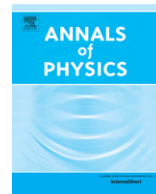




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Thermodynamic theory of equilibrium fluctuations

Y. Mishin

Department of Physics and Astronomy, George Mason University, MSN 3F3, Fairfax, VA 22030, USA

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ABSTRACT

The postulational basis of classical thermodynamics has been expanded to incorporate equilibrium fluctuations. The main additional elements of the proposed thermodynamic theory are the concept of quasi-equilibrium states, a definition of non-equilibrium entropy, a fundamental equation of state in the entropy representation, and a fluctuation postulate describing the probability distribution of macroscopic parameters of an isolated system. Although these elements introduce a statistical component that does not exist in classical thermodynamics, the logical structure of the theory is different from that of statistical mechanics and represents an expanded version of thermodynamics. Based on this theory, we present a regular procedure for calculations of equilibrium fluctuations of extensive parameters, intensive parameters and densities in systems with any number of fluctuating parameters. The proposed fluctuation formalism is demonstrated by four applications: (1) derivation of the complete set of fluctuation relations for a simple fluid in three different ensembles; (2) fluctuations in finite-reservoir systems interpolating between the canonical and micro-canonical ensembles; (3) derivation of fluctuation relations for excess properties of grain boundaries in binary solid solutions, and (4) derivation of the grain boundary width distribution for pre-melted grain boundaries in alloys. The last two applications offer an efficient fluctuation-based approach to calculations of interface excess properties and extraction of the disjoining potential in pre-melted grain boundaries. Possible future extensions of the theory are outlined.

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1. Introduction

1.1. Historical background and goal of the work

Fluctuations of thermodynamic properties play a crucial role in many physical phenomena and diverse applications. Fluctuations are especially important in nanometer-scale systems where they can lead to a large variability of mechanical and functional properties and create noises affecting performance of devices. Fluctuations are unavoidable in molecular dynamics and Monte Carlo simulations of materials, where the system dimensions rarely exceed a few nanometers. In fact, in many atomistic calculations, equilibrium properties of interest are extracted by analyzing statistical fluctuations of other properties [1–3]. Examples include the calculations of elastic coefficients of solid materials from strain and/or stress fluctuations in molecular dynamics [4–7] or Monte Carlo [8,9] simulations; calculation of partial molar properties of solutions from concentration fluctuations [10,11]; and calculation of the interface free energy of solid–liquid [12,13] and solid–solid [14–24] interfaces from capillary fluctuations or fluctuations of the interface width.

Presently, fluctuations are primarily discussed in the statistical–mechanical literature and typically in the context of specific (usually, very simple) models. At the same time, the thermodynamics community traditionally relies on classical thermodynamics [25–29] which, by the macroscopic and equilibrium nature of this discipline, disregards fluctuations and operates solely in terms of static properties. In fact, the very term “fluctuation” has a temporal connotation incompatible with the time-independent character of classical thermodynamics.

There is, however, a third direction in thermal physics that pursues a generalized form of thermodynamics that incorporates fluctuations of thermodynamic parameters around equilibrium. By contrast to the statistical–mechanical approach, such theories seek to introduce fluctuations *directly* into the thermodynamic framework via additional assumptions, postulates or similar elements of the logical structure. The goal of such theories is to expand the scope of thermodynamics by introducing statistical elements while preserving the traditional axiomatic approach that distinguishes this discipline. It is this direction in thermal physics that constitutes the subject of the present paper.¹

The logical foundations of classical thermodynamics have been the subject of research over the past hundred or more years, starting with the works of Carathéodory [30] and Ehrenfest [31] and continuing in modern times [27–29,32–37]. In spite of the fundamental importance of the traditional three laws of thermodynamics, they are essentially a reflection of the historical development of the discipline and do not constitute an autonomous and logically complete structure. The four-postulate structure proposed by Callen [27,28] is detached from the historical context, deeply thought-through, but still far from complete. The most rigorous and complete postulational basis of classical thermodynamics has been formulated by Tisza [29]. His theory, called the Macroscopic Thermodynamics of Equilibrium (MTE), presents an elegant logical structure comprising a set of interconnected definitions, postulates and corollaries. This rigor comes at a price: Tisza’s MTE is restricted to a certain class of rather simple thermodynamic systems. Nevertheless, it demonstrates an approach that can be applied for the construction of similar postulational structures for other classes of systems.

Unfortunately, attempts to create a similarly rigorous thermodynamic formalism that would include fluctuations have not been very successful. The thermodynamic fluctuation theory by Greene and Callen [38,39] and Callen’s Postulate II’ [27]² (which generalizes his entropy Postulate II to include fluctuations) turned out to be insufficient. They required additional assumptions, such as the approximation of average values of thermodynamic properties by their most probable values, and relied on the assumption that there is no distinction between the “canonical thermodynamics” and

¹ Although we do not wish to enter into terminological discussions, we point out that an expanded thermodynamic theory that incorporates statistical elements such as fluctuations could be called statistical thermodynamics. This term would distinguish it from both statistical mechanics and classical thermodynamics. Unfortunately, the term statistical thermodynamics is already used with several different meanings, most notably as a collective reference to statistical mechanics and thermodynamics (which we refer to as thermal physics).

² Callen’s Postulate II’ [27] was abandoned in a later edition of his book [28].

“microcanonical thermodynamics”. The latter assumption was later criticized by Tisza and Quay [40] from the standpoint of statistical mechanics. Tisza and Quay’s [40] own treatment of fluctuations was an amalgamation of statistical mechanics and thermodynamics, and in this sense, did not achieve the goal either. In fact, the authors [40] admit that their theory, called the Statistical Thermodynamic of Equilibrium, is only a stepping stone toward a future more general theory whose development encounters major difficulties.

There are two major challenges in the development of a thermodynamic theory of fluctuations: (1) appropriate definition of non-equilibrium entropy that would seamlessly connect with the system of other definitions and postulates of thermodynamics, and (2) formulation of a general fluctuation law of thermodynamic parameters. Historically, the first work addressing these issues was Einstein’s 1910 paper on critical opalescence [41]. In his theory, the point of departure was Boltzmann’s equation

$$S = k \ln W + \text{const}, \quad (1)$$

where k is Boltzmann’s constant and W is the probability associated with the entropy S (our notations are slightly different from Einstein’s). Einstein considered a completely isolated thermodynamic system with a fixed energy E . He assumed that all equilibrium and non-equilibrium (fluctuated) thermodynamic states of the system can be described by a set of macroscopic parameters $\lambda_1, \dots, \lambda_n$. For a discrete set of such parameters, he interpreted W as the fractions of time spent by the fluctuating system in each of the states compatible with the given energy E . This is consistent with Boltzmann’s original definition of entropy in which W is associated with the probability of finding the system in a given macro-state (see [42–44] for a review). Based on this interpretation, Einstein inverted Eq. (1) to obtain the probability of a macroscopic state and thus a given set of parameters $\lambda_1, \dots, \lambda_n$:

$$W = \text{const} \cdot \exp\left(\frac{S}{k}\right). \quad (2)$$

For continuous state variables, the probability that the parameters $\lambda_1, \dots, \lambda_n$ be found between λ_1 and $\lambda_1 + d\lambda_1, \dots, \lambda_n$ and $\lambda_n + d\lambda_n$ is

$$dW = \text{const} \cdot \exp\left(\frac{S - S_0}{k}\right) d\lambda_1 \cdots d\lambda_n, \quad (3)$$

where S_0 is the maximum entropy. Einstein’s theory does not make any reference to micro-states of the system. Instead, it relates the entropy *directly* to the probabilities of macroscopic states. As such, this theory belongs more to the realm of thermodynamics than statistical mechanics.³

Eqs. (2) and (3) essentially constitute a fluctuation law that can be built into the formalism of thermodynamics. The fluctuations described by these equations occur in an isolated system, thus the respective entropy has a micro-canonical meaning. For canonical systems, the distribution function of macroscopic parameters can be derived by considering a relatively small (but macroscopic) subsystem of an isolated system and treating the remaining part (complementary system) as a reservoir.

The situation is complicated by the fact that the most advanced thermodynamic theories of fluctuations [27,40] postulate the fluctuation law directly in a canonical form and derive properties of isolated systems as a limiting case of canonical. This approach is different from Einstein’s [41] and is rooted in statistical–mechanical arguments. The treatment of a canonical system as an asymptotic case when the complementary system tends to infinity has certain conceptual disadvantages in rigorous formulations of statistical mechanics. Alternative theories [40,47,48] postulate the canonical distribution for an infinite reservoir from the outset and derive properties of isolated and finite systems only later. Thus, postulating thermodynamic fluctuations in a canonical form is more consistent with the aforementioned statistical–mechanical theories.

³ The first statistical–mechanical theory of fluctuations was developed by Gibbs [45], whose work was apparently unknown to Einstein at the time. Gibbs’ treatment of fluctuations was based *explicitly* on classical dynamics of particles, with micro-states defined in the momentum–coordinate phase space. Einstein’s theory [41] is obviously more general, even though Eqs. (2) and (3) *per se* do not suggest any means of calculating the probabilities or the entropy for any particular system. For a more detailed comparison of the Gibbs and Einstein approaches see Tisza and Quay [40] and a more recent paper by Rudoi and Sukhanov [46].

In the present paper, we take the view that, if a thermodynamic fluctuation theory is to be relatively autonomous, then the simplicity of its internal logical structure is more important than consistency with all aspects of the formal structure of statistical mechanics. We thus propose to build the theory on a fluctuation law postulated for an isolated system. The law which will be adopted in this work will look similar to Eq. (3), except for certain refinements in justification and interpretation.

We emphasize that this paper is focused on *equilibrium* fluctuations and will not discuss driven or other strongly non-equilibrium systems. Furthermore, given that our approach is purely thermodynamic, we are only interested in statistical distributions of fluctuating parameters without attempting to describe the actual dynamics of the fluctuations [49,50].

1.2. Organization of the paper

The outline of the paper is as follows. In Sections 2–7 we formulate the basic assumptions of the theory describing equilibrium fluctuations in an isolated system. We then consider the usual quadratic expansion of the entropy around equilibrium and arrive at the Gaussian law of fluctuations and a set of relations for mean-square fluctuations and covariances of thermodynamic properties (Section 8). In Section 9 we derive the fluctuation law for generalized canonical systems, treating the system of interest and the reservoir as a combined isolated system. We derive the Gaussian law of canonical fluctuations in two forms, called the entropy scheme and the energy scheme, and present the fluctuation formalism in both schemes. To illustrate the calculation techniques, we compute fluctuations of all properties of a simple fluid in three different ensembles. In Section 10 we analyze systems connected to a finite-size reservoir. The finite-reservoir ensemble interpolates between the micro-canonical and canonical ensembles and has been implemented in recent computer simulations [21,51–59]. This section demonstrates the ease with which the theory can handle finite-size systems as opposed to alternate theories [27,40] built directly on the canonical formalism.

