaches, NET led to power laws, but these two theories are of completely different natures. By applying NET, the spatial structure is not characterized, but rather a response of the system to a mass variation which depends on the considered system. Thus, the smooth surface of a drop which grows corresponds to an extensity of dimension $m = 2/3$, whereas, as we showed, the smooth surface of cylinders which lengthen proportionally increases with their mass and leads to $m = 1$. This implies that power laws can be found for systems with smooth interfaces and not inevitably of fractal dimension.

Does this mean that there are no relations between thermodynamic dimensions and fractal dimensions? Any answer would require an explanation of how a fractal surface, of dimension D, induces a response of the system to mass variations, according to Euler's functions of order m. Currently, this question is unanswered.

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