NanoSeconds

Perspective: Nanothermodynamics

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The study of sufficiently small systems at equilibrium requires a modification of ordinary macroscopic thermodynamics. This subject, which now might appropriately be called nanothermodynamics, was investigated at some length by the author in 1961−3, and the results were published as the thermodynamics of small systems[1−4] in 1962−4. At that time there were few experimental systems that could be analyzed in this way, so almost all of the examples used in the publications were theoretical and based on statistical mechanical models.

In 1964 my interests shifted drastically and I dropped the subject of nanothermodynamics except for very occasional applications in theoretical biophysics over the next 25 years. Furthermore, during that time, with one or two exceptions, I was not aware of utilization of nanothermodynamics by others.

But, in recent years, with the explosion of interest in experimental (and theoretical) nanoscience, I have wondered whether nanothermodynamics might not, after all, find useful applications to nanosystems that are at equilibrium (or metastable equilibrium[5]). A recent paper on ferromagnetism[6] serves as an example.

For nanothermodynamics to apply, the small systems in the sample (ensemble) must be independent of each other, or approximately so. Unlike macroscopic systems, small systems have different thermodynamic properties depending on the actual experimental "environmental" independent variables (for example, for a single component: N, V, T; N, p, T; μ, V, T; or μ, p, T). The entropy would be an example

of a thermodynamic function with different values for different environments under otherwise comparable conditions. In general, the more "open" the system, the larger the entropy.

Again, unlike macroscopic systems, in a statistical mechanical treatment of a small-system model, the particular partition function appropriate to the actual environmental variables must be used.

If we take the environmental variables N, p, T as an example, applied to, say, small crystallites of various fixed sizes N, some thermodynamic properties of interest are size effects or heat capacity, melting point, sharpness or the melting transition, etc.

As another example, completely open (μ, p, T) systems are of special interest because these three intensive variables cannot all be independent in a macroscopic system but they can be in a small system. In fact, these intensive variables determine the mean size $\bar{N}$ (an extensive variable) in an ensemble of small systems of this type. The partition function $Y(\mu,p,T)$ presents no fundamental problem for a small system but it does for a macroscopic system. In fact, the practical way to handle a macroscopic system with μ, p, T is to start with the corresponding small system partition function, calculate thermodynamic properties from it, and then find the limits of these properties as μ, p, T approach their macroscopic relationship. Examples of μ, p, T systems are various open linear aggregates in biology, metastable liquid droplets in vapor,[5] the local correlations in bulk magnetic materials,[6] and a Gibbs surface excess resulting from an adsorbent molecule at the end of a one-dimensional lattice gas.[7,8]

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I turn now to the "history" of nanothermodynamics. Unfortunately, I no longer have my early working notes on the subject. But dates of the submission of three papers allow me to establish the timing. I was on sabbatical at Cambridge University for a year, starting in the summer of 1960. I submitted two papers[9,10] to the *Journal of Chemical Physics* in late 1960. Both of these have to do with the thermodynamics of macromolecular solutions and both contain a few comments that suggest to me that I was on the verge of thinking about the special connections between small systems and thermodynamics. I can remember beginning to work on the actual subject of the thermodynamics of small systems very early in 1961. I also remember making major progress in California (on the way home to Oregon) in the late summer of 1961 and continuing this in Oregon in the fall and winter of 1961. Reference 1 was submitted in January 1962. I continually added more material as I wrote the two parts of the book *Thermodynamics of Small Systems*[2,3] during 1962 and 1963.

As to the future: With plenty of space available, I tried to be exhaustive, on the thermodynamic side, while writing the book.[2,3] However, two small extensions have been made recently,[5,8] and no doubt others can be expected. On the other hand, it seems to me that a great many new analyses of (a) small-system statistical mechanical models and of (b) existing and future sets of experimental data ought to be possible.

Finally, the origin of the term "nanothermodynamics" might be of interest. I informed my friend Ralph Chamberlin of my recent occasional use of this term as a shortened and more fashionable version of "thermodynamics of small systems". He responded by including it in a recent *Nature* paper,[6] and it also appears several other places in the November 16, 2000, issue of *Nature*. This is the published birthplace as far as I know.

References

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