Sections 11 and 12 are devoted to applications of the theory to fluctuations in a single-phase interface, called a grain boundary (GB), in a binary solid solution. This is a non-trivial problem, which is addressed by conceptually partitioning the system into an imaginary perfect crystal (grain) and an excess system representing the GB, each described by their own fundamental equation. The goal is to describe fluctuations in the excess system. In Section 11 we develop a set of equations linking fluctuations of some interface properties to equilibrium values of other properties, such as the excess heat capacity, excess elastic moduli and others. An interesting result here is the prediction of fluctuations of the interface free energy, an important excess quantity that is usually treated as a static property. Next, we address the problem of width fluctuations of a pre-melted GB represented as a thin liquid layer subject to a disjoining pressure. We derive the distribution function of the GB width expressed through the disjoining potential describing interactions between the two solid–liquid interfaces bounding the liquid layer. While the functional form of the width distribution is known for single-component systems [16–18,20], it has not been previously derived for binary mixtures. Finally, in Section 13 we summarize the paper and outline future work.

To reach out to a broader audience, each time we open a new topic we briefly review the status of the field starting from early literature and up to the most recent developments. The review component is especially significant in the first half of the paper, although many of the known results appearing here are presented in a more rigorous manner and/or under a new angle. Sections 11 and 12 contain predominantly original material, with only a few paragraphs presenting a brief overview of interface thermodynamics. These sections create a theoretical framework for future systematic studies on interface fluctuations in materials.

Although the paper is focused on thermodynamics, in Sections 7 and 9.2 and a few other parts of the text we do discuss statistical distributions of micro-states and other aspects of statistical mechanics. It should be emphasized that these discussions are *not* part of the proposed fluctuation theory. They are only included here to provide a statistical–mechanical interpretation of certain thermodynamic statements or demonstrate their consistency with principles of statistical mechanics. In addition, we slightly deviate from the traditional macroscopic terminology of classical thermodynamics and talk about the number of particles (instead of moles) and ensembles (instead of types of

imposed constraints). Obviously, this is only a matter of terminology that does not compromise the thermodynamic nature of the theory.

Finally, we generally prefer a smooth development of the logic and do not follow the mathematical style of presentation [29,30,40] in which all statements are broken into definitions, postulates, corollaries and other deductive steps.

2. Definition of equilibrium fluctuations

Consider an isolated thermodynamic system, i.e., a system incapable of exchanging heat or matter with its environment or performing work on the environment. Some physical properties of an isolated system are strictly fixed by conservation laws (e.g., the total energy, total momentum, total amounts of chemical elements⁴), whereas other properties can vary. Thermodynamics postulates that all non-conserved properties averaged over a certain time scale t_{TD} , which we call the thermodynamic time scale, eventually stop varying and remain constant for as long as the system remains isolated. The quiescent state of an isolated system in which all properties remain constant on the t_{TD} time scale is called the state of thermodynamic equilibrium.

Even after thermodynamic equilibrium has been reached, non-conserved properties continue to vary on a shorter time scale, $t_f \ll t_{TD}$, called the fluctuation time scale. Such continual variations of properties of an equilibrium system are called *equilibrium fluctuations*.

For any physical property X , let \bar{X} be its value averaged over the thermodynamic time scale t_{TD} . During the equilibrium fluctuations, instantaneous values of X randomly deviate from \bar{X} . The goal of the fluctuation theory is to predict the probability distribution of any property X around its average \bar{X} and compute the moments and other statistical characteristics of this distribution.

3. The fundamental equation

Consider an isolated thermodynamic system whose equilibrium properties averaged over the t_{TD} time scale are fully defined by a set of n conserved extensive parameters X_1, \dots, X_n . (Tisza [29] refers to such conserved extensive properties as “additive invariants”.) For example, all equilibrium properties of a simple fluid enclosed in an isolated rigid box are fully defined by its energy E , volume V , and the number of particles N .⁵ As long as the parameters X_1, \dots, X_n remain fixed, the system remains in a state of equilibrium. One can temporarily break the isolation, change all or some of the parameters X_1, \dots, X_n , and then isolate and re-equilibrate the system to a new state. By repeating such perturbation/re-equilibration steps, one can vary the parameters X_1, \dots, X_n and measure all equilibrium thermodynamic properties of the system as functions of X_1, \dots, X_n .

In particular, the described procedure can be applied to measure the system entropy S as a function of the conserved parameters X_1, \dots, X_n . Here, the entropy is treated as a property defined in statistical mechanics. Namely, for an equilibrium isolated system, S is identified with the micro-canonical entropy $S = k \ln \Omega_{max}$, where Ω_{max} is the maximum number of micro-states compatible with the given set of parameters X_1, \dots, X_n (see Section 7 for a more detailed statistical–mechanical interpretation of entropy).⁶ The entropy S so defined will be referred to as the “equilibrium entropy” in order to distinguish it from the “non-equilibrium entropy” defined later.

The function

$$S = S(X_1, \dots, X_n) \quad (4)$$

⁴ In a system without nuclear reactions.

⁵ This can be considered a definition of the simple fluid. Physically, it is a homogeneous single-component fluid without electric, magnetic or other contributions to its thermodynamic properties.

⁶ Many different definitions of entropy can be found in the literature, some of which are confusing or simply incorrect. We refer the reader to recent papers by Swendsen [42–44] for a proper definition of entropy in statistical mechanics and thermodynamics and discussion of inconsistencies in alternate definitions. The definition adopted in this paper is consistent with Swendsen's work [42–44].

is called the *fundamental equation* of the system in the entropy representation [25,27–29]. More accurately, Eq. (4) is the fundamental equation of a particular phase of the system. Different phases are specified by different fundamental equation (4) [60]. For a simple fluid, the fundamental equation has the form $S = S(E, V, N)$.

It is important to recognize that, at this point of the development, the entropy S has been defined only for an equilibrium isolated system. Furthermore, the arguments X_1, \dots, X_n of the fundamental equation (4) are understood as conserved properties that remain fixed (no fluctuations!) in every given state of the isolated system.

4. The non-equilibrium entropy

When a non-equilibrium isolated system approaches equilibrium, it is often possible to define a property called the *non-equilibrium entropy*. Consider two examples.

Example 1. When the system is close enough to equilibrium, it can be mentally partitioned into small but macroscopic subsystems that can be considered as isolated and equilibrium for a period of time on the order of t_q . Such subsystems are called quasi-equilibrium and the entire isolated system is said to be in a quasi-equilibrium state.⁷ On the quasi-equilibrium time scale t_q , each subsystem α can be described by a fundamental equation $S_\alpha = S_\alpha(X_1^\alpha, \dots, X_n^\alpha)$, where $X_1^\alpha, \dots, X_n^\alpha$ are extensive properties assumed to be fixed. The non-equilibrium entropy \hat{S} is defined as the sum of the entropies of all quasi-equilibrium subsystems:

$$\hat{S}(\lambda_1, \dots, \lambda_m, X_1, \dots, X_n) \equiv \sum_{\alpha} S_{\alpha}(X_1^{\alpha}, \dots, X_n^{\alpha}). \quad (5)$$

Here, $\lambda_1, \dots, \lambda_m$ are so-called *internal parameters* describing the distribution of the conserved extensive properties X_1, \dots, X_n of the entire isolated system over its quasi-equilibrium subsystems.⁸ As the system evolves toward equilibrium, these internal parameters vary on the time scale $\gg t_q$, as do the local parameters $X_1^\alpha, \dots, X_n^\alpha$ of the subsystems and thus the non-equilibrium entropy \hat{S} . Note that the quasi-equilibrium system as a whole does not have a fundamental equation; its properties depend not only on the total amounts of the extensive quantities X_1, \dots, X_n but also on their distribution among the subsystems.

As a specific example, consider an isolated cylinder with rigid side walls, rigid top and bottom, and a movable piston dividing the cylinder in two compartments 1 and 2 (Fig. 1). The compartments are filled with different amounts of the same simple fluid obeying a fundamental equation $S = S(E, V, N)$. The system is initially not in equilibrium. Heat and particles can diffuse through the piston, but so slowly that each compartment maintains its own thermodynamic equilibrium at all times. Thus, as the system drifts toward equilibrium, it always remains in quasi-equilibrium. During this quasi-equilibrium process, the total energy $E = E_1 + E_2$, total volume $V = V_1 + V_2$ and the total number of particles $N = N_1 + N_2$ remain fixed. These properties are the additive invariants denoted as X_i . The non-equilibrium entropy of the system equals

$$\hat{S}(\underbrace{E_1, V_1, N_1}_{\lambda}, E, V, N) = S(E_1, V_1, N_1) + S(E - E_1, V - V_1, N - N_1), \quad (6)$$

where E_1, V_1 and N_1 play the role of the internal λ -parameters describing the distribution of the fixed quantities E, V and N between the compartments.

⁷ On the time scale t_q , the quasi-equilibrium system can be treated as if it was an equilibrium system with subsystems separated by isolating walls.

⁸ To avoid notational confusion, we note that our parameters $\lambda_1, \dots, \lambda_m$ are *independent* variables describing the macroscopic states subject to isolation constraints. In Einstein's work [41], $\lambda_1, \dots, \lambda_n$ are not independent variables. His Eq. (3) is only valid on the $(n - 1)$ -dimensional constant-energy surface $E(\lambda_1, \dots, \lambda_n) = \text{const}$ in the n -dimensional parameter space of $\lambda_1, \dots, \lambda_n$.

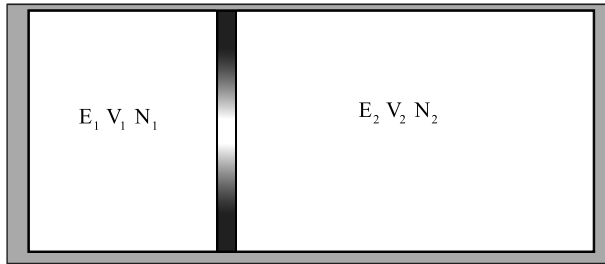


Fig. 1. A model of an isolated system: a rigid cylinder divided in two compartments containing different amounts of the same substance separated by a movable piston.

Example 2. Many systems reach equilibrium with respect to some thermodynamic properties while other properties are still in the process of equilibration. In such cases, we can talk about quasi-equilibrium as equilibrium with respect to some properties without equilibrium with respect to other properties. For example, chemical reactions usually occur much slower in comparison with thermal and mechanical equilibration. There is a certain time scale t_q on which chemical reactions can be considered as “frozen” and the system can be treated as if it were in full equilibrium. Accordingly, the system can be assigned a non-equilibrium entropy \hat{S} computed by ignoring the reactions and treating the amounts of all chemical components as fixed parameters. Of course, on the time scale much longer than t_q , the entropy slowly drifts as the system evolves toward chemical equilibrium. The non-equilibrium entropy so defined is a function of not only the conserved parameters X_1, \dots, X_n but also some progress variables $\lambda_1, \dots, \lambda_m$ describing the extents of the chemical reactions. The latter thus play the role of the internal parameters specifying the quasi-equilibrium states.

As a simple illustration, consider an isolated box containing a mixture of three chemically different gases A, B and C. In the absence of chemical reactions, this mixture is described by a fundamental equation $S = S(E, V, N_A, N_B, N_C)$. Let the system initially contain the amounts of the components $N_A^{(i)}$, $N_B^{(i)}$ and $N_C^{(i)}$. Now suppose that the components can transform to each other via a chemical reaction $A + B \rightleftharpoons C$. Assuming that the reaction is slow, the system always maintains mechanical and thermal equilibrium, while its chemical composition gradually changes. Let ΔN_A be the change in the number of particles A relative to the initial state. The non-equilibrium entropy is defined by

$$\hat{S}(\underbrace{\Delta N_A}_{\lambda}, E, V, N_A^{(i)}, N_B^{(i)}, N_C^{(i)}) = S(E, V, N_A^{(i)} - \Delta N_A, N_B^{(i)} - \Delta N_A, N_C^{(i)} + \Delta N_A). \quad (7)$$

Here, ΔN_A characterizes the progress of the chemical reaction and plays the role of an internal parameter λ , whereas $E, V, N_A^{(i)}, N_B^{(i)}, N_C^{(i)}$ is a set of fixed extensive parameters X_1, \dots, X_n .

