

Vladimir García-Morales
Technische Universität München

Javier Cervera
University of Valencia

José A. Manzanares
University of Valencia

15.1 Introduction	15-1
15.2 Historical Background.....	15-2
15.3 Presentation of State-of-the-Art.....	15-2
Surface Thermodynamics • Hill's Nanothermodynamics • Tsallis'	
Thermostatistics • Superstatistics • Nonequilibrium Approaches	
15.4 Critical Discussion and Summary.....	15-18
15.5 Future Perspectives.....	15-19
Acknowledgments.....	15-19
References.....	15-19

15.1 Introduction

Progress in the synthesis of nanoscale objects has led to the appearance of scale-related properties not seen or different from those found in microscopic/macroscale systems. For instance, monolayer-protected Au nanoparticles with average diameter of 1.9 nm have been reported to show ferromagnetism while bulk Au is diamagnetic (Hasegawa 2007). Nanotechnology brings the opportunity of tailoring systems to specific needs, significantly modifying the physicochemical properties of a material by controlling its size at the nanoscale. Size effects can be of different types. Smooth size effects can be described in terms of a size parameter such that we recover the bulk behavior when this parameter is large. The physicochemical properties then follow relatively simple scaling laws, such as a power-law dependence, that yield a monotonous variation with size. Specific size effects, on the contrary, are not amenable to size scaling because the variation of the relevant property with the size is irregular or nonmonotonic. They are characteristic of small clusters. Finally, some properties are unique for finite systems and do not have an analog in the behavior of the corresponding bulk matter (Jortner and Rao 2002, Berry 2007).

Nanothermodynamics can be defined as the study of small systems using the methods of statistical thermodynamics. Small systems are those that exhibit nonextensive behavior and contain such a small number of particles that the thermodynamic limit cannot be applied (Gross 2001). Even though Boltzmann, presumably, did not think of nonextensive systems, his formulation of statistical thermodynamics relied neither on the use of the thermodynamic limit nor on any assumption of extensivity (Gross

2001). The same applies to Gibbs ensemble theory, which can also be used to describe the behavior of small systems. However, this is not true for classical thermodynamics, which is based on a number of assumptions that may lead to questioning its validity on the nanoscale. Care must be exercised when applying thermodynamics to nanosystems. First, quantities such as interfacial energy, which could be safely neglected for large systems, must be taken into consideration (Kondepudi 2008). These and other effects lead to nonextensive character of the thermodynamic potentials. Second, the fluctuations of thermodynamic variables about their average values may be so large in a small system that these variables no longer have a clear physical meaning (Feshbach 1988, Mafé et al. 2000, Hartmann et al. 2005). Fluctuations may also lead to violations of the second law of thermodynamics (Wang et al. 2002). Third, quantum effects may also become important (Allahverdyan et al. 2004).

In this chapter, we mostly concentrate on Hill's equilibrium nanothermodynamics. For historical and pedagogical reasons, it is convenient to start the description of size effects in nanosystems using classical equilibrium thermodynamics including interfacial contributions. Thus, in Section 15.3.1, it is shown that the smooth size dependence of many thermodynamic properties can be understood without introducing any "new theory." Similarly, Section 15.3.2 shows that the methods of traditional statistical thermodynamics can be used to describe small systems under equilibrium conditions without the need of introducing significantly new ideas. The thermodynamic behavior of small systems is somehow different from the macroscopic systems. Particularly important is the fact that fluctuations break the equivalence between the different statistical ensembles and that the ensemble that accurately describes the interaction between the small system and its surroundings

* Dedicated to Prof. Julio Pellicer on occasion of his retirement.

must be used. For some of these interactions, a completely open statistical ensemble, with no macroscopic analogue, must be used. Hill's nanothermodynamics can be considered as a rigorous formulation of the consequences of nonextensivity, due to the small number of particles composing the system, on the classical thermodynamic equations. It is shown that the new degree of freedom brought about by the nonextensivity of thermodynamic potentials can be conveniently dealt with through the definition of a new thermodynamic potential, the subdivision potential. An introduction to modern applications of Hill's nanothermodynamics is included in order to show that this theory can be applied to metastable states, to interacting small systems, and to describe microscopically heterogeneous systems like glasses and ferromagnetic solids.

Hill's theory can be related to another thermodynamic theory emphasizing nonextensivity—Tsallis' theory. This theory is discussed in Section 15.3.3, where the relation between the entropic index q and Hill's subdivision potential is presented. Similarly, Hill's theory is related in Section 15.3.4 to superstatistics, a new term coined to emphasize the existence of two different statistical probability distributions in complex systems. Finally, Section 15.3.5 describes the most recent ideas on nonequilibrium nanothermodynamics and their relation to fluctuation theorems.

15.2 Historical Background

The roots of nanothermodynamics go back to the seminal works by J. W. Gibbs and Lord Kelvin in the nineteenth century when the importance of surface contributions to the thermodynamic functions of small systems was realized. These topics have taken on a new significance due to the recent development of nanoscience.

During the first half of twentieth century, there were some interesting contributions to this field. For instance, the starting point for the kinetic interpretation of condensation phenomena in supersaturated phases, the melting point depression in small metal particles, and the size-dependent chemical potential in the droplet model developed by Becker and Döring (1935). Also, in his theory of liquids, Frenkel (1946) worked out the correction to the thermodynamic functions to extend their validity to small systems.

The major contributions have occurred during the second half of twentieth century and the current decade. The formulation of nanothermodynamics as a generalization of equilibrium thermodynamics of macroscopic systems was carried out in the early 1960s. Similar to the introduction of the chemical potential by J. W. Gibbs in 1878 to describe open systems, T. L. Hill (1962) introduced the subdivision potential to describe small systems. Hill anticipated two main classes of applications of nanothermodynamics: (1) as an aid in analyzing, classifying, and correlating equilibrium experimental data on "small systems" such as (noninteracting) colloidal particles, liquid droplets, crystallites, macromolecules, polymers, polyelectrolytes, nucleic acids, proteins, etc.; and (2) to verify, stimulate, and provide a framework for statistical thermodynamic analysis of models of finite systems.

The first computer simulations of hard sphere fluids carried out in the late 1950s and early 1960s also showed the importance

of size effects. It was soon realized that the different statistical ensembles are not equivalent when applied to small systems. A key feature of small systems is that thermodynamic variables may have large fluctuations so that only the appropriate ensemble describes correctly the behavior of the system (Chamberlin 2000). Moreover, it was found that the thermodynamic functions of very small systems exhibit a variation with the number of particles that is not only due to the surface contribution and some anomalous effects may also appear (Hubbard 1971). Statistical ensembles whose natural variables are intensive were identified as the best choice to describe small systems and some specific tools were developed (Rowlinson 1987).

The development of nonextensive thermodynamics based on Tsallis entropy in the 1990s motivated a widespread interest in the modifications of classical thermodynamics for complex systems, including nanosystems. It has been shown recently, however, that Tsallis and Hill's theories can be mapped onto each other (García-Morales et al. 2005).

The interest in Hill's nanothermodynamics has grown in the 2000s after realizing that this theory can describe the behavior of a microheterogeneous material, such as a viscous liquid exhibiting complex dynamics or a ferromagnetic material, by considering it as an ensemble of small open systems. These materials have an intrinsic correlation length, which changes with the temperature. The "small systems" would then be associated to physical regions with a size related to the correlation length. These small systems would then be completely open, in the sense that they could exchange energy with the bulk material, and vary their volume and number of particles, so that they should be described using the generalized ensemble. Remarkably, Chamberlin has proved that the generalized ensemble of nanothermodynamics with unrestricted cluster sizes yields nonuniform clustering, nonexponential relaxation, and nonclassical critical scaling, similar to the behavior found near the liquid-glass and ferromagnetic transitions (Chamberlin 2003).

Besides the progress described above at equilibrium, there were some important developments on nonequilibrium statistical physics during the 1970s and 1980s coming from the modern theory of dynamical systems and the study of thermostated systems as applied to nonequilibrium fluids and molecular dynamics simulations (Evans and Morriss 2008). These developments led during the 1990s to a series of breakthroughs whose impact is today the subject of very active research at the nanoscale: the theoretical prediction (contained in the so-called fluctuation theorems), and later experimental observation, of violations of the second law of thermodynamics for small systems and short time scales, and the Jarzynski equality, which allows one to obtain equilibrium free energy differences from nonequilibrium measurements.

15.3 Presentation of State-of-the-Art

15.3.1 Surface Thermodynamics

Most modern developments of thermodynamics of nanosystems involve the introduction of new magnitudes like Hill's subdivision potential or new equations like Tsallis' entropy equation, which

are sometimes controversial or difficult to accept. On the contrary, surface thermodynamics is still considered a successful framework to analyze thermodynamic properties that show a monotonous variation on the nanoscale (Delogu 2005, Rusanov 2005, Wang and Yang 2005, Jiang and Yang 2008).

15.3.1.1 Unary Systems with Interfaces

Classical macroscopic thermodynamics deals with systems composed of one or several bulk homogeneous phases. If their interfaces have definite shape and size, they can be described using the Gibbs dividing surface model, which associates zero volume and number of particles to the interface of a unary (i.e., monocomponent) system. For a homogeneous phase β , the Gibbs equation is $dU^\beta = TdS^\beta - p^\beta dV^\beta + \mu^\beta dn^\beta$ or, in terms of molar quantities $x^\beta \equiv X^\beta/n^\beta$ ($X = S, U, V$), $du^\beta = Tds^\beta - p^\beta dv^\beta$. From the intensive character of the molar quantities, it can be concluded that phase β satisfies the Gibbs–Duhem equation

$$d\mu^\beta = -s^\beta dT + v^\beta dp^\beta \quad (15.1)$$

If another homogeneous phase α is separated from phase β by an interface σ , the Gibbs equation of the $(\alpha + \sigma)$ system is

$$dU^{\alpha+\sigma} = TdS^{\alpha+\sigma} - p^\alpha dV^\alpha + \mu^\alpha dn^\alpha + \gamma dA \quad (15.2)$$

where A is the interfacial area and γ is the interfacial free energy. The internal energy $U^{\alpha+\sigma}$ and the entropy $S^{\alpha+\sigma}$ have a bulk contribution and an interfacial contribution. The volume V^α and the bulk contributions to internal energy and to entropy are bulk extensive variables, and therefore they are proportional to the number of moles n^α . The interfacial free energy is independent of the area A , that is, γ is an interfacial intensive variable. The interfacial contributions to internal energy and to entropy are proportional to the interfacial area A , so that they are interfacial extensive variables. The concepts of bulk and interfacial extensivity would only match if A were proportional to n^α , which is not generally the case.

The Euler and Gibbs–Duhem equations of the $(\alpha + \sigma)$ system are

$$U^{\alpha+\sigma} - TS^{\alpha+\sigma} + p^\alpha V^\alpha = \mu^\alpha n^\alpha + \gamma A \quad (15.3)$$

$$A d\gamma = -S^{\alpha+\sigma} dT + V^\alpha dp^\alpha - n^\alpha d\mu^\alpha \quad (15.4)$$

In unary systems, the interfacial variables, $x^\sigma \equiv X^\sigma/A$ ($X = S, U, F$), are $s^\sigma = -d\gamma/dT$, $u^\sigma = \gamma - Td\gamma/dT$, and $\gamma = f^\sigma$, so that Equation 15.4 reduces to

$$d\mu^\alpha = -s^\alpha dT + v^\alpha dp^\alpha \quad (15.5)$$

where $v^\alpha \equiv V^\alpha/n^\alpha$ and $s^\alpha \equiv S^\alpha/n^\alpha$ are the molar volume and entropy of phase α .

Introducing the energy $E \equiv \gamma A(1 - d \ln A / d \ln n^\alpha)$ and the molar chemical potential $\mu^{\alpha+\sigma} \equiv \mu^\alpha + \gamma(dA/dn^\alpha)$, the equations of the $(\alpha + \sigma)$ system can be transformed to

$$dU^{\alpha+\sigma} = TdS^{\alpha+\sigma} - p^\alpha dV^\alpha + \mu^{\alpha+\sigma} dn^\alpha \quad (15.6)$$

$$U^{\alpha+\sigma} - TS^{\alpha+\sigma} + p^\alpha V^\alpha = \mu^{\alpha+\sigma} n^\alpha + E \quad (15.7)$$

$$dE = -S^{\alpha+\sigma} dT + V^\alpha dp^\alpha - n^\alpha d\mu^{\alpha+\sigma} \quad (15.8)$$

It is noteworthy that the energy E only appears in the Euler and Gibbs–Duhem equations and that its value is determined by the relation between A and n^α , which depends on the system geometry. Moreover, the Gibbs potential $G^{\alpha+\sigma} = \mu^{\alpha+\sigma} n^\alpha + E$ is bulk nonextensive, that is, $G^{\alpha+\sigma}$ is not proportional to n^α because neither does E .

When phase α is a spherical drop of radius r , the conditions $dV^\alpha = 4\pi r^2 dr$ and $dA = 8\pi r dr = (2/r)dV^\alpha$ are satisfied. The mechanical equilibrium condition, $(\partial F^{\alpha+\beta+\sigma}/\partial V^\alpha)_{T, n^\alpha, n^\beta} = 0$, leads to the Young–Laplace equation $p^\alpha = p^\beta + 2\gamma/r$, and the distribution equilibrium condition, $d\mu^\alpha = d\mu^\beta$ with Equations 15.1 and 15.5, requires that (DeHoff 2006)

$$(s^\beta - s^\alpha)dT - (v^\beta - v^\alpha)dp^\beta + 2\gamma v^\alpha d(1/r) = 0 \quad (15.9)$$

Equation 15.9 allows us to evaluate the dependence of the thermodynamic properties on the curvature radius r . This dependence becomes significant for the nanoscale and practically disappears for microparticles.

15.3.1.2 Phase Diagrams

The influence of curved interfaces upon the behavior of materials systems is manifested primarily through the shift of phase boundaries on phase diagrams derived from the altered condition of mechanical equilibrium (Defay and Prigogine 1966, DeHoff 2006). For a number of substances, the metastable high-pressure phases and even some more dense packing phases do not exist in the bulk state. However, these phases are easily formed at the ambient pressure when the material size decreases to the nanoscale. For instance, in the nucleation stage of clusters from gases during chemical vapor deposition (CVD), the phase stability is quite different from that of the phase diagram that is determined at ambient pressure (Figure 15.1). The high additional internal pressure associated with the interfacial free energy through Young–Laplace equation makes it possible to observe “unusual” phases (Zhang et al. 2004, Wang and Yang 2005). Thus, nanodiamond has been found to be more stable than nanographite when the crystal size approaches the deep nanoscale (Yang and Li 2008).