5. The second law of thermodynamics

In the extended thermodynamics including fluctuations, the second law (entropy postulate) can be formulated as two statements:

1. The non-equilibrium entropy \hat{S} of an isolated system averaged over the thermodynamic time scale t_{TD} , which we denote \bar{S} , increases with time and reaches a maximum value S when the system arrives at equilibrium.
2. The individual values of \hat{S} fluctuate but can never exceed the equilibrium value S .

Note that this formulation of the second law is stronger than the frequently used weak formulation. The latter only states that entropy should increase but does not guarantee that an equilibrium state

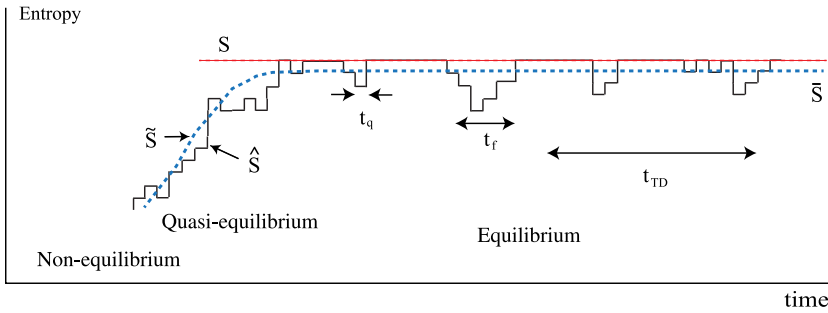


Fig. 2. Schematic temperature dependence of entropy of an isolated system. The system is initially in a highly non-equilibrium state in which the non-equilibrium entropy \hat{S} is undefined. As the system evolves toward equilibrium, it eventually reaches the quasi-equilibrium stage in which the non-equilibrium entropy \hat{S} can be defined on a time scale t_q . The subsequent time dependence of \hat{S} is shown by a broken line to emphasize that individual values of \hat{S} can only be measured within time intervals on the order of t_q . The values of \hat{S} can never exceed the maximum (micro-canonical) entropy S . By the second law of thermodynamics, \bar{S} averaged over the thermodynamic time scale t_{TD} (\bar{S} , shown by the dashed blue line) monotonically increases with time and eventually levels out when the system reaches equilibrium. In the equilibrium state, \hat{S} can randomly deviate down from its maximum value S on the fluctuation time scale t_f such that $t_q \ll t_f \ll t_{TD}$, always returning to the maximum value when the fluctuation is over. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

will be eventually reached.⁹ Clearly, to talk about equilibrium fluctuations we must first ensure that the system actually arrives at equilibrium.

Once equilibrium has been reached, the average \bar{X} of any thermodynamic property X remains constant while instantaneous values of X can randomly deviate from \bar{X} on the fluctuation time scale t_f . This includes fluctuations of the non-equilibrium entropy \hat{S} . However, the latter is a special case because it can only fluctuate down from its maximum value S . As a result, the average entropy \bar{S} is always slightly smaller than S .

The time evolution of an isolated system approaching equilibrium is illustrated schematically in Fig. 2. The plot assumes the existence of three different time scales¹⁰ such that

$$t_{TD} \gg t_f \gg t_q. \tag{8}$$

It should be remembered that \hat{S} is only defined on the quasi-equilibrium time scale t_q . The inequality (8) reflects the important assumption of the fluctuation theory that all states arising during the fluctuations are quasi-equilibrium states. As such, they can always be assigned a non-equilibrium entropy \hat{S} . The assumption that the approach to equilibrium (relaxation) and equilibrium fluctuations realize the same, quasi-equilibrium, states of the system bears a certain analogy with the fluctuation–dissipation theorem in statistical mechanics [61–63].

The non-equilibrium entropy \hat{S} reaches its maximum value S for some set of internal parameters $\lambda_1^0, \dots, \lambda_m^0$ called the equilibrium internal parameters. The latter must satisfy the necessary conditions of extremum,

$$\left(\frac{\partial \hat{S}}{\partial \lambda_i} \right)_{\lambda_{j \neq i}, X_1, \dots, X_n} = 0, \quad i = 1, \dots, m, \tag{9}$$

⁹ The weak formulation of the second law of thermodynamics has a “negative” (prohibitive) character stating what *cannot* happen—the entropy cannot decrease; whereas the strong formulation makes a “positive” statement predicting what *will* happen—the system will reach equilibrium and the entropy a maximum.

¹⁰ Generally, the time scales may depend on the observable. For the present discussion, it will suffice to represent each time scale by one “characteristic” order of magnitude.

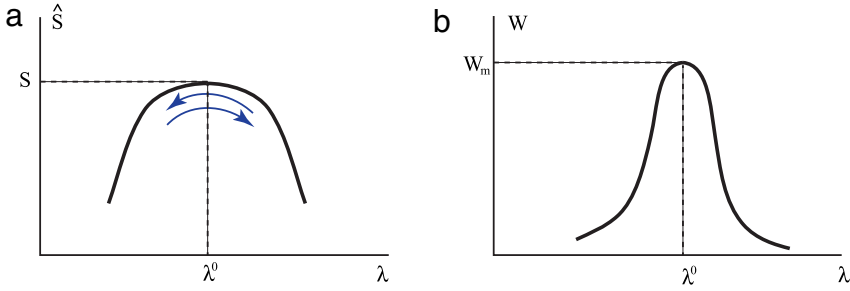


Fig. 3. Schematic diagram of equilibrium fluctuations in an isolated system with one internal parameter λ . (a) Non-equilibrium entropy \hat{S} reaches its maximum S at the equilibrium value of the internal parameter λ^0 . The arrows symbolize equilibrium fluctuations of λ on either side of λ^0 accompanied by downward deviations of \hat{S} from S . (b) The probability density of λ has a sharp maximum at $\lambda = \lambda^0$ of a height W_m .

and the relation

$$\hat{S}(\lambda_1^0, \dots, \lambda_m^0, X_1, \dots, X_n) = S(X_1, \dots, X_n), \quad (10)$$

where the right-hand side is the fundamental equation of the substance. This is illustrated schematically in Fig. 3(a) for a single internal parameter λ .

As an example, consider again the isolated cylinder with two compartments discussed in Section 4 (Fig. 1). We have three internal parameters: $\lambda_1 = E_1$, $\lambda_2 = V_1$ and $\lambda_3 = N_1$. Applying Eq. (9) to \hat{S} given by Eq. (6), we have

$$\frac{\partial \hat{S}}{\partial E_1} = \frac{\partial S(E_1, V_1, N_1)}{\partial E_1} - \frac{\partial S(E_2, V_2, N_2)}{\partial E_2} = \frac{1}{T_1} - \frac{1}{T_2} = 0, \quad (11)$$

$$\frac{\partial \hat{S}}{\partial V_1} = \frac{\partial S(E_1, V_1, N_1)}{\partial V_1} - \frac{\partial S(E_2, V_2, N_2)}{\partial V_2} = \frac{p_1}{T_1} - \frac{p_2}{T_2} = 0, \quad (12)$$

$$\frac{\partial \hat{S}}{\partial N_1} = \frac{\partial S(E_1, V_1, N_1)}{\partial N_1} - \frac{\partial S(E_2, V_2, N_2)}{\partial N_2} = -\frac{\mu_1}{T_1} + \frac{\mu_2}{T_2} = 0, \quad (13)$$

where we used the standard thermodynamic relations [26–28,63] $\partial S/\partial E = 1/T$, $\partial S/\partial V = p/T$ and $\partial S/\partial N = -\mu/T$ (T being temperature, p pressure and μ chemical potential). We thus recover the well-known thermodynamic equilibrium conditions $T_1 = T_2$, $p_1 = p_2$ and $\mu_1 = \mu_2$. These conditions must be satisfied for the equilibrium parameter set (E_1^0, V_1^0, N_1^0) .

As another example, the non-equilibrium entropy of a gas mixture with the chemical reaction $A + B \rightleftharpoons C$ is defined by Eq. (7) with a single internal parameter $\lambda = \Delta N_A$. The necessary condition of equilibrium reads

$$\begin{aligned} & \frac{\partial S(E, V, N_A^{(i)} - \Delta N_A, N_B^{(i)} - \Delta N_A, N_C^{(i)} + \Delta N_A)}{\partial \Delta N_A} \\ &= -\frac{\partial S(E, V, N_A, N_B, N_C)}{\partial N_A} - \frac{\partial S(E, V, N_A, N_B, N_C)}{\partial N_B} + \frac{\partial S(E, V, N_A, N_B, N_C)}{\partial N_C} \\ &= 0. \end{aligned} \quad (14)$$

We obtained the standard chemical equilibrium condition $\mu_A + \mu_B = \mu_C$, which must be satisfied at some $\lambda^0 = \Delta N_A^0$. The equilibrium amounts of the chemical components are then $N_A^0 = N_A^{(i)} - \Delta N_A^0$, $N_B^0 = N_B^{(i)} - \Delta N_A^0$ and $N_C^0 = N_C^{(i)} + \Delta N_A^0$.

6. The general law of fluctuations

During equilibrium fluctuations, the internal parameters randomly deviate from the equilibrium values $\lambda_1^0, \dots, \lambda_m^0$ on the time scale of t_f . These fluctuations of the internal parameters are accompanied by deviations of the non-equilibrium entropy \hat{S} down from its maximum value S [Fig. 3(a)].

The *Fundamental Postulate* of the thermodynamic theory of fluctuations states that the probability density $W(\lambda_1, \dots, \lambda_m)$ of internal parameters of an equilibrium isolated system is

$$W(\lambda_1, \dots, \lambda_m) = A \exp \left[\frac{\hat{S}(\lambda_1, \dots, \lambda_m)}{k} \right], \quad (15)$$

where A is a constant. To simplify the notations, we do not display the fixed parameters X_1, \dots, X_n as arguments of W and \hat{S} .

By definition, $W(\lambda_1, \dots, \lambda_m)d\lambda_1 \cdots d\lambda_m$ is the probability of finding the internal parameters in the infinitesimal region $d\lambda_1 \cdots d\lambda_m$ of the parameter space. The constant A can be found from the normalization condition

$$\int W(\lambda_1, \dots, \lambda_m)d\lambda_1 \cdots d\lambda_m = 1, \quad (16)$$

where the integration extends over the entire parameter space. Since \hat{S} reaches its maximum value

$$S = \hat{S}(\lambda_1^0, \dots, \lambda_m^0) \quad (17)$$

at the equilibrium parameter set $\lambda_1^0, \dots, \lambda_m^0$ [cf. Eq. (10)], W has a peak of the height

$$W_m = A \exp \left(\frac{S}{k} \right) \quad (18)$$

at $\lambda_1^0, \dots, \lambda_m^0$ [Fig. 3(b)]. In other words, $\lambda_1^0, \dots, \lambda_m^0$ is the *most probable* parameter set. Using this fact, Eq. (15) can be recast as

$$W(\lambda_1, \dots, \lambda_m) = W_m \exp \left[\frac{\hat{S}(\lambda_1, \dots, \lambda_m) - S}{k} \right]. \quad (19)$$

Eq. (19) is the central equation of the thermodynamic fluctuation theory. It is the departure point for thermodynamic analysis of all statistical properties of equilibrium fluctuations.

The average (expectation) value of any internal parameter λ_i is obtained by

$$\bar{\lambda}_i = W_m \int \lambda_i \exp \left[\frac{\hat{S}(\lambda_1, \dots, \lambda_m) - S}{k} \right] d\lambda_1 \cdots d\lambda_m. \quad (20)$$

Note that this average does not generally coincide with the most probable value λ_i^0 . It is common to use the symbol Δ to denote deviations of fluctuating properties from their average values. For example,

$$\Delta\lambda_i \equiv \lambda_i - \bar{\lambda}_i. \quad (21)$$

The covariance (second correlation moment) of any pair of internal parameters can be computed by

$$\overline{\Delta\lambda_i \Delta\lambda_j} = W_m \int \Delta\lambda_i \Delta\lambda_j \exp \left[\frac{\hat{S}(\lambda_1, \dots, \lambda_m) - S}{k} \right] d\lambda_1 \cdots d\lambda_m, \quad (22)$$

while the mean-square fluctuation of λ_i is

$$\overline{(\Delta\lambda_i)^2} = W_m \int (\Delta\lambda_i)^2 \exp \left[\frac{\hat{S}(\lambda_1, \dots, \lambda_m) - S}{k} \right] d\lambda_1 \cdots d\lambda_m. \quad (23)$$

7. Statistical–mechanical interpretation of fluctuations

In this section we will discuss the general law of fluctuations formulated above from the viewpoint of statistical-mechanics.

As before, we consider an isolated system whose equilibrium state is defined by a set of fixed parameters X_1, \dots, X_n . If multiple observations are made, the system can be found in different *macro-states*, each specified by a set of internal parameters $\lambda_1, \dots, \lambda_m$. Let us first consider a system with discrete λ -parameters. Each parameter set $\lambda_1, \dots, \lambda_m$ is implemented by a certain number Ω of *micro-states*. The latter number is sometimes called the degeneracy of the macro-state. The macro-states are analogs of the equilibrium and quasi-equilibrium states introduced in the thermodynamic theory (Section 4). The degeneracy of a given macro-state is a function of the internal parameters $\lambda_1, \dots, \lambda_m$ and the fixed parameters X_1, \dots, X_n :

$$\Omega = \Omega(\lambda_1, \dots, \lambda_m, X_1, \dots, X_n). \quad (24)$$

It is postulated that for an isolated equilibrium system, there is one unique macro-state for which the degeneracy reaches a maximum value Ω_{max} . Denoting the internal parameters corresponding to this macro-state $\lambda_1^0, \dots, \lambda_m^0$, the maximum degeneracy depends solely on the fixed parameters X_1, \dots, X_n :

$$\Omega_{max}(X_1, \dots, X_n) \equiv \Omega(\lambda_1^0, \dots, \lambda_m^0, X_1, \dots, X_n). \quad (25)$$

For a given set of fixed parameters X_1, \dots, X_n , the degeneracy Ω of an equilibrium isolated system fluctuates with time from its maximum value Ω_{max} down to smaller values. These equilibrium fluctuations follow the *Fundamental Postulate of Statistical Mechanics* stating that the probability P of a single *micro-state* is the same for all micro-states and depends only on the fixed parameters X_1, \dots, X_n :

$$P = P(X_1, \dots, X_n). \quad (26)$$

This statement is often referred to as the *micro-canonical distribution*. It immediately follows that the probability of any macro-state is simply $P\Omega$. Thus, macro-states with a larger degeneracy have a proportionately higher probability to occur. The macro-state with the largest degeneracy Ω_{max} is the most probable one.

Analysis of fluctuations relies solely on the fact that P is the same for all micro-states and does not require a specific knowledge of P . We note, however, that P can be found from the normalization condition stating that the sum of probabilities of all possible macro-states of the system be unity. In the approximation where fluctuations are neglected, only the most probable macro-state with the highest degeneracy Ω_{max} is considered. Then the normalization condition reads $P\Omega_{max} = 1$, giving

$$P = \frac{1}{\Omega_{max}}. \quad (27)$$

On the other hand, when fluctuations are significant, all possible degeneracies from $\Omega = 1$ to Ω_{max} must be included. From the normalization condition

$$\sum_{\Omega=1}^{\Omega_{max}} P\Omega = 1 \quad (28)$$

we obtain

$$P = \frac{2}{\Omega_{max}(\Omega_{max} + 1)}, \quad (29)$$

which for large systems can be approximated by $2/\Omega_{max}^2$.

Regardless of the specific value of P , the product $P\Omega$ is the probability of a given macro-state and thus the probability

$$W_{\lambda_1, \dots, \lambda_m} = P\Omega(\lambda_1, \dots, \lambda_m) \quad (30)$$

of the corresponding set of internal parameters. Here, as in Section 6, we simplify the notations by suppressing the fixed parameters X_1, \dots, X_n as arguments of P and Ω . The probability $W_{\lambda_1, \dots, \lambda_m}$ reaches a maximum value, denoted W_m , at the most probable parameter set $\lambda_1^0, \dots, \lambda_m^0$, for which

$$W_m = P\Omega(\lambda_1^0, \dots, \lambda_m^0) = P\Omega_{max}. \tag{31}$$

Combining Eqs. (30) and (31),

$$W_{\lambda_1, \dots, \lambda_m} = W_m \frac{\Omega(\lambda_1, \dots, \lambda_m)}{\Omega_{max}}. \tag{32}$$

We now define the non-equilibrium entropy of an isolated system by

$$\hat{S}(\lambda_1, \dots, \lambda_m) \equiv k \ln \Omega(\lambda_1, \dots, \lambda_m) \tag{33}$$

and the equilibrium entropy by

$$S \equiv k \ln \Omega_{max}. \tag{34}$$

It immediately follows that the non-equilibrium entropy can never exceed its equilibrium value S . It also follows that in equilibrium, \hat{S} can occasionally fluctuate down from S but eventually returns to S as the most probable value.

The probability of any given set of internal parameters given by Eq. (32) can now be rewritten in the form

$$W_{\lambda_1, \dots, \lambda_m} = W_m \exp \left[\frac{\hat{S}(\lambda_1, \dots, \lambda_m) - S}{k} \right]. \tag{35}$$

This equation treats $\lambda_1, \dots, \lambda_m$ as discrete parameters. For continuous parameters, Eq. (35) remains valid but gives the probability density of the internal parameters. The obtained Eq. (35) is identical to Eq. (19) of the thermodynamic theory of fluctuations (Section 6).

8. The Gaussian law of fluctuations

In macroscopic systems, the peak of W at the equilibrium parameter set $\lambda_1^0, \dots, \lambda_m^0$ is extremely sharp. In most cases, one can safely replace the exponent in Eq. (19) by its Taylor expansion at $\lambda_1^0, \dots, \lambda_m^0$ truncated at quadratic terms:

$$\hat{S}(\lambda_1, \dots, \lambda_m) - S = \sum_{i=1}^m \left(\frac{\partial \hat{S}}{\partial \lambda_i} \right)_0 (\lambda_i - \lambda_i^0) + \frac{1}{2} \sum_{i,j=1}^m \left(\frac{\partial^2 \hat{S}}{\partial \lambda_i \partial \lambda_j} \right)_0 (\lambda_i - \lambda_i^0)(\lambda_j - \lambda_j^0), \tag{36}$$

where the subscript 0 indicates that the derivatives are taken at $\lambda_1^0, \dots, \lambda_m^0$. The linear terms vanish by the extremum condition (9). As a result, Eq. (19) reduces to the multi-variable Gaussian distribution

$$W(\lambda_1, \dots, \lambda_m) = W_m \exp \left[-\frac{1}{2} \sum_{i,j=1}^m A_{ij} (\lambda_i - \lambda_i^0)(\lambda_j - \lambda_j^0) \right] \tag{37}$$

with the symmetrical matrix

$$A_{ij} \equiv -\frac{1}{k} \left(\frac{\partial^2 \hat{S}}{\partial \lambda_i \partial \lambda_j} \right)_0 \tag{38}$$

which we call the *stability matrix* of the system. For normally stable systems this matrix must be positive-definite.¹¹ Applying the normalization condition (16), the Gaussian distribution can be

¹¹ We follow the classification [29] dividing all systems into normally stable, critically stable, unstable and metastable. In normally stable systems, all fluctuations are finite.

rewritten as

$$W(\lambda_1, \dots, \lambda_m) = \sqrt{\frac{|\Delta|}{(2\pi)^m}} \exp \left[-\frac{1}{2} \sum_{i,j=1}^m \Delta_{ij} (\lambda_i - \lambda_i^0) (\lambda_j - \lambda_j^0) \right], \tag{39}$$

where Δ is the determinant of Δ_{ij} .¹²

We can now make use of the well-known mathematical properties of the normal distribution. The average value of any parameter λ_i coincides with its most probable value,

$$\bar{\lambda}_i = \lambda_i^0, \quad i = 1, \dots, m. \tag{40}$$

For covariances of internal parameters we have

$$\overline{\Delta\lambda_i \Delta\lambda_j} = \Delta_{ij}^{-1}, \quad i, j = 1, \dots, m, \tag{41}$$

where Δ_{ij}^{-1} is the inverse of the stability matrix Δ_{ij} . In particular, the mean-square fluctuation of a parameter λ_i equals

$$\overline{(\Delta\lambda_i)^2} = \Delta_{ii}^{-1}, \quad i = 1, \dots, m. \tag{42}$$

We can also introduce the following linear combinations of internal parameters:

$$\varphi_i \equiv \sum_{j=1}^m \Delta_{ij} \lambda_j, \quad i = 1, \dots, m. \tag{43}$$

It can be shown that

$$\overline{\Delta\varphi_i} = 0, \quad i = 1, \dots, m, \tag{44}$$

$$\overline{\Delta\varphi_i \Delta\lambda_j} = \delta_{ij}, \quad i, j = 1, \dots, m, \tag{45}$$

$$\overline{\Delta\varphi_i \Delta\varphi_j} = \Delta_{ij}, \quad i, j = 1, \dots, m, \tag{46}$$

and therefore

$$\overline{(\Delta\varphi_i)^2} = \Delta_{ii}, \quad i = 1, \dots, m. \tag{47}$$

Thus Δ_{ij} is the covariance matrix of the parameters φ_i .

An important property of Eqs. (41), (42), (46) and (47) is that their left-hand sides contain fluctuations, whereas the right-hand sides are computed in the state of equilibrium and can be obtained by the standard formalism of equilibrium thermodynamics. In other words, these equations relate fluctuations to equilibrium properties of the system.