15.3.1.3 Kelvin’s Equation for the Vapor Pressure of a Drop

If phase β is the vapor of the condensed phase α , the integration of Equation 15.9 at constant temperature making use of the approximation $v^\alpha \ll v^\beta \approx RT/p^\beta$ leads to

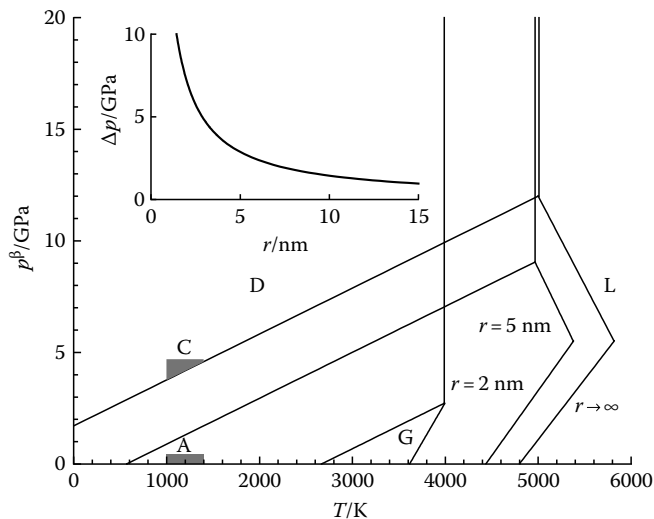


FIGURE 15.1 T - p phase diagrams of bulk ($r \rightarrow \infty$) and nanocrystalline ($r = 2$ and 5 nm) carbon: G, D, and L denote graphite, diamond, and liquid carbon. The inset shows the additional pressure ($p^\alpha - p^\beta$) as a function of the nuclei radius r . The A region means a metastable phase region of CVD diamond nucleation; the C region means a new stable phase region of CVD diamond nucleation with respect to the effect of nanosized-induced additional pressure. (Adapted from Yang, C.C. and Li, S., *J. Phys. Chem. C*, 112, 1423, 2008; Zhang, C.Y. et al., *J. Phys. Chem. B*, 108, 2589, 2004. With permission.)

$$RT \ln \frac{p^\beta(T, r)}{p^\beta(T, \infty)} = \frac{2\gamma v^\alpha}{r} \quad (15.10)$$

This equation, derived by Lord Kelvin in 1871, shows that the vapor pressure of a substance can be increased by preparing it in the form of particles of radius r . That is, the spherical particles (with a radius smaller than about $1 \mu\text{m}$) have a greater tendency to evaporate than a flat surface of the same bulk material at the same temperature. Interestingly, the term $2\gamma v^\alpha/r$ has been shown to be proportional to the interfacial energy $u^\sigma = \gamma - Td\gamma/dT$ (Dobruskin 2006) and to the enthalpy of formation of a spherical particle from bulk material (Schäfer 2003).

15.3.1.4 Chemical Potential of a Spherical Particle

The greater tendency to evaporate commented above implies that the chemical potential $\mu^\alpha = \mu^\beta = \mu$ must increase with decreasing particle size. Using $v^\alpha \ll v^\beta$ in Equation 15.9, the variation of the chemical potential at constant temperature is $d\mu = v^\beta dp^\beta \approx 2\gamma v^\alpha d(1/r)$, and integration leads to the Gibbs–Thomson–Freundlich equation

$$\mu(T, r) = \mu(T, \infty) + \frac{2\gamma v^\alpha}{r} \quad (15.11)$$

This equation is valid when the phases α and β are under conditions of thermodynamic equilibrium, so that the vapor pressure is given by Kelvin's equation and that of the condensed phase is given by Young–Laplace equation.

15.3.1.5 Solubility

The solubility of solid particles in a liquid solution is also size-dependent. In the solid phase, the chemical potential of the dissolving component (denoted by index 1) is $\mu_1^s(T, r) = \mu_1^s(T, \infty) + 2\gamma v_1^s/r$ and in the liquid solution, it is $\mu_1^l = \mu_1^{\circ l} + RT \ln(y_1^l c_1^l)$. If the activity coefficient y_1^l of this component in the liquid solution is not much affected by the change in particle radius, the equilibrium condition $\mu_1^s(r) = \mu_1^l$ implies that the molar concentration of the dissolving component under equilibrium conditions increases with decreasing particle size according to the Ostwald–Freundlich relation (Defay and Prigogine 1966, Kondepudi 2008)

$$c_1^l(r) = c_1^l(\infty) \exp \left[\frac{2\gamma v_1^s}{RT} \frac{1}{r} \right] \quad (15.12)$$

That is, in the same way that Equation 15.10 shows that a liquid drop is only in equilibrium with a supersaturated vapor, Equation 15.12 shows that a solid particle is only in equilibrium with a supersaturated solution. One of the most interesting consequences of the higher solubility of smaller particles is the Ostwald ripening phenomenon first described in 1896 and fundamental in modern technology for the solution synthesis of quantum dots (Vengrenovich et al. 2001).

15.3.1.6 Melting Point Depression

The distribution equilibrium condition can be written in terms of molar enthalpies and entropies as $h^\beta - h^\alpha = T(s^\beta - s^\alpha)$. At constant p^β , Equation 15.9 can then be integrated to give

$$\ln \frac{T(p^\beta, r)}{T(p^\beta, \infty)} = - \frac{2\gamma v^\alpha}{h^\beta - h^\alpha} \frac{1}{r} \quad (15.13)$$

When this equation is applied to the liquid–vapor equilibrium, $h^\beta - h^\alpha = \Delta H_{\text{vap}} > 0$ is the molar enthalpy of vaporization and therefore $T_{\text{vap}}(p^v, r) < T_{\text{vap}}(p^v, \infty)$, which is equivalent to Kelvin's equation for the vapor pressure.

When Equation 15.13 is applied to the equilibrium of solid particles in the liquid of the same component, $h^\beta - h^\alpha = \Delta H_m^b > 0$ is the bulk molar enthalpy of melting and $T_m(r) = T_m(p^l, r) < T_m(p^l, \infty) = T_m^b$, which shows that the spherical particles melt at lower temperature than the corresponding bulk phase. If we consider that this effect is not very large, Equation 15.13 can be transformed to Gibbs–Kelvin equation (Couchman and Jesser 1977)

$$1 - \frac{T_m(r)}{T_m^b} = \frac{2\gamma^{\text{sl}} v^s}{\Delta H_m^b} \frac{1}{r} \quad (15.14)$$

Many authors have attempted to predict the theoretical dependence of the melting point on the particle size using different thermodynamic approaches. Most studies consider spherical particles and thermodynamic equilibrium conditions between

homogeneous bulk-like phases, and deduce equations of the form (Peters et al. 1998)

$$1 - \frac{T_m(r)}{T_m^b} = \frac{2\beta_m}{\Delta H_m^b \rho^s} \frac{1}{r} \quad (15.15)$$

where ρ^s is the mass density of the solid and β_m is a parameter that depends on the model and is related to the interfacial free energy. Since atomistic features are missing, these models are expected to be valid only when the condensed phases contain at least several atomic layers. The thermodynamic equilibrium condition can be written in terms of the equality of the chemical potentials of the solid and melted particle at the melting point (Buffat and Borel 1976), equality of vapor pressures (Chushak and Bartell 2001), or extremal for the free energy (Vanfleet and Mochel 1995). In particular, using the latter type of approaches, Reiss et al. (1988) showed that the condition of equality of chemical potential is incorrect, and the work by Bartell and Chen (1992) added further caveats.

Although the $1/r$ dependence is widely accepted in the case of nanoparticles whose diameter is larger than a few nanometers, at very low radii, some studies have shown that the melting temperature depends nonlinearly on the reciprocal radius (Chushak and Bartell 2000). If we consider even smaller nanoparticles, i.e., atomic clusters, the study of the melting transition is necessarily more complicated not only because of experimental difficulties, but also because the very concept of melting has no meaning for atoms and molecules, and there must be a minimum size of the cluster that allows to classify the state of the atoms as solid- or liquid-like. At low temperatures, the atoms in a cluster make only small amplitude vibrations around a fixed position. At the melting temperature, the motion becomes quite anharmonic. At even higher temperatures, atoms in the cluster can visit neighboring places and start a diffusive motion (Schmidt and Haberland 2002).

15.3.1.7 Size Dependence of Interfacial Free Energy

The derivation of Equations 15.3 and 15.4 is based on the assumption that the interfacial contribution to the thermodynamic potentials is proportional to the interfacial area A . However, this area is not a good state variable when the particle size is very small and the interfacial variables $x^\sigma \equiv X^\sigma/A$ are no longer independent of A . This occurs because the approximation of size-independent interfacial free energy is not valid for very small particles of, e.g., $r < 1$ nm in the case of water and metal nuclei (Onischuk et al. 2006). The thermodynamic theory of Tolman (1949) suggests that the interfacial free energy of liquids changes with the droplet radius as

$$\gamma(r) = \frac{\gamma(\infty)}{1 + 2\delta/r} \quad (15.16)$$

where the Tolman length δ is of the order of 0.1 nm. This size dependence of the interfacial free energy is correlated with the mechanical instability of small objects (Samsonov et al. 2003).

15.3.1.8 Nanocrystalline Solids

Most of the results of surface thermodynamics explained above were originally devised with attention to fluids, and hence isotropic behavior is assumed. However, many nanomaterials are nonisotropic crystalline solids, like nanoparticles with faceting effects and polycrystalline solids with a nanoscale grain size. Thus, for instance, since the shape of grains can be arbitrary, there is no way to relate energy A and n^α and the Gibbs–Thomson–Freundlich equation (Equation 15.11) does not apply to the “nanograins” in polycrystalline solids. The generalization of the formalism of surface thermodynamics to solids is among the achievements in thermodynamics in the twentieth century (Weissmüller 2002).

15.3.2 Hill's Nanothermodynamics

T. L. Hill (Hill 1963) expressed the belief that “The applicability of statistical mechanical ensemble theory to small systems as well as large suggests that a parallel thermodynamics should exist.” In the nanoscale, the systems consist of only several tens to several hundred atoms and this casts some doubts on the statistical meaning of thermodynamic variables. Macroscopic thermodynamics should not be applied to a single small system, but it can be applied to, e.g., a solution of small systems which is considered as a Gibbs “ensemble” of independent small systems. Macroscopic thermodynamic functions are well defined for such a large sample of small systems. The thermodynamic variables of one small system should then be understood as averages over the ensemble of small systems, since it is this ensemble that we observe. This is one of the pillars of Hill's nanothermodynamics (Hill 1962, 1963, 1964), a theory whose fundamental thermodynamic equations for a small system involve average values of fluctuating extensive quantities. Nanothermodynamics provides thermodynamic functions and relations for a single small system, including, in general, variations in the system size. Allowance of these variations in size is, indeed, the important new feature of nanothermodynamics.

15.3.2.1 Subdivision Potential

Hill's theory is a generalization of classical thermodynamics that accounts for size effects via the introduction of a new thermodynamic potential called the subdivision potential E , and its conjugate variable, the number of small systems N . This potential can be positive or negative, depending on the nature of the small systems, and takes into account the energetic contributions usually negligible for macroscopic systems, such as surface effects, system rotation, etc. To understand its meaning, we should compare two composite systems ($i = 1$ and 2) with the same extensive variables S_i , V_i and N_i and differing in the number of small systems ($N_1 \neq N_2$). The relation between the extensive variables of a small system and those of the collection of small systems, identified with a subscript t , is $X_i = X_t/N_t$, ($X = U, S, V, N$) ($i = 1, 2$). In classical thermodynamics, the Euler equations $U_1 = TS_1 - pV_1 + \mu N_1$ and $U_2 = TS_2 - pV_2 + \mu N_2$ would lead us to the conclusion that $N_1 U_1 = N_2 U_2$ or, equivalently, that the two composite systems have the

same energy, $U_i(S_p, V_p, N_p, \mathbf{N}_1) = U_{i2}(S_p, V_p, N_p, \mathbf{N}_2)$, in agreement with the fact that the Gibbs equation, $dU_i = TdS_i - pdV_i + \mu dN_p$, forbids the variation of U_i while keeping constant S_p , V_p , and N_p . In nanothermodynamics, on the contrary, it is considered that $U_{i1}(S_p, V_p, N_p, \mathbf{N}_1) \neq U_{i2}(S_p, V_p, N_p, \mathbf{N}_2)$.

The formulation of Hill's nanothermodynamics is based on the idea that the natural variables of the internal energy U_i are $(S_p, V_p, N_p, \mathbf{N})$ and that they can be varied independently. Thus, the Gibbs equation in nanothermodynamics is

$$dU_i = TdS_i - pdV_i + \mu dN_i + E d\mathbf{N} \quad (15.17)$$

where, unlike that used in Equations 15.1 through 15.8, the chemical potential $\mu \equiv (\partial U_i / \partial N_i)_{S_p, V_p, \mathbf{N}}$ is defined here per particle. The last two terms in Equation 15.17 bear some similarity, so that the subdivision potential $E \equiv (\partial U_i / \partial \mathbf{N})_{S_p, V_p, N_i}$ is like the chemical potential of a small system; but the energy required to add another identical small system to the ensemble is $(\partial U_i / \partial \mathbf{N})_{S_p, V_p, N} = U \neq E$. Strictly, E is the energy required to increase in one unit the number of subdivisions of the composite system, while keeping constant the total number of particles and other extensive parameters. That is, Hill's theory incorporates the possibility that processes taking place in a closed system produce or destroy small systems \mathbf{N} (Chamberlin 2002).

In classical thermodynamics, the energy U_i is assumed to be a first-order homogeneous function of its natural variables, that is, U_i is extensive. This leads, for instance, to the Euler equation $G_i(T, p, N) = U_i - TS_i + pV_i = \mu N_i$. We then say that the intensive state of the system is determined by intensive variables such as T and p , and that N_i determines the size of the system. The extensive character of the thermodynamic potentials like U_i and G_i means that, for a given intensive state, they are proportional to N_i .

In nanothermodynamics the energy U_i is also assumed to be a first-order homogeneous function of all its natural variables, \mathbf{N} included. This can be justified because the composite system is macroscopic and the small systems are noninteractive. Therefore, the Euler and Gibbs-Duhem equations take the form

$$U_i = TS_i - pV_i + \mu N_i + E\mathbf{N} \quad (15.18)$$

$$N dE = -S_i dT + V_i dp - N_i d\mu \quad (15.19)$$

The Gibbs and Euler equations can also be presented as $dG_i = -S_i dT + V_i dp + \mu dN_i + E d\mathbf{N}$ and $G_i(T, p, N_p, \mathbf{N}) = \mu N_i + E\mathbf{N}$. Interestingly, we cannot conclude that G_i is proportional to N_i at constant T, p because N_i and \mathbf{N} are independent variables. That is, G_i is no longer an extensive potential, and the same applies to other potentials like U_i .

Dividing Equations 15.18 and 15.19 by \mathbf{N} , and remembering that $X = X_i/\mathbf{N}$, the thermodynamic equations for a small system are

$$U = TS - pV + \mu N + E \quad (15.20)$$

$$dE = -SdT + Vdp - Nd\mu \quad (15.21)$$

From Equations 15.20 and 15.21, the Gibbs equation for a small system is

$$dU = TdS - pdV + \mu dN \quad (15.22)$$

which turns out to be the same as in classical thermodynamics. In classical thermodynamics, the Gibbs equation can be written in terms of intensive quantities, $x = X/N$, as $du = Tds - pdv$, and the chemical potential does not show up in this equation because N is not a natural variable of u . Similarly, the subdivision potential does not show up in Equation 15.22 because \mathbf{N} is not a natural variable of U . On the contrary, the subdivision potential appears in Equation 15.17 because \mathbf{N} is a natural variable of U_p , in the same way as μ appears in Equation 15.22 because N is a natural variable of U .

The Gibbs potential of a small system is $G(T, p, N) = \mu N + E$ and its Gibbs equation is $dG = -SdT + Vdp + \mu dN$. The important point to be noticed is that μ and E can still vary when T and p are kept constant (see Equation 15.21) and therefore we cannot conclude that G is proportional to N . In multicomponent small systems, the Gibbs potential is $G = \sum_i \mu_i N_i + E$. The presence of the subdivision potential is characteristic of small systems and evidences the nonextensive character of the Gibbs potential (Gilányi 1999).