As a simple illustration, let us revisit the isolated system divided in two compartments (Fig. 1). Suppose the system is in equilibrium. Consider a particular type of fluctuations in which the compartments can only exchange energy at fixed volumes and numbers of particles. Thus, the only internal parameter is $\lambda_1 = E_1$. The stability matrix (38) reduces to the scalar

$$\Delta = -\frac{1}{k} \left(\frac{\partial^2 \hat{S}}{\partial E_1^2} \right)_0. \tag{48}$$

From Eq. (11),

$$\frac{\partial \hat{S}}{\partial E_1} = \frac{1}{T_1} - \frac{1}{T_2} \tag{49}$$

¹² The Gaussian distribution (39) can be interpreted as a consequence of the central limit theorem for a system composed of many statistically independent subsystems, see for example Chapter V of Khinchin [48].

and thus

$$\Lambda = \frac{1}{k} \left(\frac{1}{T_1^2} \frac{\partial T_1}{\partial E_1} + \frac{1}{T_2^2} \frac{\partial T_2}{\partial E_2} \right)_0 = \frac{1}{kT_0^2 c_v} \left(\frac{1}{N_1} + \frac{1}{N_2} \right), \tag{50}$$

where T_0 is the equilibrium temperature of both compartments and

$$c_v = \frac{1}{N} \left(\frac{\partial E}{\partial T} \right)_{V,N} \tag{51}$$

is the specific heat of the substance per particle at the equilibrium temperature T_0 . Applying Eq. (42) we obtain the energy fluctuation of compartment 1:

$$\left(\overline{(\Delta E_1)^2} \right)_{V_1, N_1} = \frac{1}{\Lambda} = kT_0^2 c_v \frac{N_1 N_2}{N_1 + N_2}. \tag{52}$$

When the second compartment is much larger than the first, $N_2 \gg N_1$, this equation reduces to

$$\left(\overline{(\Delta E_1)^2} \right)_{V_1, N_1} = N_1 kT_0^2 c_v. \tag{53}$$

In this limit, the second compartment serves as a heat bath (reservoir) for the first. The relative fluctuation (variance) of E_1 becomes

$$\frac{\left[\left(\overline{(\Delta E_1)^2} \right)_{V_1, N_1} \right]^{1/2}}{\bar{E}_1} = \frac{T_0 (c_v k)^{1/2}}{\varepsilon \sqrt{N_1}}, \tag{54}$$

where $\varepsilon = \bar{E}_1/N_1$ is the equilibrium energy per particle. This relation shows that the relative fluctuation of energy decreases with the system size as $1/\sqrt{N}$.

9. Fluctuations in canonical systems

9.1. General relations

We now return to the general fluctuation law formulated in Section 6 and will apply it to a relatively small (but still macroscopic) subsystem of an equilibrium isolated system. We will adopt the terminology in which we refer to the selected subsystem as the “canonical system”, or simply “system”, and to the remaining part of the isolated system as the “complementary system” or “reservoir”.

An example of the situation was already given by the system with two compartments (Fig. 1) when the second compartment is much larger than the first. We will now consider a more general case in which the entire isolated system is characterized by a set of conserved extensive properties (additive invariants) $\tilde{X}_1, \dots, \tilde{X}_n$. These properties are partitioned between our system, X_1, \dots, X_n , and the reservoir, X_1^r, \dots, X_n^r (Fig. 4). For some of these properties, the partitioning is fixed once and for all, while m remaining properties can “flow” between the system and the reservoir as a result of equilibrium fluctuations. Such fluctuations are subject to the conservation constraints

$$X_i + X_i^r = \tilde{X}_i = \text{const}, \quad i = 1, \dots, m. \tag{55}$$

We assume that the exchange of the quantities X_i occurs slowly enough that we can consider both the system and the reservoir as quasi-equilibrium systems. Accordingly, they obey the fundamental equations

$$S = S(X_1, \dots, X_n) \tag{56}$$

for the system and

$$S_r = S_r(X_1^r, \dots, X_n^r) \tag{57}$$

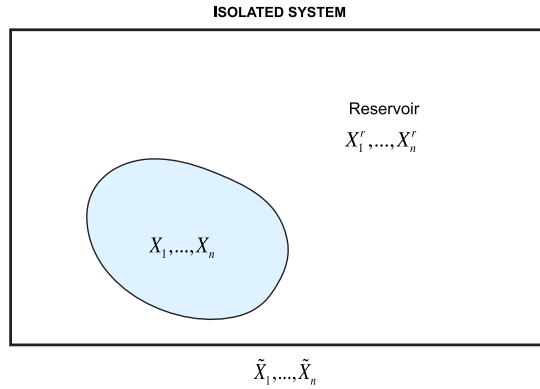


Fig. 4. A subsystem chosen inside an isolated system characterized by a set extensive properties $\tilde{X}_1, \dots, \tilde{X}_n$. These properties are partitioned between the subsystem and the complementary system (reservoir). The partitioning is specified by the parameter sets X_1, \dots, X_n and X'_1, \dots, X'_n , respectively.

for the reservoir. Note that these two equations are generally different, allowing the system and the reservoir to be composed of different substances.

In the subsequent analysis, a special role will be played by the entropy derivatives

$$F_i \equiv \frac{\partial S}{\partial X_i}, \tag{58}$$

called the thermodynamic “forces” conjugate to the extensive variables X_i . Similar derivatives $\partial S_r / \partial X'_i$ define the forces F'_i in the reservoir. For example, for a simple fluid with the fundamental equation $S(E, V, N)$, the thermodynamic forces are $F_1 = 1/T$, $F_2 = p/T$ and $F_3 = -\mu/T$. Note that the thermodynamic forces are intensive variables.

We define the non-equilibrium entropy of the entire isolated system as

$$\hat{S}(\underbrace{X_1, \dots, X_m}_{\lambda}, X_{m+1}, \dots, X_n, \tilde{X}_1, \dots, \tilde{X}_n) \equiv S(X_1, \dots, X_n) + S_r(\tilde{X}_1 - X_1, \dots, \tilde{X}_n - X_n), \tag{59}$$

where X_1, \dots, X_m play the role of the fluctuating internal parameters λ_i , whereas the remaining parameters $X_{m+1}, \dots, X_n, \tilde{X}_1, \dots, \tilde{X}_n$ remain fixed. The equilibrium value of this entropy is

$$\tilde{S} = S(X_1^0, \dots, X_m^0, X_{m+1}, \dots, X_n) + S_r(\tilde{X}_1 - X_1^0, \dots, \tilde{X}_m - X_m^0, \tilde{X}_{m+1} - X_{m+1}, \dots, \tilde{X}_n - X_n), \tag{60}$$

where X_1^0, \dots, X_m^0 are the equilibrium values of the fluctuating parameters. To simplify the notations, from now on we will suppress the fixed parameters in all equations, writing Eqs. (59) and (60) in the form

$$\hat{S}(X_1, \dots, X_m) \equiv S(X_1, \dots, X_m) + S_r(\tilde{X}_1 - X_1, \dots, \tilde{X}_m - X_m), \tag{61}$$

$$\tilde{S} = S(X_1^0, \dots, X_m^0) + S_r(\tilde{X}_1 - X_1^0, \dots, \tilde{X}_m - X_m^0). \tag{62}$$

Before analyzing fluctuations, we will apply the equilibrium conditions (9) to the internal parameters $\lambda_i = X_i$ ($i = 1, \dots, m$):

$$\left(\frac{\partial \hat{S}}{\partial \lambda_i} \right)_0 = \left(\frac{\partial S}{\partial X_i} \right)_0 - \left(\frac{\partial S_r}{\partial X'_i} \right)_0 = F_i^0 - (F'_i)^0 = 0, \quad i = 1, \dots, m, \tag{63}$$

where, as usual, the symbol 0 indicates that the derivatives are computed for the equilibrium parameters X_1^0, \dots, X_m^0 . We thus conclude that in equilibrium, the system and the reservoir have equal values of the thermodynamic forces conjugate to the fluctuating parameters.

We now turn to fluctuations. The probability density of the internal parameters X_1, \dots, X_m is given by Eq. (19), which takes the form

$$\begin{aligned}
 W(X_1, \dots, X_m) &= W_m \exp \left[\frac{\hat{S}(X_1, \dots, X_m) - \tilde{S}}{k} \right] \\
 &= W_m \exp \left[\frac{S(X_1, \dots, X_m) - S(X_1^0, \dots, X_m^0)}{k} \right] \\
 &\quad \times \exp \left[\frac{S_r(\tilde{X}_1 - X_1, \dots, \tilde{X}_m - X_m) - S_r(\tilde{X}_1 - X_1^0, \dots, \tilde{X}_m - X_m^0)}{k} \right]. \quad (64)
 \end{aligned}$$

In the second exponential factor, we will expand S_r around the equilibrium parameters X_1^0, \dots, X_m^0 :

$$\begin{aligned}
 S_r(\tilde{X}_1 - X_1, \dots, \tilde{X}_m - X_m) - S_r(\tilde{X}_1 - X_1^0, \dots, \tilde{X}_m - X_m^0) &= - \sum_{i=1}^m F_i^0 (X_i - X_i^0) \\
 &\quad + \frac{1}{2} \sum_{i,j=1}^m \left(\frac{\partial^2 S_r}{\partial X_i^r \partial X_j^r} \right)_0 (X_i - X_i^0)(X_j - X_j^0). \quad (65)
 \end{aligned}$$

As will be shown later, the second derivatives appearing in the quadratic terms scale as $1/N^r$, where N^r is the number of particles in the reservoir. Since the reservoir is assumed to be much larger than our system, the quadratic terms in Eq. (65) can be neglected in comparison with the linear terms. Neglecting the quadratic terms constitutes what can be called the “reservoir approximation”, in which

$$S_r(\tilde{X}_1 - X_1, \dots, \tilde{X}_m - X_m) - S_r(\tilde{X}_1 - X_1^0, \dots, \tilde{X}_m - X_m^0) = - \sum_{i=1}^m F_i^0 (X_i - X_i^0). \quad (66)$$

Inserting this equation in Eq. (64), we obtain

$$W(X_1, \dots, X_m) = W_m \exp \left[\frac{S(X_1, \dots, X_m) - S(X_1^0, \dots, X_m^0) - \sum_{i=1}^m F_i^0 (X_i - X_i^0)}{k} \right]. \quad (67)$$

Note that this equation contains only properties of the canonical system and does not depend on properties of the reservoir. The role of the reservoir is only to impose the thermodynamic forces F_i^0 .

Eq. (67) is an important relation that will serve as the starting point for deriving all fluctuation properties of canonical systems.

In some canonical systems, there can be additional internal parameters, say Y_1, Y_2, \dots, Y_l , that can fluctuate without affecting the reservoir parameters X_1^r, \dots, X_m^r . In such cases, the set of internal parameters is $X_1, \dots, X_m, Y_1, Y_2, \dots, Y_l$ and Eq. (61) is replaced by

$$\begin{aligned}
 \hat{S}(X_1, \dots, X_m, Y_1, Y_2, \dots, Y_l) &\equiv S(X_1, \dots, X_m, Y_1, Y_2, \dots, Y_l) \\
 &\quad + S_r(\tilde{X}_1 - X_1, \dots, \tilde{X}_m - X_m). \quad (68)
 \end{aligned}$$

The equilibrium conditions with respect to the parameters decoupled from the reservoir is

$$\left(\frac{\partial \hat{S}}{\partial Y_i} \right)_0 = \left(\frac{\partial S}{\partial Y_i} \right)_0 \equiv F_{i+m}^0 = 0, \quad (69)$$

where $i = 1, 2, \dots, l$. It is easy to see that the additional parameters can be incorporated into the parameter list X_1, \dots, X_m by simply assigning them zero thermodynamic forces. Accordingly, Eq. (67) remains valid, except that the sum with F_i^0 excludes the terms corresponding to the decoupled parameters Y_1, Y_2, \dots, Y_l .

9.2. *The generalized canonical distribution*

Before proceeding with applications of Eq. (67), we return for a moment to the statistical–mechanical interpretation of fluctuations discussed in Section 7. For discrete internal parameters X_1, \dots, X_m , Eq. (67) gives the probability W_{X_1, \dots, X_m} of a given parameter set X_1, \dots, X_m . Recall that on the quasi-equilibrium time scale t_q , our system can be treated as if it were equilibrium and isolated with fixed values of X_1, \dots, X_m . Thus, its fundamental equation $S(X_1, \dots, X_m)$ gives the equilibrium entropy $S = k \ln \Omega_{max}$. The probability P of a single *micro-state* can be obtained from the relation $W_{X_1, \dots, X_m} = P \Omega_{max}$, which gives

$$P = \frac{W_{X_1, \dots, X_m}}{\Omega_{max}} = W_{X_1, \dots, X_m} \exp \left[-\frac{S(X_1, \dots, X_m)}{k} \right]. \tag{70}$$

Combining this relation with Eq. (67) we obtain

$$P = W_m \exp \left[-\frac{S(X_1^0, \dots, X_m^0) + \sum_{i=1}^m F_i^0 (X_i - X_i^0)}{k} \right], \tag{71}$$

which can be rewritten as

$$P = A \exp \left(-\frac{1}{k} \sum_{i=1}^m F_i^0 X_i \right), \tag{72}$$

where

$$A = W_m \exp \left[-\frac{S(X_1^0, \dots, X_m^0) - \sum_{i=1}^m F_i^0 X_i^0}{k} \right] \tag{73}$$

is a constant.

Eq. (72) constitutes the *generalized canonical distribution* describing several statistical ensembles.¹³

Assuming that one of the extensive parameters, say X_1 , is energy, Eq. (72) can be rewritten in the form

$$P = A \exp \left(-\frac{E + \sum_{i=2}^m T_0 F_i^0 X_i}{kT_0} \right). \tag{74}$$

As an illustration, suppose our system is a simple fluid. Either one or two of its extensive parameters E , V and N can fluctuate with the third parameter fixed (otherwise the system is undefined). For example,

¹³ The way we arrived at Eq. (72) is not intended to be a rigorous statistical–mechanical derivation of the canonical distribution. The goal was only to show that the thermodynamic fluctuation relation (67) is consistent with the distribution of micro-states known from statistical mechanics.

suppose only energy can fluctuate while V and N remain fixed. From Eq. (74), the probability of a micro-state is

$$P = A \exp\left(-\frac{E}{kT_0}\right), \quad \text{fixed } V, N, \tag{75}$$

a relation which is known as the canonical, or NVT , distribution. If both energy and volume are allowed to fluctuate, we have $X_2 = V$ with $F_2 = p/T$, giving the NpT distribution

$$P = A \exp\left(-\frac{E + p_0V}{kT_0}\right), \quad \text{fixed } N. \tag{76}$$

If the energy and the number of particles can fluctuate at a fixed volume (open system), we have $X_2 = N$ and $F_2 = -\mu/T$. Eq. (74) gives the grand-canonical, or μVT , distribution

$$P = A \exp\left(-\frac{E - \mu_0N}{kT_0}\right), \quad \text{fixed } V. \tag{77}$$

Of course, the pre-exponential factor A is different in all three distributions and is related to the respective partition functions through the probability normalization condition.

Note that the distributions (75)–(77) contain the temperature T_0 , pressure p_0 and the chemical potential μ_0 corresponding to the exact equilibrium with the reservoir. These properties are fixed parameters imposed by the reservoir, by contrast to the fluctuating temperature, pressure and chemical potential inside the system.

We re-emphasize the important difference between Eq. (72) and the previously derived Eq. (67): Eq. (72) gives the probability of a single *micro-state* of the system, whereas Eq. (67) is the probability distribution of the parameters X_1, \dots, X_m characterizing different *macro-states*.

9.3. The Gaussian law of canonical fluctuations

We now return to the probability distribution of the fluctuating parameters given by Eq. (67). Let us expand the entropy of the system around its equilibrium value, keeping only linear and quadratic terms:

$$S(X_1, \dots, X_m) - S(X_1^0, \dots, X_m^0) = \sum_{i=1}^m F_i^0 (X_i - X_i^0) + \frac{1}{2} \sum_{i,j=1}^m \left(\frac{\partial^2 S}{\partial X_i \partial X_j}\right)_0 (X_i - X_i^0)(X_j - X_j^0). \tag{78}$$

Inserting this expansion in Eq. (67), we arrive at the multi-variable Gaussian distribution

$$W(X_1, \dots, X_m) = W_m \exp\left[-\frac{1}{2} \sum_{i,j=1}^m \Lambda_{ij} (X_i - X_i^0)(X_j - X_j^0)\right], \tag{79}$$

with the stability matrix

$$\Lambda_{ij} \equiv -\frac{1}{k} \left(\frac{\partial^2 S}{\partial X_i \partial X_j}\right)_0 = -\frac{1}{k} \left(\frac{\partial F_i}{\partial X_j}\right)_0. \tag{80}$$

In this approximation, the average values \bar{X}_i are numerically equal to the most probable values X_i^0 . Using the standard properties of the Gaussian distribution (Section 8), we obtain the fluctuation relations

$$\overline{\Delta X_i \Delta X_j} = \Lambda_{ij}^{-1}, \quad i, j = 1, \dots, m, \tag{81}$$

and thus

$$\overline{(\Delta X_i)^2} = \Lambda_{ii}^{-1}, \quad i = 1, \dots, m. \quad (82)$$

We can also introduce the parameters

$$\varphi_i \equiv \sum_{j=1}^m \Lambda_{ij} X_j, \quad i = 1, \dots, m, \quad (83)$$

for which

$$\varphi_i - \bar{\varphi}_i = -\frac{1}{k} \sum_{j=1}^m \left(\frac{\partial F_i}{\partial X_j} \right)_0 (X_j - X_j^0) \equiv -\frac{1}{k} \Delta F_i. \quad (84)$$

Here, ΔF_i is the deviation of F_i from its equilibrium value evaluated in the quadratic approximation (78). Using the properties (46) and (47) of the Gaussian distribution, we obtain the fluctuation relations for thermodynamic forces:

$$\overline{\Delta X_i \Delta F_j} = -k \delta_{ij}, \quad i, j = 1, \dots, m, \quad (85)$$

$$\overline{\Delta F_i \Delta F_j} = k^2 \Lambda_{ij}, \quad i, j = 1, \dots, m, \quad (86)$$

and therefore

$$\overline{(\Delta F_i)^2} = k^2 \Lambda_{ii}, \quad i = 1, \dots, m. \quad (87)$$

Eqs. (82) and (87) show that for normally stable states, the derivatives $(\partial X_i / \partial F_i)_0$ and $(\partial F_i / \partial X_i)_0$ must be positive. At critical points one of these derivatives tends to infinity and the respective fluctuation diverges (unless the reservoir has a finite size, see Section 10).

Another form of the foregoing equations is obtained by introducing the thermodynamic potential

$$\Theta(F_1, \dots, F_m) \equiv S - \sum_{i=1}^m F_i X_i \quad (88)$$

as the Legendre transform of the entropy (Massieu function) [26–28]. Then,

$$X_i = -\frac{\partial \Theta}{\partial F_i} \quad (89)$$

and

$$\Lambda_{ij}^{-1} = k \left(\frac{\partial^2 \Theta}{\partial F_i \partial F_j} \right)_0. \quad (90)$$

For normally stable states $(\partial^2 \Theta / \partial F_i^2)_0 > 0$ for all $i = 1, \dots, m$.

It is interesting to evaluate canonical fluctuations of entropy relative to its equilibrium value $S(X_1^0, \dots, X_m^0)$. Using the quadratic approximation (78), we have

$$\Delta S = \sum_{i=1}^m F_i^0 \Delta X_i - \frac{1}{2} k \sum_{i,j=1}^m \Lambda_{ij} \Delta X_i \Delta X_j. \quad (91)$$

Averaging this equation over the distribution (79) and taking into account Eq. (81), we obtain

$$\overline{\Delta S} = \sum_{i=1}^m F_i^0 \overline{\Delta X_i} - \frac{1}{2} k \sum_{i,j=1}^m \Lambda_{ij} \overline{\Delta X_i \Delta X_j} = -\frac{1}{2} k. \quad (92)$$

Thus, in the Gaussian approximation the canonical entropy equals

$$\bar{S} = S(X_1^0, \dots, X_m^0) - \frac{1}{2} k. \quad (93)$$

Considering that entropy scales in proportion to the total of number of particles N , the relative fluctuation $\overline{\Delta S}/\bar{S} \propto N^{-1}$. Using the same Gaussian approximation, the mean-square fluctuation of entropy scales in proportion to N ,

$$\overline{(\Delta S)^2} = \sum_{i,j=1}^m F_i^0 F_j^0 \overline{\Delta X_i \Delta X_j} = \sum_{i,j=1}^m F_i^0 F_j^0 \Lambda_{ij}^{-1} \propto N. \tag{94}$$

where we neglected higher-order moments of the distribution. Thus, the relative fluctuation $\left(\overline{(\Delta S)^2}\right)^{1/2} / \bar{S} \propto N^{-1/2}$. Both estimates show that, with increasing size of the system, the canonical entropy \bar{S} tends to the micro-canonical entropy S satisfying the fundamental equation (4). While the two entropies are conceptually different, they converge to the same numerical value in the thermodynamic limit.

It should be emphasized that the existence of equilibrium fluctuations of intensive parameters in a canonical system and their correlations with extensive parameters has long been the subject of debate in the literature. While for some authors [27,28,38,39,41,63], the canonical fluctuation relations such as Eqs. (85)–(87) reflect the actual physics and can be subject to experimental verification [64], others consider such relations meaningless [65] and a mere manipulation of symbols [66]. It is our opinion that the controversy arises from different definitions of the intensive parameters adopted by different authors. As argued by Kittel [65], if temperature of a canonical system is only defined as the temperature of the infinite reservoir with which it has been equilibrated, then of course it cannot fluctuate. This argument equally applies to pressure, chemical potentials and all other intensive properties. In response to Kittel, Mandelbrot [67] offered a different approach in which the temperature of an isolated system is defined by attempts to estimate the temperature of the thermostat with which the system was in equilibrium prior to isolation. In this approach, temperature fluctuations are well-defined while the temperature itself cannot be defined unambiguously. The present analysis is based on the micro-canonical definition of temperature as the derivative $(\partial S/\partial E)^{-1}$ computed by considering different equilibrium isolated states of the same system (Section 3). Likewise, all other intensive properties are defined through the derivatives $F_i = \partial S/\partial X_i$ (or $P_i = \partial E/\partial Z_i$, see below) computed in the same manner. In the sense of this definition, not only infinite reservoirs but also finite systems have their own temperature, pressure and other intensive parameters. Accordingly, they continue to fluctuate when the system is equilibrated with an infinite reservoir. It is in this sense that Eqs. (85)–(87) and similar fluctuation relations should be understood in this paper.

9.4. Canonical fluctuations in the energy scheme

The treatment of fluctuations based on the fundamental equation (4) is called the entropy scheme. In practical situations, energy is always one of the extensive parameters fluctuating between the canonical system and the reservoir.¹⁴ Suppose $X_1 = E$ and thus $F_1 = 1/T$. Eq. (4) can be inverted to obtain

$$E = E(Z_1, \dots, Z_n), \tag{95}$$

where $Z_1 = S$ and $Z_i = X_i, i = 2, \dots, n$. This equation is called the fundamental equation in the energy representation, or the energy scheme [29]. In the energy scheme, the thermodynamic forces $P_i = \partial E/\partial Z_i$ conjugate to the extensive arguments Z_1, \dots, Z_n are $P_1 = T$ and $P_i = -TF_i, i = 2, \dots, n$. For example, for a simple fluid $E = E(S, V, N)$ and thus $P_1 = T, P_2 = -p$ and $P_3 = \mu$.