15.3.2.2 Relation between Nano, Surface, and Nonextensive Thermodynamics

Hill's nanothermodynamics can describe interfacial contributions in a very natural way; and it can also describe nonextensive contributions of different nature. When the nonextensivity of the thermodynamic potentials arises from interfacial effects, Equations 15.20 through 15.22 would become identical to Equations 15.6 through 15.8 if we choose to define the subdivision potential as $E \equiv \gamma A(1 - d \ln A / d \ln n^\alpha)$, where γ is the interfacial free energy. In relation to Equations 15.6 through 15.8, we should remember that the interfacial quantities are proportional to the interfacial area A , that the bulk extensive quantities are proportional to the number of moles n^α of the single component in bulk phase α and, more importantly, that the relation between A and n^α depends on the system geometry. If A were directly proportional to n^α then the subdivision potential $E \equiv \gamma A(1 - d \ln A / d \ln n^\alpha)$ would vanish. However, this is not generally the case and the subdivision potential then accounts for the interfacial contributions to the thermodynamic potentials.

In relation to this, it can be mentioned that some authors present the Gibbs equation in nonextensive thermodynamics as

$$dU = TdS - pdV + \mu dn + \tau d\chi \quad (15.23)$$

where n is the number of moles, μ is the chemical potential (per mole), and τ and χ are the quantities introduced to account for nonextensivity. Equation 15.23 holds a close resemblance to Equations 15.2 and 15.17, so that τ is associated with γ and χ with

A in the case of interfacial systems. Letellier et al. (2007a,b) have used Equation 15.23 to derive the Ostwald–Freundlich relation (Equation 15.12) and the Gibbs–Kelvin equation for the melting point depression (Equation 15.13). The magnitudes τ and χ could be used to describe nonextensive contributions other than interfacial, and power laws of the type $\chi \propto n^m$ with $m \neq 2/3$ can also be used. The value of m becomes thus a free parameter that must be determined by comparison with experiments (Letellier et al. 2007b).

15.3.2.3 Generalized or Completely Open (T, p, μ) Ensemble

The extensive character of internal energy and entropy in macroscopic thermodynamics implies that the intensive state of a monocomponent system can be characterized by two variables, e.g., T and p . If we consider a collection of macroscopic small systems, T and p take the same values for a single small system and for the collection of small systems. These variables contain no information on the size of the small systems. In nonextensive small systems, on the contrary, T and p do vary with system size and we need one additional variable to specify the state of the system. The Gibbs–Duhem equation (Equation 15.21) evidences one of the key features of nanothermodynamics: the intensive parameters T, p , and μ can be varied independently due to the additional degree of freedom brought by nonextensivity. This enables the possibility of using the completely open or generalized (T, p, μ) statistical ensemble. This ensemble describes the behavior of small systems in which the extensive variables, such as the amount of matter in the system, fluctuate under the constraint that intensive variables (T, p, μ) are fixed by the surroundings.

The equilibrium probability distribution in the completely open ensemble is

$$p_j = \frac{1}{Y} e^{-\beta(E_j + pV_j - \mu N_j)} \quad (15.24)$$

where $\beta \equiv 1/k_B T$ and $Y(T, p, \mu) \equiv \sum_j e^{-\beta(E_j + pV_j - \mu N_j)}$ is the generalized partition function and the sum extends over microstates. Introducing the absolute activity $\lambda \equiv e^{\beta\mu}$, this partition function can also be written as $Y(T, p, \lambda) \equiv \sum_N \lambda^N \Xi(T, p, N)$. The relation with the subdivision potential is

$$E = -k_B T \ln Y \quad (15.25)$$

and the Gibbs–Duhem equation (Equation 15.21) allows us to obtain the extensive variables of the small system as $S = -(\partial E / \partial T)_{p, \mu}$, $\langle V \rangle = (\partial E / \partial p)_{T, \mu}$, $\langle N \rangle = -(\partial E / \partial \mu)_{T, p}$, and $U = TS - p\langle V \rangle + \mu\langle N \rangle + E$. When the small systems can be assumed to be incompressible, so that p and V are not state variables, the partition function Y becomes equal to the grand partition function, and the subdivision potential becomes then equal to the grand potential. The generalized ensemble is incompatible with the thermodynamic limit, $N \rightarrow \infty$.

15.3.2.4 The Incompressible, Spherical Aggregate, and the Critical Wetting Transition

In macroscopic thermodynamics, all the ensembles are equivalent and predict the same values and relations for the thermodynamics potentials and variables. In nanothermodynamics, on the contrary, this is no longer true. The state of the nanosystem is affected by the fluctuations in its thermodynamic variables and these are determined by the surroundings, so the statistical description of the nanosystem has to be done using the ensemble that correctly describes the constraints imposed to the nanosystem. We can illustrate this statement by describing a spherical aggregate under two different environmental constraints: canonical (T, N) and grand canonical (T, μ). The crystallite is assumed to be incompressible, so that p and V are not state variables; and there is no difference between the Gibbs and Helmholtz potentials, G and F , on the one hand, and the subdivision and grand potentials, E and Ω , on the other hand.

Consider first that each aggregate contains N particles in a volume V . Each particle has an intrinsic partition function $z(T) = z'(T)e^{\beta\epsilon}$, which also includes the energy of interaction per particle, $-\epsilon$. The canonical partition function is then

$$Z(T, N) = z^N e^{-\beta a N^{2/3}} \quad (15.26)$$

where $aN^{2/3} = \gamma A = F\sigma$ is the surface contribution to the free energy of the crystallite. This partition sum is valid only when $N \gg 1$ (though not macroscopic) since it assumes that it is possible to distinguish a surface and a bulk in the aggregate. The subdivision potential is

$$E(T, N) = G - \mu N = -k_B T \left[\ln Z - N \left(\frac{\partial \ln Z}{\partial N} \right)_\beta \right] = \frac{1}{3} a N^{2/3} \quad (15.27)$$

In the thermodynamic limit, $N \rightarrow \infty$, the surface contribution is negligible and $E/N \rightarrow 0$. This result is in agreement with Equation 15.7, since $E \equiv \gamma A (1 - d \ln A / d \ln N) = \gamma A / 3$ for spherical particles, $A \propto N^{2/3}$. Note also that, since $A = 4\pi (3V/4\pi)^{2/3}$ and the molar volume in the condensed phase is $v^l = VN_A/N$, the relation between parameter a and the interfacial free energy is $a = \gamma \pi^{1/3} (6v^l/N_A)^{2/3}$.

Consider now that the aggregates are in (distribution) equilibrium with a solution of the particles, which fixes T and μ . The generalized partition function $Y(T, \mu)$ or $Y(T, \lambda)$ is

$$Y(T, \lambda) = \sum_{N=0}^{\infty} Z(T, N) \lambda^N \approx \sum_{N=0}^{\infty} e^{-\beta a N^{2/3}} (z\lambda)^N \quad (15.28)$$

where $\lambda = e^{\beta\mu}$ is the absolute activity of the particles. The approximation sign is used because this form of $Z(T, N)$ is expected to be good for relatively large N only. The chemical potential in a bulk liquid is $\mu^\infty = -k_B T \ln z$ and the corresponding absolute activity is $\lambda^\infty = 1/z$. If $\lambda > \lambda^\infty$ the sum diverges and a finite system is not possible. In order to obtain aggregates of reasonable size we must choose $\lambda^\infty - \lambda \geq 0$, that is the aggregate must be approximately in

equilibrium with the bulk liquid; the aggregates could be clusters in a saturated vapor phase in equilibrium with a liquid. But even with a saturated vapor, the aggregate will be sizeable only near the critical temperature, when the interfacial energy is very small, $a(T)N^{2/3} \ll k_B T$.

Because we are interested only in $\langle N \rangle$ being fairly large, we can replace the sum in Y by an integral and extend the integration to $N = 0$. Even though the expression used for $Z(T, N)$ is not good when N is very small, the error introduced in this region of the integration is not serious when $\langle N \rangle$ is large enough (Hill 1964). Thus, the partition function is

$$Y(T, \lambda) \approx \int_0^{\infty} e^{-\beta a N^{2/3}} (z\lambda)^N dN \approx \int_0^{\infty} e^{-\beta a N^{2/3}} [1 + N \ln(z\lambda)] dN$$

$$= \frac{3\sqrt{\pi}}{4(\beta a)^{3/2}} + \frac{3}{(\beta a)^3} \ln(z\lambda) \quad (15.29)$$

The average number of particles in an aggregate is then

$$\langle N \rangle = \lambda \left(\frac{\partial \ln Y}{\partial \lambda} \right)_T \approx \frac{4}{\sqrt{\pi} (\beta a)^{3/2}} = \frac{2N_A}{3\pi v^1} \left(\frac{k_B T}{\gamma} \right)^{3/2} \quad (15.30)$$

and the subdivision potential is

$$E(T, \lambda) = -k_B T \ln Y \approx -k_B T \ln \frac{3\sqrt{\pi}}{4(\beta a)^{3/2}} = -k_B T \ln \frac{3\pi \langle N \rangle}{16} \quad (15.31)$$

As it should be expected, the aggregate size $\langle N \rangle$ increases as the interfacial free energy decreases.

This example illustrates two interesting characteristics of nanothermodynamics. First, the state of the small system is determined by the environment and different ensembles are not equivalent. For instance, the subdivision potential is different in the two ensembles, $E(T, N) = aN^{2/3}/3$ and $E(T, \lambda) = -k_B T \ln(3\pi \langle N \rangle / 16)$, and any magnitude related to the aggregate size fluctuation can only be described in the generalized ensemble. Second, we can determine an extensive variable, like the average aggregate size $\langle N \rangle$, from the intensive variables T and μ . In macroscopic thermodynamics, this would be impossible since, for example, the amount of water in a container cannot be determined from the values of T and μ . However, in nanothermodynamics, considering a completely open ensemble characterized by intensive parameters and evaluating the generalized partition function, all the equilibrium information on the small system is known, including the extensive parameters.

These results are found useful in analyzing the liquid–vapor equilibrium near the critical temperature and, particularly, cluster formation in metastable states. A recent successful application of nanothermodynamics to determine the critical wetting parameter is based on a modification of Equation 15.29. When

rotational and translational degrees of freedom of the aggregate are taken into account, the generalized partition function is

$$Y(T, \lambda) \propto \int_0^{\infty} e^{-\beta a N^{2/3}} [1 + N \ln(z\lambda)] N^d dN$$

$$\approx \frac{3[(3d+1)2]!}{2(\beta a)^{3(1+d)/2}} + \frac{3[(3d+4)2]!}{2(\beta a)^{3(1+d)/2}} \ln(z\lambda) \quad (15.32)$$

where d is related to the aggregate dynamics. The average number of particles in an aggregate is then

$$\langle N \rangle = \lambda \left(\frac{\partial \ln Y}{\partial \lambda} \right)_T \approx \frac{[(3d+4)2]! \ln(z\lambda)}{[(3d+1)2]! (\beta a)^{3/2}} \quad (15.33)$$

and the critical wetting parameter is obtained as (García-Morales et al. 2003)

$$\omega_c = 4 \frac{[(3d+4)2]!}{[(3d+1)2]!} \quad (15.34)$$

Good agreement with the experimentally determined value is obtained for $d = 2$, which corresponds to a combination of translation and vortex rotational motion of the aggregate.

15.3.2.5 Lattice Model for the Ideal Gas

As a second example, we discuss the lattice ideal gas. In this model, N particles are distributed in a lattice of sites of volume v_s so that every site can accommodate only one particle. In the isothermal–isobaric ensemble, the partition sum is

$$\Xi(T, p, N) = \sum_{N_s=N}^{\infty} \frac{N_s!}{N!(N_s-N)!} x^{N_s} z^N = \frac{(xz)^N}{(1-x)^{N+1}} \quad (15.35)$$

where $x \equiv e^{-\beta p v_s}$ and $z(T)$ is the intrinsic partition function. The average number of sites is

$$\langle N_s \rangle = x \left(\frac{\partial \ln \Xi}{\partial x} \right)_{T, N} = \frac{N+x}{1-x} \quad (15.36)$$

and its relative fluctuation is

$$\frac{\sigma_{N_s}}{\langle N_s \rangle} = \frac{\sqrt{\langle N_s^2 \rangle - \langle N_s \rangle^2}}{\langle N_s \rangle} = \frac{\sqrt{(N+x)x}}{N+x} \propto \frac{1}{\sqrt{N}} \quad (15.37)$$

where we have used that $x \approx 1$. That is, the fluctuations in the volume vanish when the system becomes macroscopic. This is a consequence of the fact that the extensive variable N is fixed in this ensemble. The subdivision potential is $E(T, p, N) = G - \mu N = k_B T \ln(1-x) \approx p v_s$, where $G = -k_B T \ln \Xi$ is the Gibbs potential and

$\mu = -k_B T (\partial \ln \Xi / \partial N)_{T,p}$ is the chemical potential. The chemical potential μ equals to G/N only for macroscopic systems, $N \gg 1$. The relation between T , p , and μ for the latter is $(1 + \lambda z)x = 1$, where $\lambda \equiv e^{\beta\mu}$ is the absolute activity.

Similarly, in the grand canonical ensemble the partition sum is

$$Q(T, V, \mu) = \sum_{N_s=0}^{N_s} \frac{N_s!}{N!(N_s - N)!} (\lambda z)^N = (1 + \lambda z)^{N_s} \quad (15.38)$$

The macroscopic equilibrium relation between T , p , and μ is again $(1 + \lambda z)x = 1$, where pressure is determined as $p = (k_B T / v_s) (\partial \ln Q / \partial N_s)_{T,\mu}$. The average number of particles is

$$\langle N \rangle = \lambda z \left(\frac{\partial \ln Q}{\partial (\lambda z)} \right)_{T,V} = \frac{N_s \lambda z}{1 + \lambda z} \quad (15.39)$$

and its relative fluctuation is

$$\frac{\sigma_N}{\langle N \rangle} = \frac{\sqrt{\langle N^2 \rangle - \langle N \rangle^2}}{\langle N \rangle} = \frac{1}{\sqrt{N_s \lambda z}} \propto \frac{1}{\sqrt{\langle N \rangle}} \quad (15.40)$$

That is, the fluctuations in the number of particles is again normal and vanish when the system becomes macroscopic, which is a consequence of the fact that the extensive variable V is fixed in this ensemble. The subdivision potential is $\mathbf{E}(T, V, \mu) = G - \mu \langle N \rangle = \Omega - pV = 0$.