In many applications, we are more interested in fluctuations of the P -forces rather than F -forces. The formalism presented below expresses canonical fluctuations in terms of the variable sets Z_1, \dots, Z_n and P_1, \dots, P_n corresponding to the energy scheme.

¹⁴ While “adiabatic ensembles” in which the system is adiabatically isolated but can still exchange particles with the reservoir are helpful theoretical constructions, their practical implementation in experiments or atomistic simulations is unfeasible.

As before, we consider a system coupled to a reservoir and described by n extensive properties X_1, \dots, X_n . Out of them, m properties X_1, \dots, X_m can flow between the system and the reservoir while the remaining properties X_{m+1}, \dots, X_n are fixed. Assuming $X_1 = E$, we transform the variable set X_1, \dots, X_m to Z_1, \dots, Z_m and perform a Legendre transformation to obtain the thermodynamic potential appropriate for the energy scheme:

$$\Phi(P_1, \dots, P_m) \equiv E - \sum_{i=1}^m P_i Z_i. \tag{96}$$

This potential has the property

$$\frac{\partial \Phi}{\partial P_i} = -Z_i. \tag{97}$$

Returning to the parameter distribution (67), we can now recast it in the form

$$W = W_m \exp \left[-\frac{E - E_0 - \sum_{i=1}^m P_i^0 (Z_i - Z_i^0)}{kT_0} \right] \equiv W_m \exp \left(-\frac{\mathcal{R}}{kT_0} \right), \tag{98}$$

where we denote

$$\mathcal{R} \equiv E - E_0 - \sum_{i=1}^m P_i^0 (Z_i - Z_i^0). \tag{99}$$

It can be shown that \mathcal{R} has the meaning of the reversible work required for the creation of the fluctuated state of the canonical system at a fixed value of the total entropy of the system and the reservoir [25,63].

Eq. (98) is the canonical distribution function of the extensive parameters Z_1, \dots, Z_m . For small fluctuations, we can expand $E - E_0$ in these parameters and neglect all terms beyond quadratic to obtain the multi-variable Gaussian distribution

$$W(Z_1, \dots, Z_m) = W_m \exp \left[-\frac{1}{2} \sum_{i,j=1}^m K_{ij} (Z_i - Z_i^0)(Z_j - Z_j^0) \right], \tag{100}$$

where the matrix

$$K_{ij} \equiv \frac{1}{kT_0} \left(\frac{\partial^2 E}{\partial Z_i \partial Z_j} \right)_0 = \frac{1}{kT_0} \left(\frac{\partial P_i}{\partial Z_j} \right)_0 \tag{101}$$

can be called [29] the generalized stiffness matrix. Its inverse

$$K_{ij}^{-1} = kT_0 \left(\frac{\partial Z_i}{\partial P_j} \right)_0 = -kT_0 \frac{\partial^2 \Phi}{\partial P_i \partial P_j} \tag{102}$$

can be then called [29] the generalized compliance matrix.

Using the standard properties of the Gaussian distribution (Section 8), we obtain at once the covariances and mean-square fluctuations of all extensive and intensive properties of the canonical system in the energy scheme:

$$\overline{\Delta Z_i \Delta Z_j} = K_{ij}^{-1}, \quad i, j = 1, \dots, m, \tag{103}$$

$$\overline{(\Delta Z_i)^2} = K_{ii}^{-1}, \quad i = 1, \dots, m, \tag{104}$$

$$\overline{\Delta Z_i \Delta P_j} = kT_0 \delta_{ij}, \quad i, j = 1, \dots, m, \tag{105}$$

$$\overline{\Delta P_i \Delta P_j} = (kT_0)^2 K_{ij}, \quad i, j = 1, \dots, m, \tag{106}$$

$$\overline{(\Delta P_i)^2} = (kT_0)^2 K_{ii}, \quad i = 1, \dots, m. \tag{107}$$

Having these fluctuation relations, it is straightforward to find the covariance of any two thermodynamic properties $y = y(Z_1, \dots, Z_m)$ and $z = z(Z_1, \dots, Z_m)$. Indeed, for small fluctuations,

$$\Delta y = \sum_{i=1}^m \left(\frac{\partial y}{\partial Z_i} \right)_0 \Delta Z_i, \quad (108)$$

$$\Delta z = \sum_{i=1}^m \left(\frac{\partial z}{\partial Z_i} \right)_0 \Delta Z_i, \quad (109)$$

from which

$$\overline{\Delta y \Delta z} = \sum_{i,j=1}^m \left(\frac{\partial y}{\partial Z_i} \right)_0 \left(\frac{\partial z}{\partial Z_j} \right)_0 \overline{\Delta Z_i \Delta Z_j} = \sum_{i,j=1}^m \left(\frac{\partial y}{\partial Z_i} \right)_0 \left(\frac{\partial z}{\partial Z_j} \right)_0 K_{ij}^{-1}. \quad (110)$$

Similarly, for any two functions $y = y(P_1, \dots, P_m)$ and $z = z(P_1, \dots, P_m)$,

$$\overline{\Delta y \Delta z} = \sum_{i,j=1}^m \left(\frac{\partial y}{\partial P_i} \right)_0 \left(\frac{\partial z}{\partial P_j} \right)_0 \overline{\Delta P_i \Delta P_j} = (kT_0)^2 \sum_{i,j=1}^m \left(\frac{\partial y}{\partial P_i} \right)_0 \left(\frac{\partial z}{\partial P_j} \right)_0 K_{ij}. \quad (111)$$

The same calculation method can be applied when y is a function Z_1, \dots, Z_m while z is a function of P_1, \dots, P_m , or when both are functions of mixed sets of Z 's and P 's.

9.5. Canonical fluctuations in a simple fluid

To demonstrate the foregoing formalism for computing canonical fluctuations, we will apply it to a simple fluid coupled to a reservoir. We will consider three different ensembles, deriving equations for the mean-square fluctuations and covariances of all thermodynamic properties in each case. The calculations will be conducted in the energy scheme, although the entropy scheme could be applied just as well. We are working with the extensive and intensive parameter sets $(Z_1, Z_2, Z_3) = (S, V, N)$ and $(P_1, P_2, P_3) = (T, -p, \mu)$, respectively. To simplify the notations, we will suppress the index 0 but it is implied that all derivatives are taken at the equilibrium state.

While a number of fluctuation relations for fluids can be found in the literature, in this paper we present a *complete* set of such relations for each ensemble. For the NVT ensemble, there are 5 fluctuating parameters (E, S, T, p, μ) . Out of 25 covariances that can be formed among them, only 15 are distinct due to the symmetry of the covariance. Similarly, in the NpT and μVT ensembles, there are 6 fluctuating parameters (E, S, V, T, p, μ) and (E, S, N, T, p, μ) , respectively.¹⁵ Taking into account the symmetry of covariances, 21 distinct fluctuation relations exist for each of these ensembles. All these fluctuation relations will be derived below in a systematic manner enabled by the proposed formalism.

The equilibrium properties appearing on right-hand sides of the fluctuation relations will be presented in simplest possible form. They can be further transformed to many other forms expressing them through specific heats, moduli or other experimentally accessible properties. We do not pursue such transformations as they lie outside the fluctuation topic and depend on the problem at hand.

9.5.1. NVT ensemble

Suppose the volume and number of particles in the system are fixed while the energy and entropy can fluctuate (canonical ensemble). The stiffness and compliance matrices reduce to the scalars

$$K_{11} = \frac{1}{kT_0} \left(\frac{\partial T}{\partial S} \right)_{V,N} = \frac{1}{Nk c_v} \quad (112)$$

¹⁵ Recall that all intensive properties of a canonical system are allowed to fluctuate, including those which are imposed by the reservoir. For example, in the μVT ensemble, the reservoir imposes a certain temperature T_0 and chemical potential μ_0 ; however, the actual temperature and chemical potential inside the system fluctuate around the imposed values. See the last paragraph of Section 9.3 for further discussion.

and

$$K_{11}^{-1} = Nk c_v. \quad (113)$$

By Eq. (104),

$$\overline{(\Delta S)^2} = K_{11}^{-1} = Nk c_v. \quad (114)$$

Applying Eq. (110), we find the energy fluctuation

$$\overline{(\Delta E)^2} = \left(\frac{\partial E}{\partial S} \right)_{V,N}^2 K_{11}^{-1} = Nk T_0^2 c_v \quad (115)$$

and the energy-entropy covariance

$$\overline{\Delta E \Delta S} = \left(\frac{\partial E}{\partial S} \right)_{V,N} K_{11}^{-1} = Nk T_0 c_v, \quad (116)$$

where we used the relation $(\partial E/\partial S)_{V,N} = T_0$. For temperature fluctuations, we follow Eq. (107) to obtain

$$\overline{(\Delta T)^2} = (kT_0)^2 K_{11} = \frac{kT_0^2}{Nc_v}. \quad (117)$$

We next derive fluctuations of the chemical potential and pressure. Both are dependent variables that can be expressed as functions of temperature and the number density of particles, $\rho \equiv N/V$. The latter is fixed, leaving only T as an independent argument. Applying Eq. (111) we obtain

$$\overline{(\Delta \mu)^2} = (kT_0)^2 \left(\frac{\partial \mu}{\partial T} \right)_\rho^2 K_{11} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial \mu}{\partial T} \right)_\rho^2, \quad (118)$$

$$\overline{(\Delta p)^2} = (kT_0)^2 \left(\frac{\partial p}{\partial T} \right)_\rho^2 K_{11} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial p}{\partial T} \right)_\rho^2, \quad (119)$$

$$\overline{\Delta \mu \Delta p} = (kT_0)^2 \left(\frac{\partial \mu}{\partial T} \right)_\rho \left(\frac{\partial p}{\partial T} \right)_\rho K_{11} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial \mu}{\partial T} \right)_\rho \left(\frac{\partial p}{\partial T} \right)_\rho, \quad (120)$$

$$\overline{\Delta \mu \Delta T} = (kT_0)^2 \left(\frac{\partial \mu}{\partial T} \right)_\rho K_{11} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial \mu}{\partial T} \right)_\rho, \quad (121)$$

$$\overline{\Delta p \Delta T} = (kT_0)^2 \left(\frac{\partial p}{\partial T} \right)_\rho K_{11} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial p}{\partial T} \right)_\rho. \quad (122)$$

For “cross-fluctuations” between extensive and intensive properties, we first apply Eq. (105) to obtain

$$\overline{\Delta S \Delta T} = kT_0. \quad (123)$$

The remaining “cross-fluctuations” are easily computed by the method outlined by Eqs. (108)–(111):

$$\overline{\Delta E \Delta T} = \left(\frac{\partial E}{\partial S} \right)_{V,N} \overline{\Delta S \Delta T} = kT_0^2, \quad (124)$$

$$\overline{\Delta S \Delta p} = \left(\frac{\partial p}{\partial T} \right)_\rho \overline{\Delta S \Delta T} = kT_0 \left(\frac{\partial p}{\partial T} \right)_\rho, \quad (125)$$

$$\overline{\Delta E \Delta p} = \left(\frac{\partial E}{\partial S} \right)_{V,N} \left(\frac{\partial p}{\partial T} \right)_\rho \overline{\Delta S \Delta T} = kT_0^2 \left(\frac{\partial p}{\partial T} \right)_\rho, \quad (126)$$

Table 1

Complete set of fluctuation relations for a simple fluid in the *NVT* ensemble.