Finally, the generalized partition sum is

$$\begin{aligned} Y(T, p, \mu) &= \sum_{N_s=0}^{\infty} \sum_{N=0}^{N_s} \frac{N_s!}{N!(N_s - N)!} x^{N_s} (\lambda z)^N \\ &= \sum_{N_s=0}^{\infty} (1 + \lambda z)^{N_s} x^{N_s} = \frac{1}{1 - (1 + \lambda z)x} \end{aligned} \quad (15.41)$$

where the condition $(1 + \lambda z)x < 1$, required for the convergence of the sum, determines when the small system can exist. The subdivision potential is $\mathbf{E}(T, p, \mu) = -k_B T \ln Y = k_B T \ln [1 - (1 + \lambda z)x]$. From this partition sum the average number of particles is

$$\langle N \rangle = \lambda \left(\frac{\partial \ln Y}{\partial \lambda} \right)_{T,x} = \frac{\lambda z x}{1 - (1 + \lambda z)x} \quad (15.42)$$

and the average number of sites is $\langle N_s \rangle = x (\partial \ln Y / \partial x)_{T,\lambda} = \langle N \rangle (1 + 1/\lambda z)$. The important result now is that the relative fluctuation is $\sigma_N / \langle N \rangle = \sqrt{(1 - x) / \lambda z x} > 1$. The fact that no extensive variable is held constant in the generalized ensemble has an important consequence: since there is no fixed extensive variable that provides some restraint on the fluctuations of extensive properties, they are of a larger magnitude than in other ensembles

(Hill and Chamberlin 2002). This example also shows that different ensembles lead to different results and stress the importance of choosing the right ensemble for the problem at hand.

15.3.2.6 Micelle Formation

Hill's nanothermodynamics has been applied to study ionic (Tanaka 2004) and nonionic micelles in solution (Hall 1987), as well as to describe polymer-surfactant complex formation (Gilányi 1999). The micellar solution of surfactant is treated as a completely open ensemble of small systems (micelles or polymer-surfactant complexes) dispersed in monomeric solution. The main advantage of the nanothermodynamics approach is that it imposes no restrictions on the distribution of micelles sizes.

15.3.2.7 Reactions Inside Zeolite Cavities and Other Confined Spaces

Crystalline zeolites with well-defined cavities and pores have long been used in the chemical industry as nanospaces for catalytic reactions. During the last decades, a variety of tailor-made "nanoreactors," with confined nanospaces where selected chemical reactions can take place very efficiently in controlled environments, have been fabricated and studied. The growing research activity in this area is also justified from the observed increased reactivity in nanospaces.

Hill (1963) applied nanothermodynamics to the study of the isomerization reaction in small closed systems and found no difference in the reaction extent from the macroscopic behavior. However, Polak and Rubinovich (2008) have considered other reactions and found a universal confinement effect that explains why the equilibrium constants of exothermic reactions are significantly enhanced in confined geometries that contain a small number of reactant and product molecules. The effect is universal in the sense that it has an entropic origin associated to the fact that when the number of molecules is small the Stirling approximation cannot be used to evaluate the number of microstates, that is, it is related to the nonextensivity of the entropy in small systems.

15.3.2.8 Mean-Field Theory of Ferromagnetism

In the classical mean-field theory of ferromagnetism, the material is described as a lattice of N particles (or spins) that can have two orientations. Let $s_i = \pm 1$ be the orientation variable of spin i , l be the number of particles in the up state ($s_i = +1$), J be the strength of the exchange interaction, and c be the coordination number of the lattice. The average energy per particle within the mean-field approximation is (Chamberlin 2000)

$$\epsilon(l, N) = -\frac{cJ}{2} \left(4 \frac{l(l-1)}{N(N-1)} - 4 \frac{l}{N} + 1 \right) \quad (15.43)$$

In the macroscopic limit, $N \geq l \gg 1$, this equation simplifies to $u^\infty(m) = -cJm^2/2$, where $m = (1/N) \sum_{i=1}^N s_i = (2l/N) - 1$ is the average value of the spin orientation variable. In this

limit, the thermodynamic potentials are extensive and the canonical partition sum factorizes, $Z^\infty(T, N) = [z^\infty(T)]^N$ where $z^\infty = 2e^{-\beta c/m^2/2} \cosh[\beta c/m]$. Introducing the macroscopic critical temperature $T_c^\infty \equiv c/k_B$, the relation between T and m under thermodynamic equilibrium conditions is $T/T_c^\infty = m/\text{arctanh}(m)$, and the absolute activity $\lambda^\infty = e^{\beta\mu^\infty} = 1/z^\infty$ can be presented as $\lambda^\infty(m) = \exp[\text{marctanh}(m)/2]\sqrt{1-m^2/2}$, and the entropy per particle is $s^\infty(m)/k_B = (u^\infty - \mu^\infty)/k_B T = -\text{marctanh}(m) + \ln\left(2/\sqrt{1-m^2}\right)$. These two functions are represented together with $u^\infty(m)$ in Figures 15.2 through 15.4. Note that $m = 0$ and $\lambda^\infty = 0.5$ at $T \geq T_c^\infty$.

In the case of finite clusters, the canonical partition sum is

$$Z(T, N) = \sum_{l=0}^N \frac{N!}{l!(N-l)!} e^{-\beta N \epsilon(l, N)} \quad (15.44)$$

and the equilibrium thermodynamic properties per particle are obtained as $\lambda(T, N) = Z^{-1/N}$, $u(T, N) = -(\partial \ln Z / \partial \beta)_N / N$ and $s(T, N) = [\partial (k_B T \ln Z) / \partial T]_N / N$. These functions have also been represented in Figures 15.2 through 15.4 for $N = 20, 50,$ and 100 . Interestingly, the absolute activity and hence the free energy per particle is lower for finite-size clusters than for a macroscopic sample, and this effect is particularly significant for temperatures in the vicinity of T_c^∞ . The reduction in free energy mostly

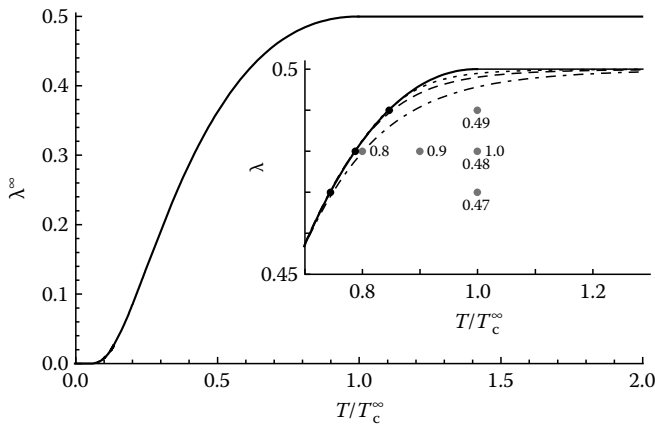


FIGURE 15.2 Temperature dependence of the absolute activity of ferromagnetic particles in the classical mean-field theory. In the case of finite-size ferromagnetic clusters, the mean-field theory predicts a decrease in the absolute activity, which is only noticeable in the vicinity of the macroscopic critical temperature T_c^∞ . The inset shows the mean-field activity for restricted-size finite cluster with number of particles $N = 20$ (dot-dashed), 50 (dashed), 100 (dotted), and ∞ (solid line). The gray points in the inset describe the unrestricted-size finite clusters studied below. Some of them correspond to fixed temperature $T = T_c^\infty$ and variable activity $\lambda = 0.47, 0.48,$ and 0.49 ; note that $\lambda^\infty(T_c^\infty) = 0.5$. The other gray points correspond to fixed activity $\lambda = 0.48$ and variable temperature $T/T_c^\infty = 1.0, 0.9,$ and 0.8 . Finally, the black points mark the finite-size critical temperatures for $\lambda = 0.48$ ($T_c/T_c^\infty = 0.846$), 0.48 ($T_c/T_c^\infty = 0.788$), and 0.47 ($T_c/T_c^\infty = 0.745$); note that $\lambda = \lambda^\infty(T)$.

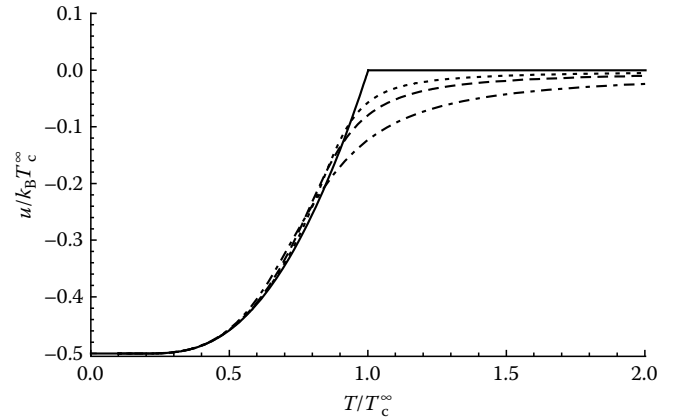


FIGURE 15.3 Internal energy per particle in the mean-field theory for restricted-size finite ferromagnetic cluster with number of particles $N = 20$ (dot-dashed), 50 (dashed), 100 (dotted), and ∞ (solid line). The classical Weiss transition at T_c^∞ is suppressed by finite-size effects.

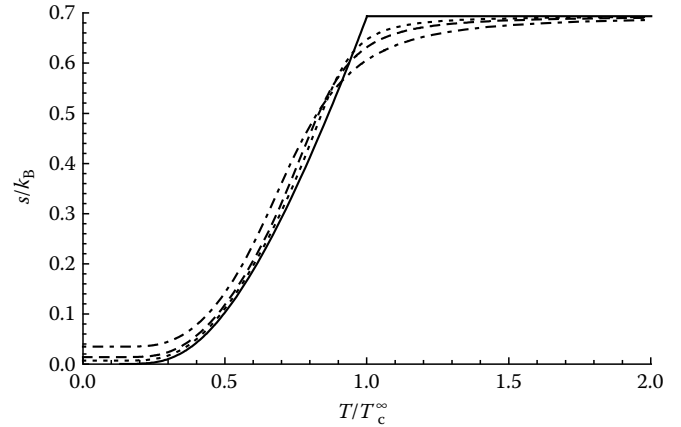


FIGURE 15.4 Entropy per particle in the mean-field theory for restricted-size finite ferromagnetic cluster with number of particles $N = 20$ (dot-dashed), 50 (dashed), 100 (dotted), and ∞ (solid line). The residual entropy $s(0) = k_B \ln 2/N$ appears because of the degeneracy associated to all-up and all-down spin states, and vanishes for macroscopic systems.

arises from the reduction in internal energy per particle due to fractionation in finite-size clusters. In particular, $m = 0$ and $u^\infty = 0$ for $T \geq T_c^\infty$ under equilibrium conditions but a macroscopic system can decrease its internal energy by subdividing into finite-size clusters, which can then become magnetized even for $T \geq T_c^\infty$.

Clusters with unrestricted sizes can be described by the generalized partition sum

$$Y(T, \lambda) = \sum_{N=2}^{\infty} \lambda^N \sum_{l=0}^N \frac{N!}{l!(N-l)!} e^{-\beta N \epsilon(l, N)} \quad (15.45)$$

where $\lambda \equiv e^{\beta\mu}$ and the sum over particles numbers start at $N = 2$ to avoid the ill-defined interaction energy of an isolated spin. The probability of finding a cluster of size N is then

$$p(N, T, \lambda) = \frac{\lambda^N}{Y(T, \lambda)} \sum_{l=0}^N \frac{N!}{l!(N-l)!} e^{-\beta N \varepsilon(l, N)} \quad (15.46)$$

and the average cluster size is $\langle N \rangle = \lambda (\partial \ln Y / \partial \lambda)_T = \sum_{N=2}^{\infty} N p(N, T, \lambda^N)$. The generalized partition sum only converges for $\lambda < \lambda^{\infty}(T)$, and the average cluster size becomes increasingly large as λ approaches $\lambda^{\infty}(T)$. The divergence of the average cluster size is associated to critical behavior and can be used to define a critical temperature $T_c(\lambda)$ for unrestricted finite-size clusters from the condition $\lambda^{\infty}(T_c) = \lambda$. Figure 15.5 shows $p(N, T_c^{\infty}, \lambda)$ for $\lambda^{\infty}(T_c^{\infty}) - \lambda = 0.03, 0.02$, and 0.01 . Similarly, Figure 15.6 shows $p(N, T, 0.48)$ for $T/T_c^{\infty} = 0.8, 0.9$, and 1.0 . It is observed that the probability distribution flattens and the average cluster size increases as λ approaches $\lambda^{\infty}(T_c^{\infty}) = 0.5$ in Figure 15.5 and as T approaches $T_c(0.48) = 0.788T_c^{\infty}$ in Figure 15.6. Thus, it is predicted from this theory that $\langle N \rangle \gg 100$ near the critical temperature, so that the magnetic order parameter increases rapidly with decreasing temperature near T_c .

The subdivision potential is $E(T, \lambda) = -k_B T \ln Y$ and the equilibrium thermodynamic properties of clusters with unrestricted sizes can be evaluated as $u(T, \lambda) = -(\partial \ln Y / \partial \beta)_{\lambda} / \langle N \rangle$ and $s(T, \lambda) = (u - \mu - E / \langle N \rangle) / T$. Figures 15.7 and 15.8 show $u(T, \lambda)$ and $s(T, \lambda)$ for $\lambda^{\infty}(T_c^{\infty}) - \lambda = 0.01, 0.02$, and 0.03 . It is remarkable that, by subdividing into clusters with unrestricted sizes, a macroscopic ferromagnet can do both decrease its energy per particle and increase its entropy per particle. It should be remembered that in the case of fixed cluster size (i.e., in the canonical ensemble), the entropy per particle in the vicinity of T_c^{∞} was $s(T_c^{\infty}, N) < s^{\infty}(T_c^{\infty}) = 0$. If we denote the entropy per particle obtained from the canonical ensemble for $\langle N \rangle(T, \lambda)$ as $s(T, \langle N \rangle)$, it can be shown that (Hill 1964)

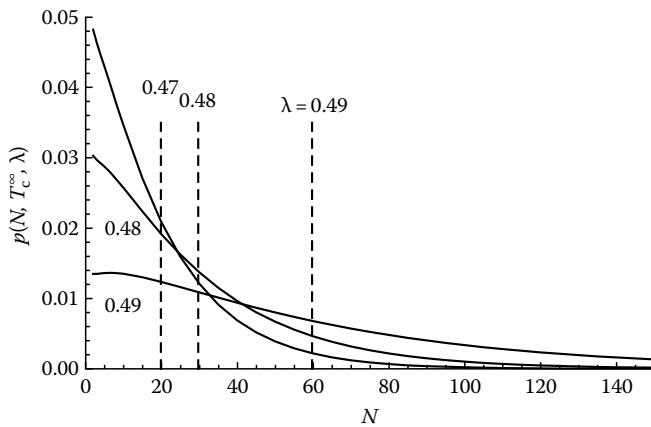


FIGURE 15.5 Probability function $p(N, T_c^{\infty}, \lambda)$ characterizing the distribution of cluster sizes at temperature $T = T_c^{\infty}$. The curves correspond to the activity values $\lambda = 0.47, 0.48$, and 0.49 . The size distribution broadens and the average size (marked with the dashed vertical lines) increases when λ approaches $\lambda^{\infty}(T_c^{\infty}) = 0.5$.

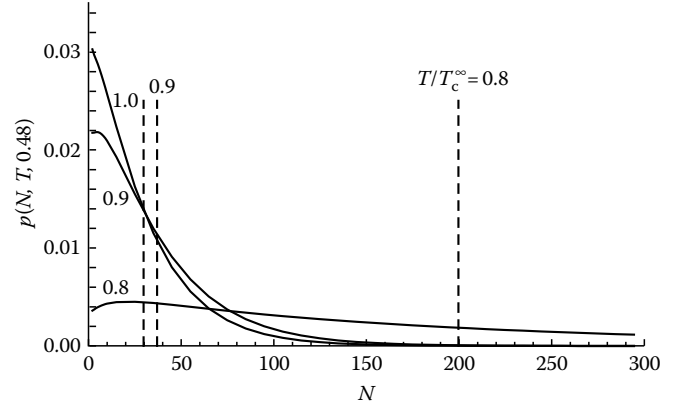


FIGURE 15.6 Probability function $p(N, T, 0.48)$ characterizing the distribution of cluster sizes for $\lambda = 0.48$. The curves correspond to temperatures $T/T_c^{\infty} = 1.0, 0.9$, and 0.8 . The size distribution broadens and the average size (marked with the dashed vertical lines) increases when the critical temperature $T_c(0.48)/T_c^{\infty} = 0.788$ is approached.

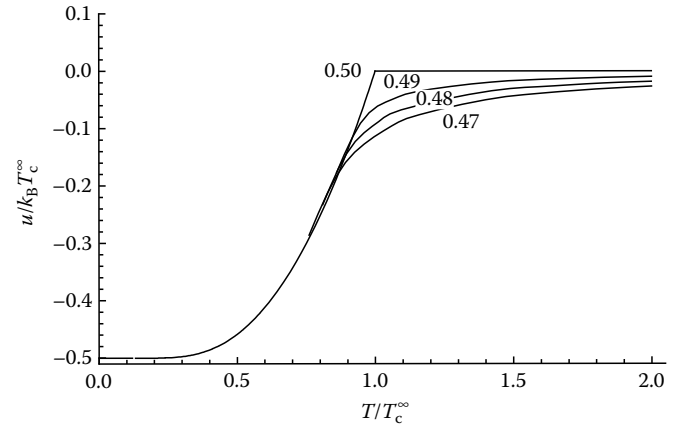


FIGURE 15.7 Internal energy per particle in the mean-field theory for unrestricted-size finite ferromagnetic cluster with absolute activity $\lambda = 0.47, 0.48$, and 0.49 . The solid line that covers the whole temperature range corresponds to the macroscopic system. The classical Weiss transition at T_c^{∞} is suppressed by finite-size effects.

$$[s(T, \lambda) - s(T, \langle N \rangle)] \langle N \rangle = -k_B \sum_{N=2}^{\infty} p(N, T, \lambda) \ln p(N, T, \lambda) \quad (15.47)$$

That is, the increased entropy in the generalized ensemble arises from the different ways in which the total number of particles can be distributed into clusters of average size $\langle N \rangle$.

In the previous paragraphs, we have considered a single cluster (or small system) with average size $\langle N \rangle$, which may become infinite at the critical point. Furthermore, the sample can increase its entropy by forming aggregates of indistinguishable clusters. These aggregates are described by the partition sum (Chamberlin 1999)

$$\Gamma(T, \lambda) = \sum_{N=0}^{\infty} \frac{1}{N!} [Y(T, \lambda)]^N \quad (15.48)$$

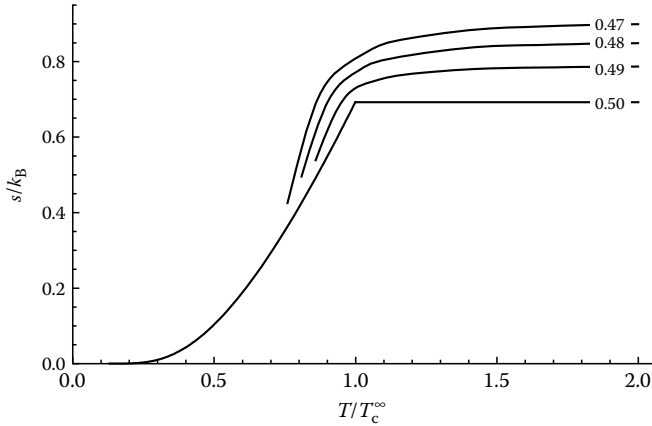


FIGURE 15.8 Entropy per particle in the mean-field theory for unrestricted-size finite ferromagnetic cluster with absolute activity $\lambda = 0.47, 0.48,$ and 0.49 . The solid line that covers the whole temperature range corresponds to the macroscopic system.

and the average number of clusters per aggregate is

$$\langle N \rangle = Y \left(\frac{\partial \ln \Gamma}{\partial Y} \right)_{T, \lambda} \quad (15.49)$$

In the case of ferromagnetic clusters in the presence of external magnetic field H , the energy per particle within the mean-field approximation is

$$\varepsilon(H, l, N) = -h \left(2 \frac{l}{N} - 1 \right) - \frac{cJ}{2} \left(4 \frac{l(l-1)}{N(N-1)} - 4 \frac{l}{N} + 1 \right) \quad (15.50)$$

where $h \equiv \mu_m \mu_0 H$, μ_m is the magnetic moment of the spin and μ_0 is the magnetic permeability of vacuum. The generalized partition sum is

$$Y(T, H, \lambda) = \sum_{N=2}^{\infty} \lambda^N \sum_{l=0}^N \frac{N!}{l!(N-l)!} e^{-\beta N \varepsilon(H, l, N)} \quad (15.51)$$

The magnetization of the cluster is $\langle M \rangle = (\mu_m k_B T / V) (\partial \ln Y / \partial h)_{T, \lambda}$ and its magnetic susceptibility is $\chi_m = (\partial \langle M \rangle / \partial H)_{T, \mu} = (\mu_0 \mu_m^2 k_B T / V) (\partial^2 \ln Y / \partial h^2)_{T, \lambda}$. In the absence of external field ($H \rightarrow 0$), the average magnetization vanishes above T_c^∞ and, therefore, the susceptibility reduces to

$$\begin{aligned} \chi_m^{H \rightarrow 0}(T, \lambda) &= \mu_0 \mu_m^2 \frac{k_B T}{V} \frac{1}{Y} \left(\frac{\partial^2 Y}{\partial h^2} \right)_{T, \lambda} \\ &= \frac{\mu_0 \mu_m^2}{V k_B T} \frac{1}{Y} \sum_{N=2}^{\infty} \lambda^N \sum_{l=0}^N \frac{N!(2l-N)^2}{l!(N-l)!} e^{-\beta N \varepsilon(H, l, N)} \quad (15.52) \end{aligned}$$

The value of the absolute activity λ is determined by comparison with experimental data and typical values are found in the range $0.0006 < \lambda^\infty(T_c^\infty) - \lambda < 0.004$ (Chamberlin 2000).

Two separate theories are often used to characterize the paramagnetic properties of ferromagnetic materials (Chamberlin 2000). Above the Weiss temperature Θ , classical mean-field theory yields the Curie–Weiss law for the magnetic susceptibility $\chi_m(T) = C/(T - \Theta)$. Close to the Curie or critical temperature T_c , however, the standard mean-field approach breaks down so that better agreement with experimental data is provided by the critical scaling theory $\chi_m(T) \propto (T - T_c)^{-\gamma}$ where γ is a scaling exponent. However, there is no known model capable of predicting either the measured values of γ or its variation among different substances.

By combining the mean-field approximation with Hill's nanothermodynamics, as explained above, the extra degrees of freedom from considering clusters with unrestricted sizes give the correct critical behavior, because the fraction of clusters with a specific amount of order diverges at T_c . At all temperatures above T_c , the model matches the measured magnetic susceptibilities of crystalline EuO, Gd, Co, and Ni, thus providing a unified picture for both the critical-scaling and Curie–Weiss regimes (Chamberlin 2000). Interestingly, Equation 15.52 gives a better agreement with experimental results for the entire paramagnetic phase with less fitting parameters and without introducing a separate transition temperature and amplitude prefactor for the scaling regime. Furthermore, when the average number of clusters per aggregate $\langle N \rangle$ is evaluated from Equation 15.49, the results are also in agreement with measurements of the correlation length in crystalline cobalt.

In conclusion, Chamberlin (2000) proved that the critical behavior of ferromagnets can be described by the mean-field theory, thereby eliminating the need for a separate scaling regime, provided that the clusters are described using the generalized or completely open ensemble because this is the only ensemble that does not artificially restrict the internal fluctuations of a bulk sample.

15.3.2.9 Supercooled Liquids and the Glass Transition

Motivated by the close similarity between the Vogel–Tamman–Fulcher (VTF) law for the characteristic relaxation time of supercooled liquids and the Curie–Weiss law of ferromagnetism, Chamberlin (1999, 2002) applied the Weiss mean-field theory to finite systems with unrestricted sizes, as explained in Section 15.3.2.8, to derive a generalized partition function for supercooled liquids. Finite-size effects broaden the transition and induce a Curie–Weiss-like energy reduction which provides an explanation for the VTF law. Moreover, the distribution of aggregate sizes derived from the generalized partition function of this nanothermodynamic theory provides an explanation for the Kohlrausch–Williams–Watt law. And standard fluctuation theory also helps to explain the measured specific heats.

15.3.3 Tsallis' Thermostatistics

Nonextensivity may appear in systems that are not in the thermodynamic limit because correlations are of the order of the system size, and this can be due to finite size effects, the presence of

long-range interactions, the existence of dissipative structures, etc. Tsallis considered that the Boltzmann–Gibbs–Shannon (BGS) entropy is not appropriate to nonextensive behavior and proposed to adopt the Havrda–Charvat structural entropy inspired by the multifractal formalism. Tsallis’ equation for the nonextensive entropy is (Tsallis 2001)

$$S_q \equiv k \frac{\sum_{j=1}^W p_j^q - 1}{1-q}, \quad \sum_{j=1}^W p_j = 1 \quad (15.53)$$

where q is a real number known as the entropic index and W is the total number of microstates of the system. The entropic index q characterizes the degree of nonextensivity reflected in the following pseudoadditivity rule:

$$S_q(A+B) = S_q(A) + S_q(B) + [(1-q)/k] S_q(A) S_q(B) \quad (15.54)$$

where A and B are two independent systems in the sense that the probabilities of $A+B$ factorize into those of A and of B . Since $S_q \geq 0$, the cases $q < 1$, $q = 1$, and $q > 1$ correspond, respectively, to superextensivity, extensivity, and subextensivity. Equation 15.53 is the only entropic form that satisfies the nonextensivity rule given in Equation 15.54, in the same way as BGS entropy is the only one that satisfies the extensivity rule $S(A+B) = S(A) + S(B)$.

The constant, k , in Equation 15.53 differs from Boltzmann’s constant, k_B , but reduces to it when $q = 1$. Moreover, S_q tends to the BGS entropy $S = -k_B \sum_j p_j \ln p_j$ when $q = 1$. In the microcanonical ensemble, all microstates are equally probable, $p_j = 1/W$, and Tsallis’ entropy becomes $S_q = k \ln_q W$ where \ln_q is a function called the q -logarithm defined as $\ln_q x \equiv (x^{1-q} - 1)/(1-q)$. Its inverse function is the q -exponential $e_q^x \equiv [1 + (1-q)x]^{1/(1-q)}$ and the equation $\ln_q(e_q^x) = e_q^{\ln_q x} = x$ is satisfied. Obviously, these functions have been introduced to resemble Boltzmann’s expression $S = k_B \ln W$, which is the limit of S_q when $q = 1$.

The probability distribution in Tsallis’ statistics is the q -exponential distribution

$$p_j = \frac{[1 - (1-q)\beta U_j]^{1/(1-q)}}{Z_q} = \frac{e_q^{-\beta U_j}}{Z_q} \quad (15.55)$$

where $Z_q = \sum_j e_q^{-\beta U_j}$ is a generalized canonical partition function. Equation 15.55 can be obtained by maximizing Equation 15.53 under the constraint that a generalized average energy $\langle U \rangle_q \equiv \left(\sum_j p_j^q U_j \right) / \sum_j p_j^q$ is fixed. To some extent, Equation 15.55 is responsible for the great success that Tsallis’ theory has experienced since it replaces the classical Boltzmann distribution by a family of distributions with a parameter q that can be determined by fitting the experimental data (Luzzi et al. 2002).

At the same time, this widespread use of q as a fitting parameter is one of the major drawbacks of Tsallis’ theory. Phenomena

characterized by the probability distribution in Equation 15.55 abound in nature. This type of statistics may arise from the convolution of the normal distribution with either a gamma or a power-law distribution, the latter being, for instance, a manifestation of the polydispersity of the system. The fact that they can be satisfactorily explained without any assumption of nonergodicity, long-range correlations, or thermodynamic nonequilibrium casts some doubts on the relevance of Tsallis formalism for many systems (Gheorghiu and Coppens 2004).

Yet, Tsallis’ entropy has got a place in modern statistical mechanics, which is supported by the growing evidence of its relevance to many complex physical systems and the great success in some of its applications. For instance, the entropic index q has been shown to be intimately related to the microscopic dynamics (Cohen 2002). Furthermore, in systems with fractal phase space, the entropic index q has been shown to be equal to the fractal dimension of the available phase space (García-Morales and Pellicer 2006). This connection has allowed to interpret unequivocally the observation that q tends to vanish in the strong coupling regime found in ionic solutions, since the available phase space collapses into regions of strikingly lower dimensions when the multivalent ions of the same charge are located close to a highly charged surface and crystallize forming a Wigner crystal (García-Morales et al. 2004).

The thermodynamic equations corresponding to Tsallis’ statistics have been deduced by García-Morales et al. (2005) after work by Vives and Planes (2002) and take the form

$$dS_q = \frac{1}{T} d\langle U \rangle_q + \frac{P}{T} d\langle V \rangle_q - \frac{\mu}{T} d\langle N \rangle_q \quad (15.56)$$

$$k \frac{\Sigma_q \ln \Sigma_q}{1-q} = \frac{\langle U \rangle_q}{T} + \frac{P \langle V \rangle_q}{T} - \frac{\mu \langle N \rangle_q}{T} \quad (15.57)$$

$$\ln \Sigma_q dS_q = \langle U \rangle_q d\frac{1}{T} + \langle V \rangle_q d\frac{P}{T} - \langle N \rangle_q d\frac{\mu}{T} \quad (15.58)$$

where $\Sigma_q \equiv \sum_{j=1}^W p_j^q = 1 + (1-q)S_q/k$, and $\langle X \rangle_q \equiv (\sum_j p_j^q X_j) / \Sigma_q$ for $X = U, V, N$. The comparison of these equations with those obtained in Hill’s nanothermodynamics shows that it is possible to connect these two nonextensive formalisms through the relation (García-Morales et al. 2005)

$$E = kT \frac{\Sigma_q \ln \Sigma_q}{1-q} - TS_q \quad (15.59)$$

Note that when $q = 1$, the first term becomes equal to $TS_q (=TS)$ and hence $E = 0$, so that extensivity is recovered. This relation between Hill’s subdivision potential E and Tsallis’ entropic index q may help to clarify the physical foundations of Tsallis’ entropy, and shows that, when the thermodynamic forces are properly defined, Tsallis’ entropy can be used to describe the size-effects on thermodynamic magnitudes.

15.3.4 Superstatistics

In Hill's theory, the ensemble contain N -independent nanosystems, each of which is in thermal contact with the thermal bath and has a fixed temperature, that of the bath. The energy of every nanosystem u_i fluctuates, and the same applies to the mean internal energy

$$\langle u \rangle_N = \frac{\langle U \rangle_N}{N} = \frac{1}{N} \sum_{i=1}^N u_i \quad (15.60)$$

The probability that the nanosystem i is found in a microstate of energy u_i is

$$p(u_i) = \frac{e^{-\beta_0 u_i}}{Z(\beta_0)} \quad (15.61)$$

and the joint probability distribution, i.e., the probability that the ensemble is found in the microstate $\{u_1, u_2, \dots, u_N\}$ is

$$P_N(U_N) = \prod_{i=1}^N p(u_i) = \frac{e^{-\beta_0 u_1}}{Z(\beta_0)} \frac{e^{-\beta_0 u_2}}{Z(\beta_0)} \dots \frac{e^{-\beta_0 u_N}}{Z(\beta_0)} = \left[\frac{e^{-\beta_0 \langle u \rangle_N}}{Z(\beta_0)} \right]^N = \frac{e^{-\beta_0 \langle U \rangle_N}}{Z_N(\beta_0)} \quad (15.62)$$

which is the usual Boltzmann distribution.

An alternative approach proposed by Rajagopal et al. (2006) would be to consider that the temperature of each nanosystem *fluctuates* around the temperature of the reservoir. The Boltzmann parameter $\beta \equiv 1/k_B T$ of a nanosystem would then be a fluctuating magnitude and the thermal equilibrium of the ensemble with the bath would only ensure that the ensemble average value of β is determined by the bath, $\langle \beta \rangle = \beta_0$; (the averaging routine to calculate $\langle \beta \rangle$ is still to be defined). The origin of these fluctuations lies in the very same nanosize and thus they come to quasithermodynamic equilibrium with the reservoir. This means that the Boltzmann–Gibbs distribution has to be averaged over the temperature fluctuations induced by the reservoir. Recently, this idea has been further developed in different physical contexts using a noisy reservoir (Wilk and Włodarczyk 2000, Beck 2002).

When temperature fluctuations are taken into account, the probability distribution that replaces that shown in Equation 15.62 can be derived by taking an integral over all possible fluctuating (inverse) temperatures. Let us work out this idea in detail starting from the concept of *superstatistics* (i.e., from the superposition of two different statistics) (Beck 2002). If all nanosystems in the ensemble had the same temperature, their probability distribution would be described by ordinary statistical mechanics, i.e., by Boltzmann factors $e^{-\beta u_i}$. However, if the nanosystems differ in temperature, we also need another statistics to describe the ensemble (the Boltzmann statistics $e^{-\beta u_i}$ and that of β), hence the name “superstatistics.” One may define an average Boltzmann factor $B(u_i)$ as

$$B(u_i) \equiv \int_0^{\infty} f(\beta) e^{-\beta u_i} d\beta \quad (15.63)$$

where $f(\beta)$ is the probability distribution of β . The stationary long-term probability distribution is obtained by normalizing this effective Boltzmann factor as

$$p(u_i) = \frac{B(u_i)}{\int_0^{\infty} B(u_i) du_i} \equiv \frac{1}{Z} B(u_i) \quad (15.64)$$

which can be considered as the generalization of Equation 15.61.

It should be noticed that we have linked the concepts of Hill's ensemble of nanosystems and the description of temperature fluctuations through superstatistics to make clear the limitations of the former. However, the concepts of superstatistics and temperature fluctuations can be applied to many other situations. For example, spatiotemporal fluctuations in temperature (or in other intensive magnitudes) may arise in driven nonequilibrium system with a stationary state. The different spatial regions (cells) with different values of β would then play the role of different nanosystems.

Among all possible probability distributions $f(\beta)$, there is one that has received much attention. This is the χ^2 distribution (also called Γ distribution) and is given by

$$f(\beta) = \frac{1}{\Gamma(\gamma)} \frac{(\gamma \beta / \langle \beta \rangle)^\gamma e^{-\gamma \beta / \langle \beta \rangle}}{\beta} \quad (15.65)$$

where $\langle \beta \rangle = \int_0^{\infty} \beta f(\beta) d\beta$ is the average value of β . The parameter γ is a measure of the variance, $\langle \beta^2 \rangle - \langle \beta \rangle^2$, of the distribution such that

$$\langle \beta^2 \rangle = \int_0^{\infty} \beta^2 f(\beta) d\beta = \left(1 + \frac{1}{\gamma}\right) \langle \beta \rangle^2 \quad (15.66)$$

and

$$\frac{\langle (\beta - \langle \beta \rangle)^2 \rangle}{\langle \beta \rangle^2} = \frac{\langle \beta^2 \rangle - \langle \beta \rangle^2}{\langle \beta \rangle^2} = \frac{1}{\gamma} \geq 0 \quad (15.67)$$

The average Boltzmann factor $B(u_i)$ corresponding to the χ^2 distribution in Equation 15.65 is

$$B(u_i) = \int_0^{\infty} f(\beta) e^{-\beta u_i} d\beta = [1 + \langle \beta \rangle u_i / \gamma]^{-\gamma} \quad (15.68)$$

Introducing the entropic index as $q \equiv 1 + 1/\gamma$, this factor can also be presented as $B(u_i) = e_q^{-\langle \beta \rangle u_i}$, which turns out to be the Tsallis distribution corresponding to the average temperature. Hence,

it can be concluded that the entropy associated with small systems with temperature fluctuations is Tsallis' entropy. The Boltzmann–Gibbs statistics corresponds to $1/\gamma = 0$ and absence of temperature fluctuations.

In conclusion, the theory of superstatistics contains Tsallis' statistics as a particular case that corresponds to the χ^2 distribution. The validity of Tsallis' distributions observed in a large variety of physical systems, many of them in a driven stationary state far from equilibrium, can thus be justified because the χ^2 distribution naturally arises in many circumstances.

Since these or similar distributions are often observed in experiments, it seems justified to look for dynamical arguments for the occurrence of Tsallis statistics in suitable classes of non-equilibrium systems (Beck 2001). And this is indeed possible: Tsallis statistics can be generated from stochastic differential equations with fluctuating parameters. For many systems, the reason why Tsallis distributions are observed can be related to the fact that there are spatiotemporal fluctuations of an intensive parameter (e.g., the temperature). If these fluctuations evolve on a long time scale and are distributed according to a particular distribution, the χ^2 distribution, one ends up with Tsallis' statistics in a natural way.

15.3.5 Nonequilibrium Approaches

As in macroscopic systems, there exist nonequilibrium steady states with net currents flowing across small systems where physical properties do not display any observable time dependence. For example, a small system in contact with two thermal sources at different temperatures has a heat flux as current. Another example is a resistor connected to a voltage source, which has an electric current across it. Such systems require a constant input of energy to maintain their steady state because the systems constantly dissipate net energy and operate away from equilibrium. Most biological systems, including molecular machines and even whole cells, are found in nonequilibrium steady states. Out of a steady state, the most general case, one or more of the system's properties change in time. The entropy production σ is perhaps the most important fact in nonequilibrium thermodynamics, since it is totally absent in thermostatics. In macroscopic irreversible thermodynamics (de Groot and Mazur 1962), it is usual to look at it as a function of two sets of variables, the thermodynamic fluxes $\{\phi_i\}$ and forces $\{y_i\}$, defined so that the entropy production can be expressed as a sum of products of conjugates, $\sigma = \sum_i \phi_i y_i$, the fluxes being zero at equilibrium.

This expression is supplemented by a set of phenomenological relations, which gives the fluxes as functions of the forces, these relations being such that the forces cancel at equilibrium. It is an experimental fact that there exists a neighborhood of equilibrium where the relations between the two sets of variables are linear, that is, $\phi_i = \sum_j L_{ij} y_j$ so that $\sigma = \sum_{i,j} L_{ij} y_j y_i$.

Onsager's result is the symmetry of the phenomenological coefficients $L_{ij} = L_{ji}$, proven on the basis of two general

hypothesis: regression of fluctuations and microscopic dynamic reversibility (de Groot and Mazur 1962). This implies that the matrix of Onsager coefficients is definite positive, and, therefore, that entropy production is always a positively defined quantity. This situation can change for a nanosystem where violations of the second law for short times have been observed experimentally (Wang et al. 2002). Dissipation and thermal properties out of equilibrium in nanosystems and small times have been the subject of intense research in the last two decades and remarkable rigorous results have been derived that have been found experimentally to hold out of equilibrium. In this section, we summarize some of these results.

15.3.5.1 Jarzynski Equality (JE)

C. Jarzynski derived an expression allowing the equilibrium free energy difference ΔF between two configurations A (initial) and B (final) of the system to be determined from finite-time measurements of the work W performed in parametrically switching from one configuration to the other. This result, which is independent of both the path γ from A to B, and the rate at which the parameters are switched along the path, is surprising: It says that we can extract equilibrium information from an ensemble of *nonequilibrium* (finite-time) measurements. Jarzynski equality reads (Jarzynski 1997a, 1997b)

$$\left\langle e^{-\beta W} \right\rangle_{\chi(t)} = e^{-\beta \Delta F} \quad (15.69)$$

where $\chi(t)$ is the time-dependent protocol specifying the switching between the two configurations and the brackets $\langle \dots \rangle$ denote an average over an ensemble of measurements of W . Each measurement is made after first allowing the system and reservoir to equilibrate at temperature T , with parameters fixed at A. (The path in parameter space γ from A to B, and the protocol at which the parameters are switched along this path, remain unchanged from one measurement to the next.) Formally, W is defined by

$$W = \int_0^{t_s} dt \chi \frac{\partial H_\chi(\mathbf{z}(t))}{\partial \chi} \quad (15.70)$$

where $\mathbf{z}(t)$ is the mechanical (stochastic) trajectory followed by the system and the dynamical role of χ , a parameter that is tuned externally in the experiments, is clarified. The system's Hamiltonian H_χ depends explicitly on the latter external parameter. χ varies between 0 (at configuration A) and 1 (at configuration B) over a total switching time t_s . Now imagine an ensemble of realizations of the switching process (with γ and t_s fixed), with initial conditions for the system and reservoir generated from a canonical ensemble at temperature T . Then W may be computed for each trajectory $\mathbf{z}(t)$ in the ensemble, and the brackets in Equation 15.69 indicate an average over the distribution of values of W thus obtained. This provides a means for a numerical checking of Equation 15.69. Alternatively W defined

by Equation 15.70 can be readily measured in the experiments and then brackets in Equation 15.69 denote the average obtained from the set of measurements. Equation 15.69 holds independently of the path γ . In the limiting case of an infinitely slow switching of the external parameters the system is in quasistatic equilibrium with the reservoir throughout the switching process and Equation 15.69 takes the form

$$\Delta F = \int_0^1 d\chi \left\langle \frac{\partial H_\chi(\mathbf{z}(t))}{\partial \chi} \right\rangle \quad (15.71)$$

In the opposite limit of infinitely fast switching ($t_s \rightarrow 0$), the switching is instantaneous and therefore $W = \Delta H = H_1 - H_0$ in Equation 15.70. Since we have a canonical distribution of initial conditions Equation 15.69 becomes

$$\Delta F = -k_B T \ln \left\langle e^{-\beta \Delta H} \right\rangle_0 \quad (15.72)$$

Equations 15.71 and 15.72 are well known from previous work (Kirkwood 1935, Zwanzig 1954) and the JE generalizes them to *any* switching protocol $\chi(t)$. “The free energy difference between initial and final equilibrium states can be determined not just from a reversible or quasistatic process that connects those states, but also via a nonequilibrium, irreversible process that connects them” (Bustamante et al. 2005). This property makes the JE to have enormous practical importance. The exponential average appearing in Equation 15.69 implies that $\langle W \rangle \geq \Delta F$, which, for macroscopic systems, is the statement of the second law of thermodynamics in terms of free energy and work. The Clausius inequality combined with the JE allows relating mean entropy dissipation to experimental observables (Ben-Amotz and Honig 2006). The Carnot engine has been then elegantly shown to emerge as a limiting case of a family of irreversible processes arising from an interface between materials at different temperatures. The following expression for the entropy change during an irreversible process has been proposed (Ben-Amotz and Honig 2006)

$$dS = \frac{\langle \delta W_{\text{dis}} \rangle_{\chi(t)}}{T} + k_B \ln \left\langle e^{-\beta \delta W_{\text{dis}}} \right\rangle_{\chi(t)} \quad (15.73)$$

The JE considers processes where the system is driven out of equilibrium by a mechanical external agent while remaining in contact with a thermal reservoir at a fixed temperature. Quite recently, a generalization of the JE to situations where the reservoir drives the system out of equilibrium through temperature changes has also been provided (Williams et al. 2008). The JE has also been extended to quantum systems (Mukamel 2003, Teifel and Mahler 2007).

The biophysical relevance of the JE was recently demonstrated through single-molecule experiments carried out under nonequilibrium conditions, which allowed extracting free energy differences (Hummer and Szabo 2001). The JE was also tested by

mechanically stretching a single molecule of RNA, both reversibly and irreversibly, between its folded and unfolded conformations (Liphardt et al. 2002).

15.3.5.2 Fluctuation Theorems (FTs)

The question of how reversible microscopic equations of motion can lead to irreversible macroscopic behavior has been the object of intense work in the last two decades. The fluctuation theorem (FT) was formulated heuristically in 1993 for thermostated dissipative nonequilibrium systems (Evans et al. 1993) and gives an answer to the problem of macroscopic irreversibility under reversible microscopic dynamics. The theorem, which was successfully tested in a recent experimental work (Wang et al. 2002), is entirely grounded on the postulates of causality and ergodicity at equilibrium states. Gallavotti and Cohen derived rigorously the FT in 1995 (Gallavotti and Cohen 1995) for thermostated deterministic steady-state ensembles. The authors proved the following asymptotic expression:

$$\frac{P_\tau(+\sigma)}{P_\tau(-\sigma)} = e^{\sigma\tau} \quad (15.74)$$

Here $P_\tau(\pm\sigma)$ is the probability of observing an average entropy production σ on a trajectory of time τ . Equation 15.74 establishes that *there is a nonvanishing probability of observing a negative entropy production* (thus violating the second law of thermodynamics) which is, however, exponentially small with increasingly longer times compared to the probability of observing a positive entropy production. In small systems (and short-trajectory times), the probability of observing a violation of the second law is, however, significant. A FT for stochastic dynamics was also derived (Kurchan 1998, Lebowitz and Spohn 1999, Maes 1999). Other FTs have been reported differing in details on as whether the kinetic energy or some other variable is kept constant, and whether the system is initially prepared in equilibrium or in a nonequilibrium steady state (Evans and Searles 2002). FTs can be of crucial interest for nanosystems and especially for the development of nanoelectronics (van Zon et al. 2004, Garnier and Ciliberto 2005).

Another result that connects the FT to the JE was obtained by Crooks (1999) who derived a generalized FT for stochastic microscopic dynamics. Crooks FT, which was experimentally tested in recovering RNA folding free energies (Collin et al. 2005), provides an independent and succinct proof of the JE and has similar practical relevance as the JE. Crooks theorem has been extended to quantum systems in the microcanonical ensemble yielding interesting insights on the concept of nonequilibrium entropy in the quantum regime (Talkner et al. 2008).

15.3.5.3 Thermodynamics Based on the Principle of Least-Abbreviated Action

In invoking concepts as microscopic reversibility and deterministic or stochastic trajectories, all works mentioned above point directly to several aspects of the dynamical foundations of

statistical thermodynamics. These were already the concern of Boltzmann and Clausius at the end of the nineteenth century (see Baily 1994) and are still open issues. Recently, a dynamical definition of nonequilibrium entropy based solely in the Hamiltonian dynamics of conservative systems has been introduced (García-Morales et al. 2008). The theory is based on the Maupertuis principle of least-abbreviated action and the definition of the entropy is of relevance to *systems of any size*, since it is grounded directly on the Hamiltonian H of the system. Finite-size effects and non-extensivity in small systems are satisfactorily captured by the formulation. The nonequilibrium entropy takes the form

$$S = k_B \ln \left(\prod_{i=1}^N J_i \right) \quad (15.75)$$

where the $J_i = \oint p_i dq_i$ are suitable action variables (q_i and p_i are, respectively, generalized position and momenta and the integral extends over the region that bounds each degree of freedom). When all degrees of freedom are separable in the Hamiltonian and the system is integrable, the system remains forever *out of equilibrium*, since the degrees of freedom cannot thermalize. Under this picture, macroscopic irreversibility is entirely grounded in the *nonintegrability* of the dynamics coming from complicated interactions between the degrees of freedom that lead to their thermalization. The propagation of the error in using approximate action variables to describe the nonintegrable dynamics of the system is directly linked to the entropy production (García-Morales et al. 2008), which is defined through Hamiltonian mechanics as

$$\sigma = -k_B \sum_{i=1}^N \frac{1}{J_i} \frac{\partial H}{\partial \theta_i} \quad (15.76)$$

where θ_i are the angle variables conjugate to the J_i , which are present in the Hamiltonian H , making the dynamics of the system nonintegrable.

15.3.5.4 Nonequilibrium Nanothermodynamics

In the entropic representation, the thermodynamic equations for the average small system in Hill's nanothermodynamics are (García-Morales et al. 2005, Carrete et al. 2008)

$$dS = \sum_{\alpha} y_{\alpha} d\langle X_{\alpha} \rangle \quad (15.77)$$

$$S = \sum_{\alpha} y_{\alpha} \langle X_{\alpha} \rangle - \frac{E}{T} \quad (15.78)$$

$$d\left(-\frac{E}{T}\right) = -\sum_{\alpha} \langle X_{\alpha} \rangle dy_{\alpha} \quad (15.79)$$

The E -dependence of Equations 15.78 (Euler equation) and 15.79 (Gibbs–Duhem equation) makes entropy to be a

nonhomogeneous function of the extensive variables. By using Equations 15.73 and 15.78 a statistical definition can be given to the subdivision potential change ΔE of the nanosystem under an irreversible process (Carrete et al. 2008)

$$\Delta E|_{\chi(t)} = T \sum_{\alpha} y_{\alpha} \langle X_{\alpha} \rangle \Big|_0^{t_0} + \int_0^{t_0} \left[\delta W_{\text{dis}} + k_B T \ln \langle e^{-\beta \delta W_{\text{dis}}} \rangle \right] \chi(t) \quad (15.80)$$

Nonequilibrium nanothermodynamics (Carrete et al. 2008) follows Hill's course of reasoning to establish nonequilibrium transport equations in the linear regime that generalize macroscopic irreversible thermodynamics. The key idea is to consider a macroscopic ensemble of nanosystems, with a possible gradient in their number. Assuming that linear macroscopic irreversible thermodynamics holds for the entire ensemble, transport equations can be derived for quantities regarding each nanosystem. The nanoscopic transport coefficients are also found to be symmetric (Carrete et al. 2008), ensuring that the second law of thermodynamics is obeyed by the average systems although it can be transitorily violated by a small system.

It is important to note that Hill's equilibrium nanothermodynamics is consistent with Gibbs definition of the equilibrium entropy. Out of equilibrium a link of thermodynamic properties and statistical properties of nanosystems is provided by the Gibbs' entropy postulate (Reguera et al. 2005):

$$S = S_{\text{eq}} - k_B \int P(\gamma, t) \ln [P(\gamma, t) / P_{\text{eq}}(\gamma)] d\gamma \quad (15.81)$$

where S_{eq} denotes the equilibrium Gibbs entropy when the degrees of freedom γ are at equilibrium (where the integrand of the second term in the r.h.s. cancels). The probability distribution at an equilibrium state of a given configuration in γ -space is given by

$$P_{\text{eq}}(\gamma) \approx e^{-\beta \Delta W(\gamma)} \quad (15.82)$$

where $\Delta W(\gamma)$ is the minimum reversible work to create such a state. Taking variations of Equation 15.81, we have

$$\delta S = -k_B \int \delta P(\gamma, t) \ln [P(\gamma, t) / P_{\text{eq}}(\gamma)] d\gamma \quad (15.83)$$

The evolution of the probability density in the γ -space is governed by the continuity equation

$$\frac{\partial P}{\partial t} = -\frac{\partial J}{\partial \gamma} \quad (15.84)$$

where $J(\gamma, t)$ is a current or density flux in γ -space which has to be specified. Its form can be obtained by taking the time derivative in Equation 15.83 and by using Equation 15.84. After a partial integration, one then arrives at

$$\frac{dS}{dt} = -\int \frac{\partial J_s}{\partial \gamma} d\gamma + \sigma \quad (15.85)$$

where $J_s = k_B J \ln [P/P_{eq}]$ is the entropy flux and

$$\sigma = -k_B \int J(\gamma, t) \frac{\partial \ln [P(\gamma, t)/P_{eq}(\gamma)]}{\partial \gamma} d\gamma \quad (15.86)$$

is the entropy production. In this scheme, the thermodynamic forces are identified as the gradients in the space of mesoscopic variables of the logarithm of the ratio of the probability density to its equilibrium value. By assuming a linear dependence between fluxes and forces and establishing a linear relationship between them we have

$$J(\gamma, t) = -k_B L(\gamma, P(\gamma)) \frac{\partial \ln [P(\gamma, t)/P_{eq}(\gamma)]}{\partial \gamma} \quad (15.87)$$

where $L(\gamma, P(\gamma))$ is an Onsager coefficient, which, in general, depends on the state variable $P(\gamma)$ and on the mesoscopic parameters γ . To derive this expression, locality in γ -space is taken into account, and only fluxes and forces with the same value of γ become coupled. The resulting kinetic equation follows by substituting Equation 15.87 back into the continuity Equation 15.84:

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial \gamma} \left(D P_{eq} \frac{\partial P}{\partial \gamma} \right) \quad (15.88)$$

where the diffusion coefficient is defined as

$$D(\gamma) \equiv \frac{k_B L(\gamma, P)}{P} \quad (15.89)$$

By using Equation 15.82, Equation 15.88 can be written as

$$\frac{\partial P}{\partial t} = \frac{\partial}{\partial \gamma} \left(D \frac{\partial P}{\partial \gamma} + \frac{D}{k_B T} \frac{\partial \Delta W}{\partial \gamma} P \right) \quad (15.90)$$

which is the Fokker-Planck equation for the evolution of the probability density in γ -space. The dynamics of the probability distribution depends explicitly on equilibrium thermodynamic properties through the reversible work ΔW . This formalism allows to analyze the effects of entropic barriers $\Delta W = -T\Delta S$ in the nonequilibrium dynamics of the system. Entropic barriers are present in many situations, such as the motion of macromolecules through pores, protein folding, and in general in the dynamics of small confined systems (Reguera et al. 2005). As we have seen above, in mesoscopic physics, besides the diffusion processes coming from, for example, mass transport, one finds a diffusion process for the probability density of measuring certain values for experimental observables in the space of mesoscopic degrees of freedom γ .

15.4 Critical Discussion and Summary

Usually, there is some arbitrariness in all thermostatical approaches that arise from the difficulty of relating a very limited number of macroscopic variables to an enormous number of microscopic degrees of freedom. The existence of mesoscopic degrees of freedom, like rotation and translation of mesoscopic clusters, pose additional problems since the robustness of the thermodynamic limit is lost, and efficient ways of handling a very complicated and rich dynamics coming from a sufficiently high number of degrees of freedom need to be devised. Hill's nanothermodynamics constitutes an elegant approach whose philosophy, as we have seen, is averaging over the mesoscopic degrees of freedom and over ensembles of mesoscopic systems in order to bridge the mesoscopic dynamics with the macroscopic behavior that might be expected from a huge collection of mesoscopic samples. Although Hill's nanothermodynamics is based on equilibrium statistical thermodynamics, and hence it is strictly valid only for systems in equilibrium states, it has also proved to be successful in describing metastable states in the liquid-gas phase transition (Hill and Chamberlin 1998).

The nanosystems considered in Hill's ensembles are all identical, and they are all in equilibrium with their surroundings, so that fluctuations in intensive parameters such as temperature are neglected. Fluctuations in extensive parameters such as the number of particles in the nanosystem are considered, however, and this makes it useful to describe systems close to phase transitions. Chamberlin has adapted Hill's theory to treat finite-sized thermal fluctuations inside bulk materials (Javaheri and Chamberlin 2006). Thus, for example, in the study of supercooled liquids, Chamberlin and Stangel (2006) incorporated the fact that every "small system" was in thermal contact with an ensemble of similar systems, not an infinite external bath, and this yielded a self-consistent internal temperature.

Since the direct interactions between the nanosystems are neglected in Hill's theory, some authors consider that it cannot be applied to systems where local correlations are important. Indeed, the correction terms predicted in Hill's theory do not depend on temperature, whereas it is well known that correlations become more important the lower the temperature (Hartmann et al. 2004). However, Chamberlin has proved in several systems that interactions can be satisfactorily described using the mean-field approach when the "small systems" are considered as completely open, like in the generalized ensemble. Furthermore, the use of the partition function Γ describing a collection of completely open small systems somehow also accounts for interactions among small systems, because the small systems are then allowed to vary in size due to a redistribution of the components among the small systems. This partially solves the criticism raised against Hill's theory.

Other formulations valid for nanosystems and systems exhibiting nonextensivity, like Tsallis thermostatics, can be shown to be related to Hill's nanothermodynamics (García Morales et al. 2005) and therefore the same considerations apply.

Because of the increased importance of the specificities of the microscopic dynamics out of equilibrium, the problems to lay

a general foundation of nonequilibrium nanothermodynamics are much harder than in the equilibrium case. These difficulties are partially softened in the linear branch of nonequilibrium thermodynamics, where linear relationships between fluxes and thermodynamic forces are expected. Out of this linear branch, nonlinear effects cause couplings between microscopic degrees of freedom and it is a far from a trivial task in many problems to decide which of these degrees of freedom are irrelevant to the collective dynamics or can be accounted for, for example, by means of adiabatic elimination. Despite all these problems, rigorous results of general validity have been derived in the last two decades from which we have given an overview here. These results include the Jarzynski equality and the fluctuation theorems, which can be of enormous interest for the understanding of thermal properties at the nanoscale. We have also pointed out how, in the linear regime of nonequilibrium thermodynamics, the macroscopic approach can be extended to nanosystems both from a thermodynamic and a statistical point of view.

15.5 Future Perspectives

Besides the further development of nanothermodynamics, especially of its nonequilibrium branch, there are also some other topics that might likely be of great interest in a near future. Fluctuations play a significant role in the thermodynamics of small systems, near critical points, in processes taking place at small time scales, and in nonequilibrium thermodynamics (Lebon et al. 2008). One of the consequences of fluctuations is the nonequivalence of statistical ensembles that we have shown above in small systems, and also occurs at critical points and in other systems that are mesoscopically inhomogeneous, like complex fluids. A common feature of these systems is that they possess a mesoscopic length scale, known as the correlation length which is associated with fluctuations. Finite-size scaling (Bruce and Wilding 1999) is a powerful theoretical approach that has already been applied to small systems (Anisimov 2004) and may yield more interesting results in the near future.

The development of thermodynamic concepts at the nanoscale is also of crucial interest for the development of Brownian motors. The dynamical behavior of machines based on chemical principles can be described as a random walk on a network of states. In contrast to macroscopic machines whose function is determined predominately by the connections between the elements of the machine, the function of a Brownian machine in response to an external stimulus is completely specified by the equilibrium energies of the states and of the heights of the barriers between them. The thermodynamic control of mechanisms will be crucial in the next steps of interfacing synthetic molecular machines with the macroscopic world (Astumian 2007).

Interesting thermodynamic ideas that have arisen recently in applied physics and engineering and which might be of interest for nonequilibrium nanosystems are provided by the so-called *constructal theory* (Bejan 2000, 2006). We have refrained from discussing this theory here because, until now, the applications that it has found concern purely macroscopic systems. However,

an extension of these ideas to nanosystems might have great interest for the engineering of nanodevices and, specially, in the field of nanofluidics. The heart of constructal theory is contained in what might be arguably considered a new law of thermodynamics (Bejan 2000): “For a finite-size system to persist in time (to live), it must evolve in such a way that it provides easier access to the imposed currents that flow through it.” This principle connects global optimization techniques employed in engineering with local constraints and has been extremely successful in providing a foundation for scaling laws found in nature as, for example, the relationship between metabolic rate and body size known as Kleiber’s law, or different empirical relationships found in the locomotion of living beings. This principle also connects for the first time thermodynamics with the occurrence of definite shapes in nature: it explains, for example, why human beings have a bronchial tree with 23 levels of bifurcation. The constructal theory of the flow architecture of the lung predicts and offers an explanation for the dimensions of the alveolar sac, the total length of the airways, the total alveolar surface area and the total resistance to oxygen transport in the respiratory tree. Further research relating the constructal principle to the microscopic physical dynamics might yield valuable insight for all branches of nanoengineering.

Acknowledgments

This research was funded by the European Commission through the New and Emerging Science and Technology programme, DYNAMO STREP, project No. FP6-028669-2. Financial support from the excellence cluster NIM (Nanosystems Initiative München) is also gratefully acknowledged.

References

- Allahverdyan, A. E., Balian, R., and Nieuwenhuizen, Th. M. 2004. Quantum thermodynamics: Thermodynamics at the nanoscale. *J. Modern Opt.* 51: 2703–2711.
- Anisimov, M. A. 2004. Thermodynamics at the meso- and nanoscale. In *Dekker Encyclopedia of Nanoscience and Nanotechnology*, J. A. Schwarz, C. I. Contescu, and K. Putyera (Eds.), pp. 3893–3904. New York: Marcel Dekker.
- Astumian, R. D. 2007. Design principles for Brownian molecular machines: How to swim in molasses and walk in a hurricane. *Phys. Chem. Chem. Phys.* 9: 5067–5083.
- Bailyn, A. 1994. *A Survey of Thermodynamics*. New York: American Institute of Physics Press.
- Bartell, L. S. and Chen, J. 1992. Structure and dynamics of molecular clusters. 2. Melting and freezing of carbon tetrachloride clusters. *J. Phys. Chem.* 96: 8801–8808.
- Beck, C. 2001. Dynamical foundations of nonextensive statistical mechanics. *Phys. Rev. Lett.* 87: 180601.
- Beck, C. 2002. Non-additivity of Tsallis entropies and fluctuations of temperature. *Europhys. Lett.* 57: 329–333.
- Becker, R. and Döring, W. 1935. Kinetische Behandlung der Keimbildung in übersättigten Dämpfen. *Ann. Phys.* 24: 719–752.

- Bejan, A. 2000. *Shape and Structure: From Engineering to Nature*. Cambridge, U.K.: Cambridge University Press.
- Bejan, A. 2006. Constructal theory of generation of configuration in nature and engineering. *J. Appl. Phys.* 100: 041301.
- Ben-Amotz, D. and Honig, J. M. 2006. Average entropy dissipation in irreversible mesoscopic processes. *Phys. Rev. Lett.* 96: 020602.
- Berry, R. S. 2007. The power of the small. *Eur. Phys. J. D* 43: 5–6.
- Bruce, A. D. and Wilding, N. B. 1999. Critical-point finite-size scaling in the microcanonical ensemble. *Phys. Rev. E* 60: 3748–3760.
- Buffat, Ph. and Borel, J. P. 1976. Size effect on the melting temperature of gold particles. *Phys. Rev. A* 13: 2287–2298.
- Bustamante, C., Liphardt, J., and Ritort, F. 2005. The nonequilibrium thermodynamics of small systems. *Phys. Today* 58: 43–48.
- Carrete, J., Varela, L. M., and Gallego, L. J. 2008. Nonequilibrium nanothermodynamics. *Phys. Rev. E* 77: 022102.
- Chamberlin, R. V. 1999. Mesoscopic mean-field theory for supercooled liquids and the glass transition. *Phys. Rev. Lett.* 82: 2520–2523.
- Chamberlin, R. V. 2000. Mean-field cluster model for the critical behaviour of ferromagnets. *Nature* 408: 337–339.
- Chamberlin, R. V. 2002. Nanoscopic heterogeneities in the thermal and dynamic properties of supercooled liquids. *ACS Symp. Ser.* 820: 228–248.
- Chamberlin, R. V. 2003. Critical behavior from Landau theory in nanothermodynamic equilibrium. *Phys. Lett. A* 315: 313–318.
- Chamberlin, R. V. and Stangel, K. J. 2006. Monte Carlo simulation of supercooled liquids using a self-consistent local temperature. *Phys. Lett. A* 350: 400–404.
- Chushak, Y. G. and Bartell, L. S. 2000. Crystal nucleation and growth in large clusters of SeF₆ from molecular dynamics simulations. *J. Phys. Chem. A* 104: 9328–9336.
- Chushak, Y. G. and Bartell, L. S. 2001. Melting and freezing of gold nanoclusters. *J. Phys. Chem. B* 105: 11605–11614.
- Cohen, E. G. D. 2002. Statistics and dynamics. *Physica A* 305: 19–26.
- Collin, D., Ritort, F., Jarzynski, C., Smith, S., Tinoco Jr., I., and Bustamante, C. 2005. Verification of the Crooks fluctuation theorem and recovery of RNA folding free energies. *Nature* 437: 231–234.
- Couchman, P. R. and Jesser, W. A. 1977. Thermodynamic theory of size dependence of melting temperature in metals. *Nature* 269: 481–483.
- Crooks, G. E. 1999. Entropy production fluctuation theorem and the nonequilibrium work relation for free-energy differences. *Phys. Rev. E* 60: 2721–2726.
- de Groot, S. R. and Mazur, P. 1962. *Non-Equilibrium Thermodynamics*. Amsterdam, the Netherlands: North-Holland Publishing Co.
- Defay, R. and Prigogine, I. 1966. *Surface Tension and Adsorption*. London, U.K.: Longmans.
- DeHoff, R. 2006. *Thermodynamics in Materials Science*. Boca Raton, FL: Taylor & Francis.
- Delogu, F. 2005. Thermodynamics on the nanoscale. *J. Phys. Chem. B* 109: 21938–21941.
- Dobruskin, V. K. 2006. Size-dependent enthalpy of condensation. *J. Phys. Chem. B* 110: 19582–19585.
- Evans, D. J. and Morriss, G. 2008. *Statistical Mechanics of Nonequilibrium Liquids*. Cambridge, U.K.: Cambridge University Press.
- Evans, D. J. and Searles, D. J. 2002. The fluctuation theorem. *Adv. Phys.* 51: 1529–1585.
- Evans, D. J., Cohen, E. G. D., and Morriss, G. P. 1993. Probability of second law violations in shearing steady states. *Phys. Rev. Lett.* 71: 2401–2404.
- Feshbach, H. 1988. Small systems: When does thermodynamics apply? *IEEE J. Quant. Electron.* 24: 1320–1322.
- Frenkel, J. 1946. *Kinetic Theory of Liquids*. New York: Oxford University Press.
- Gallavotti, G. and Cohen, E. G. D. 1995. Dynamical ensembles in stationary states. *J. Stat. Phys.* 80: 931–970.
- García-Morales, V. and Pellicer, J. 2006. Microcanonical foundation of nonextensivity and generalized thermostatics based on the fractality of the phase space. *Physica A* 361: 161–172.
- García-Morales, V., Cervera, J., and Pellicer, J. 2003. Calculation of the wetting parameter from a cluster model in the framework of nanothermodynamics. *Phys. Rev. E* 67: 062103.
- García-Morales, V., Cervera, J., and Pellicer, J. 2004. Coupling theory for counterion distributions based in Tsallis statistics. *Physica A* 339: 482–490.
- García-Morales, V., Cervera, J., and Pellicer, J. 2005. Correct thermodynamic forces in Tsallis thermodynamics: Connection with Hill nanothermodynamics. *Phys. Lett. A* 336: 82–88.
- García-Morales, V., Pellicer, J., and Manzanares, J. A. 2008. Thermodynamics based on the principle of least abbreviated action: Entropy production in a network of coupled oscillators. *Ann. Phys. (NY)* 323: 1844–1858.
- Garnier, N. and Ciliberto, S. 2005. Nonequilibrium fluctuations in a resistor. *Phys. Rev. E* 71: 060101.
- Gheorghiu, S. and Coppens, M. O. 2004. Heterogeneity explains features of “anomalous” thermodynamics and statistics. *Proc. Natl. Acad. Sci. USA* 101: 15852–15856.
- Gilányi, T. 1999. Small systems thermodynamics of polymer-surfactant complex formation. *J. Phys. Chem. B* 103: 2085–2090.
- Gross, D. H. E. 2001. *Microcanonical Thermodynamics. Phase Transitions in “Small” Systems*. Singapore: World Scientific.
- Hall, D. G. 1987. Thermodynamics of micelle formation. In *Nonionic Surfactants. Physical Chemistry*, M. J. Schick (Ed.), pp. 233–296. New York: Marcel Dekker.
- Hartmann, M., Mahler, G., and Hess, O. 2004. Local versus global thermal states: Correlations and the existence of local temperatures. *Phys. Rev. E* 70: 066148.
- Hartmann, M., Mahler, G., and Hess, O. 2005. Nanothermodynamics: On the minimal length scale for the existence of temperature. *Physica E* 29: 66–73.
- Hasegawa, H. 2007. Non-extensive thermodynamics of transition-metal nanoclusters. *Prog. Mat. Sci.* 52: 333–351.

- Hill, T. L. 1962. Thermodynamics of small systems. *J. Chem. Phys.* 36: 153–168.
- Hill, T. L. 1963. *Thermodynamics of Small Systems. Part I.* New York: W.A. Benjamin.
- Hill, T. L. 1964. *Thermodynamics of Small Systems. Part II.* New York: W.A. Benjamin.
- Hill, T. L. and Chamberlin, R.V. 1998. Extension of the thermodynamics of small systems to open metastable states: An example. *Proc. Natl. Acad. Sci. USA*, 95: 12779–12782.
- Hill, T. L. and Chamberlin, R. V. 2002. Fluctuations in energy in completely open small systems. *Nano Lett.* 2: 609–613.
- Hubbard, J. 1971. On the equation of state of small systems. *J. Chem. Phys.* 55: 1382–1385, and references therein.
- Hummer, G. and Szabo, A. 2001. Free energy reconstruction from nonequilibrium single-molecule pulling experiments. *Proc. Natl. Acad. Sci. USA* 98: 3658–3661.
- Jarzynski, C. 1997a. Nonequilibrium equality for free energy differences. *Phys. Rev. Lett.* 78: 2690–2693.
- Jarzynski, C. 1997b. Equilibrium free-energy differences from nonequilibrium measurements: A master-equation approach. *Phys. Rev. E* 56: 5018–35.
- Javaheri, M. R. H. and Chamberlin, R. V. 2006. A free-energy landscape picture and Landau theory for the dynamics of disordered materials. *J. Chem. Phys.* 125: 154503.
- Jiang, Q. and Yang, C. C. 2008. Size effect on the phase stability of nanostructures. *Curr. Nanosci.* 4: 179–200.
- Jortner, J. and Rao, C. N. R. 2002. Nanostructured advanced materials. Perspectives and directions. *Pure Appl. Chem.* 74: 1491–1506.
- Kirkwood, J. G. 1935. Statistical mechanics of fluid mixtures. *J. Chem. Phys.* 3: 300–313.
- Kondepudi, D. 2008. *Introduction to Modern Thermodynamics.* New York: Wiley.
- Kurchan, J. 1998. Fluctuation theorem for stochastic dynamics. *J. Phys. A: Math. Gen.* 31 3719–3729.
- Lebon, G., Jou, D., and Casas-Vázquez, J. 2008. *Understanding Non-Equilibrium Thermodynamics.* Berlin, Germany: Springer-Verlag.
- Lebowitz, J. L. and Spohn, H. 1999. A Gallavotti-Cohen-type symmetry in the large deviation functional for stochastic dynamics. *J. Stat. Phys.* 95: 333–365.
- Letellier, P., Mayaffre, A., and Turmine, M. 2007a. Solubility of nanoparticles: Nonextensive thermodynamics approach. *J. Phys.: Condens. Matter* 19: 436229.
- Letellier, P., Mayaffre, A., and Turmine, M. 2007b. Melting point depression of nanoparticles: Nonextensive thermodynamics approach. *Phys. Rev. B* 76: 045428.
- Liphardt, J., Dumont, S., Smith, S. B., Tinoco Jr., I., and Bustamante, C. 2002. Equilibrium information from nonequilibrium measurements in an experimental test of Jarzynski's equality. *Science* 296: 1832–1835.
- Luzzi, R., Vasconcellos, A. R., and Galvao Ramos, J. 2002. Trying to make sense out of order. *Science* 298: 1171–1172.
- Maes, C. 1999. The fluctuation theorem as a Gibbs property. *J. Stat. Phys.* 95: 367–392.
- Mafé, S., Manzanares, J. A., and de la Rubia, J. 2000. On the use of the statistical definition of entropy to justify Planck's form of the third law of thermodynamics. *Am. J. Phys.* 68: 932–935.
- Mukamel, S. 2003. Quantum extension of the Jarzynski relation: Analogy with stochastic dephasing, *Phys. Rev. Lett.* 90:170604.
- Onischuk, A. A., Purtov, P. A., Bakalnov, A. M., Karasev, V. V., and Vosel, S. K. 2006. Evaluation of surface tension and Tolman length as a function of droplet radius from experimental nucleation rate and supersaturation ratio: Metal vapor homogenous nucleation. *J. Chem. Phys.* 124: 014506.
- Peters, K. F., Cohen, J. B., and Chung, Y. W. 1998. Melting of Pb nanocrystals. *Phys. Rev. B* 57: 13430–13438.
- Polak, M. and Rubinovich, L. 2008. Nanochemical equilibrium involving a small number of molecules: A prediction of a distinct confinement effect. *Nano Lett.* 8: 3543–3547.
- Rajagopal, A. K., Pande, C. S., and Abe, S. 2006. Nanothermodynamics—A generic approach to material properties at nanoscale. In *Nano-Scale Materials: From Science to Technology*, S. N. Sahu, R. K. Choudhury, and P. Jena (Eds.), pp. 241–248. Hauppauge, NY: Nova Science.
- Reguera, D., Rubí, J. M., and Vilar, J. M. G. 2005. The mesoscopic dynamics of thermodynamic systems. *J. Phys. Chem. B* 109: 21502–21515.
- Reiss, H., Mirabel, P., and Whetten, R. L. 1988. Capillary theory for the coexistence of liquid and solid clusters. *J. Phys. Chem.* 92: 7241–7246.
- Rowlinson, J. S. 1987. Statistical thermodynamics of small systems. *Pure Appl. Chem.* 59: 15–24.
- Rusanov, A. I. 2005. Surface thermodynamics revisited. *Surf. Sci. Rep.* 58: 111–239.
- Samsonov, V. M., Sdobnyakov, N. Yu., and Bazulev, A. N. 2003. On thermodynamic stability conditions for nanosized particles. *Surf. Sci.* 532–535: 526–530.
- Schäfer, R. 2003. The chemical potential of metal atoms in small particles. *Z. Phys. Chem.* 217: 989–1001.
- Schmidt, M. and Haberland, H. 2002. Phase transitions in clusters. *C. R. Physique* 3: 327–340.
- Talkner, P., Hänggi, P., and Morillo, M. 2008. Microcanonical quantum fluctuation theorems. *Phys. Rev. E* 77: 051131.
- Tanaka, M. 2004. New interpretation of small system thermodynamics applied to ionic micelles in solution and Corrin-Harkins equation. *J. Oleo Sci.* 53: 183–196.
- Teifel, J. and Mahler, G. 2007. Model studies on the quantum Jarzynski relation. *Phys. Rev. E* 76: 051126.
- Tolman, R. C. 1949. The effect of droplet size on surface tension. *J. Chem. Phys.* 17: 333–337.
- Tsallis, C. 2001. Nonextensive statistical mechanics and thermodynamics: Historical background and present status. In *Nonextensive Statistical Mechanics and Its Applications*, S. Abe and Y. Okamoto (Eds.), pp. 3–98. Berlin, Germany: Springer-Verlag.
- van Zon, R., Ciliberto, S., and Cohen, E. G. D. 2004. Power and heat fluctuation theorems for electric circuits. *Phys. Rev. Lett.* 92: 130601.

- Vanfleet, R. R. and Mochel, J. M. 1995. Thermodynamics of melting and freezing in small particles. *Surf. Sci.* 341: 40–50.
- Vengrenovich, R. D., Gudyma, Yu. V., and Yarema, S. V. 2001. Ostwald ripening of quantum-dot nanostructures. *Semiconductors* 35: 1378–1382.
- Vives, E. and Planes, A. 2002. Is Tsallis thermodynamics nonextensive? *Phys. Rev. Lett.* 88: 020601.
- Wang, C. X. and Yang, G. W. 2005. Thermodynamics of metastable phase nucleation at the nanoscale. *Mater. Sci. Eng. R* 49: 157–202.
- Wang, G. M., Sevick, E. M., Mittag, E., Searles, D. J., and Evans, D. J. 2002. Experimental demonstration of violations of the second law of thermodynamics for small systems and short time scales. *Phys. Rev. Lett.* 89: 050601.
- Weissmüller, J. 2002. Thermodynamics of nanocrystalline solids. In *Nanocrystalline Metals and Oxides. Selected Properties and Applications*, P. Knauth and J. Schoonman (Eds.), pp. 1–39. Boston, MA: Kluwer.
- Wilk, G. and Włodarczyk, Z. 2000. Interpretation of the nonextensivity parameter q in some applications of Tsallis statistics and Lévy distributions. *Phys. Rev. Lett.* 84: 2770–2773.
- Williams, S. R., Searles, D. J., and Evans, D. J. 2008. Nonequilibrium free-energy relations for thermal changes. *Phys. Rev. Lett.* 100: 250601.
- Yang, C. C. and Li, S. 2008. Size-dependent temperature-pressure phase diagram of carbon. *J. Phys. Chem. C*, 112: 1423–1426.
- Zhang, C. Y., Wang, C. X., Yang, Y. H., and Yang, G. W. 2004. A nanoscaled thermodynamic approach in nucleation of CVD diamond on nondiamond surfaces. *J. Phys. Chem. B* 108: 2589–2593.
- Zwanzig, R. W. 1954. High-temperature equation of state by a perturbation method. I. Nonpolar gases. *J. Chem. Phys.* 22: 1420–1426.