$\overline{(\Delta E)^2} = NkT_0^2 c_v$	$\overline{\Delta\mu\Delta p} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial\mu}{\partial T}\right)_\rho \left(\frac{\partial p}{\partial T}\right)_\rho$
$\overline{(\Delta S)^2} = Nkc_v$	$\overline{\Delta S\Delta T} = kT_0$
$\overline{(\Delta E)(\Delta S)} = NkT_0 c_v$	$\overline{\Delta E\Delta T} = kT_0^2$
$\overline{(\Delta T)^2} = \frac{kT_0^2}{Nc_v}$	$\overline{\Delta S\Delta p} = kT_0 \left(\frac{\partial p}{\partial T}\right)_\rho$
$\overline{(\Delta\mu)^2} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial\mu}{\partial T}\right)_\rho^2$	$\overline{\Delta E\Delta p} = kT_0^2 \left(\frac{\partial p}{\partial T}\right)_\rho$
$\overline{(\Delta p)^2} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial p}{\partial T}\right)_\rho^2$	$\overline{\Delta S\Delta\mu} = kT_0 \left(\frac{\partial\mu}{\partial T}\right)_\rho$
$\overline{\Delta T\Delta p} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial p}{\partial T}\right)_\rho$	$\overline{\Delta E\Delta\mu} = kT_0^2 \left(\frac{\partial\mu}{\partial T}\right)_\rho$
$\overline{\Delta\mu\Delta T} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial\mu}{\partial T}\right)_\rho$	

$$\overline{\Delta S\Delta\mu} = \left(\frac{\partial\mu}{\partial T}\right)_\rho \overline{\Delta S\Delta T} = kT_0 \left(\frac{\partial\mu}{\partial T}\right)_\rho, \tag{127}$$

$$\overline{\Delta E\Delta\mu} = \left(\frac{\partial E}{\partial S}\right)_{V,N} \left(\frac{\partial\mu}{\partial T}\right)_\rho \overline{\Delta S\Delta T} = kT_0^2 \left(\frac{\partial\mu}{\partial T}\right)_\rho. \tag{128}$$

Table 1 summarizes all fluctuation relations derived for the *NVT* ensemble.

9.5.2. *NpT* ensemble

Now suppose that the volume of the system can also fluctuate while $N = \text{const}$. The stiffness matrix is now 2×2 and its K_{11} component is still given by Eq. (112). For the remaining components we have

$$K_{12} = \frac{1}{kT_0} \left(\frac{\partial T}{\partial V}\right)_{S,N} = -\frac{1}{kT_0} \left(\frac{\partial S}{\partial V}\right)_{T,N} = -\frac{\left(\frac{\partial p}{\partial T}\right)_\rho}{Nkc_v}, \tag{129}$$

where we used the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_{T,N} = \left(\frac{\partial p}{\partial T}\right)_{V,N}, \tag{130}$$

and

$$K_{22} = -\frac{1}{kT_0} \left(\frac{\partial p}{\partial V}\right)_{S,N} = \frac{1}{Nkc_v} \left(\frac{\partial p}{\partial T}\right)_\rho^2 - \frac{1}{kT_0} \left(\frac{\partial p}{\partial V}\right)_{T,N}, \tag{131}$$

where we used the identity

$$\left(\frac{\partial p}{\partial V}\right)_{S,N} = \left(\frac{\partial p}{\partial V}\right)_{T,N} - \frac{T}{Nc_v} \left(\frac{\partial p}{\partial T}\right)_{V,N}^2. \tag{132}$$

Note that the derivatives $(\partial p/\partial V)_{T,N}$ and $(\partial p/\partial V)_{S,N}$ are related to the isothermal and adiabatic moduli, respectively.

Thus, the stiffness matrix of the fluid takes the form

$$K = \frac{1}{Nkc_v} \begin{pmatrix} 1 & -\left(\frac{\partial p}{\partial T}\right)_\rho \\ -\left(\frac{\partial p}{\partial T}\right)_\rho & \left(\frac{\partial p}{\partial T}\right)_\rho^2 - \frac{Nc_v}{T_0} \left(\frac{\partial p}{\partial V}\right)_{T,N} \end{pmatrix} \tag{133}$$

with the compliance matrix

$$K^{-1} = -kT_0 \left(\frac{\partial V}{\partial p} \right)_{T,N} \begin{pmatrix} \left(\frac{\partial p}{\partial T} \right)_\rho^2 - \frac{Nc_v}{T_0} \left(\frac{\partial p}{\partial V} \right)_{T,N} & \left(\frac{\partial p}{\partial T} \right)_\rho \\ \left(\frac{\partial p}{\partial V} \right)_{T,N} & 1 \end{pmatrix}. \quad (134)$$

We are ready to calculate the fluctuations. To find the entropy and volume fluctuations, we apply Eq. (103):

$$\overline{(\Delta S)^2} = K_{11}^{-1} = Nkc_v - kT_0 \left(\frac{\partial V}{\partial p} \right)_{T,N} \left(\frac{\partial p}{\partial T} \right)_\rho^2 \equiv Nkc_p, \quad (135)$$

$$\overline{(\Delta V)^2} = K_{22}^{-1} = -kT_0 \left(\frac{\partial V}{\partial p} \right)_{T,N}, \quad (136)$$

$$\overline{\Delta S \Delta V} = K_{12}^{-1} = -kT_0 \left(\frac{\partial V}{\partial p} \right)_{T,N} \left(\frac{\partial p}{\partial T} \right)_\rho = kT_0 \left(\frac{\partial V}{\partial T} \right)_{p,N}, \quad (137)$$

where c_p is the specific heat at constant pressure. Fluctuation relations involving energy are calculated by Eq. (110):

$$\begin{aligned} \overline{(\Delta E)^2} &= \left(\frac{\partial E}{\partial S} \right)_{V,N}^2 K_{11}^{-1} + \left(\frac{\partial E}{\partial V} \right)_{S,N}^2 K_{22}^{-1} + 2 \left(\frac{\partial E}{\partial S} \right)_{V,N} \left(\frac{\partial E}{\partial V} \right)_{S,N} K_{12}^{-1} \\ &= NkT_0^2 c_v - kT_0^3 \left(\frac{\partial V}{\partial p} \right)_{T,N} \left[\left(\frac{\partial p}{\partial T} \right)_\rho - \frac{p_0}{T_0} \right]^2. \end{aligned} \quad (138)$$

$$\begin{aligned} \overline{\Delta E \Delta S} &= \left(\frac{\partial E}{\partial S} \right)_{V,N} K_{11}^{-1} + \left(\frac{\partial E}{\partial V} \right)_{S,N} K_{12}^{-1} \\ &= NkT_0 c_v - kT_0^2 \left(\frac{\partial V}{\partial p} \right)_{T,N} \left(\frac{\partial p}{\partial T} \right)_\rho \left[\left(\frac{\partial p}{\partial T} \right)_\rho - \frac{p_0}{T_0} \right]. \end{aligned} \quad (139)$$

$$\begin{aligned} \overline{\Delta E \Delta V} &= \left(\frac{\partial E}{\partial S} \right)_{V,N} K_{12}^{-1} + \left(\frac{\partial E}{\partial V} \right)_{S,N} K_{22}^{-1} \\ &= -kT_0^2 \left(\frac{\partial V}{\partial p} \right)_{T,N} \left[\left(\frac{\partial p}{\partial T} \right)_\rho - \frac{p_0}{T_0} \right]. \end{aligned} \quad (140)$$

Turning to fluctuations of intensive parameters, we use Eqs. (106) and (107) to obtain

$$\overline{(\Delta T)^2} = (kT_0)^2 K_{11} = \frac{kT_0^2}{Nc_v}, \quad (141)$$

$$\overline{(\Delta p)^2} = (kT_0)^2 K_{22} = -kT_0 \left[\left(\frac{\partial p}{\partial V} \right)_{T,N} - \frac{T_0}{Nc_v} \left(\frac{\partial p}{\partial T} \right)_\rho^2 \right], \quad (142)$$

$$\overline{\Delta T \Delta p} = -(kT_0)^2 K_{12} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial p}{\partial T} \right)_\rho. \quad (143)$$

To derive fluctuation relations involving the chemical potential, we treat it as a function of T and p . Using Eq. (111),

$$\overline{(\Delta \mu)^2} = (kT_0)^2 \left[\left(\frac{\partial \mu}{\partial T} \right)_p^2 K_{11} + \left(\frac{\partial \mu}{\partial p} \right)_T^2 K_{22} - 2 \left(\frac{\partial \mu}{\partial T} \right)_p \left(\frac{\partial \mu}{\partial p} \right)_T K_{12} \right]$$

$$\begin{aligned}
&= (kT_0)^2 [s_0^2 K_{11} + v_0^2 K_{22} + 2s_0 v_0 K_{12}] \\
&= \frac{kT_0^2}{Nc_v} \left[v_0 \left(\frac{\partial p}{\partial T} \right)_\rho - s_0 \right]^2 - kT_0 v_0^2 \left(\frac{\partial p}{\partial V} \right)_{T,N}, \tag{144}
\end{aligned}$$

where

$$s_0 = - \left(\frac{\partial \mu}{\partial T} \right)_p \tag{145}$$

is the equilibrium entropy per particle and

$$v_0 = \left(\frac{\partial \mu}{\partial p} \right)_p \tag{146}$$

is the equilibrium volume per particle ($v_0 = 1/\rho_0$). Similarly,

$$\overline{\Delta \mu \Delta T} = (kT_0)^2 \left[\left(\frac{\partial \mu}{\partial T} \right)_p K_{11} - \left(\frac{\partial \mu}{\partial p} \right)_T K_{12} \right] = \frac{kT_0^2}{Nc_v} \left[v_0 \left(\frac{\partial p}{\partial T} \right)_\rho - s_0 \right], \tag{147}$$

$$\overline{\Delta \mu \Delta p} = (kT_0)^2 \left[- \left(\frac{\partial \mu}{\partial T} \right)_p K_{12} + \left(\frac{\partial \mu}{\partial p} \right)_T K_{22} \right] \tag{148}$$

$$= -kT_0 v_0 \left(\frac{\partial p}{\partial V} \right)_{T,N} + \frac{kT_0^2}{Nc_v} \left(\frac{\partial p}{\partial T} \right)_\rho \left[v_0 \left(\frac{\partial p}{\partial T} \right)_\rho - s_0 \right]. \tag{149}$$

Eq. (105) gives the “cross-fluctuations”

$$\overline{\Delta S \Delta T} = - \overline{\Delta V \Delta p} = kT_0, \tag{150}$$

$$\overline{\Delta S \Delta p} = 0, \tag{151}$$

$$\overline{\Delta V \Delta T} = 0. \tag{152}$$

The remaining “cross-fluctuations” are computed in a manner similar to Eqs. (108)–(111):

$$\overline{\Delta S \Delta \mu} = \left(\frac{\partial \mu}{\partial T} \right)_p \overline{\Delta S \Delta T} = -kT_0 s_0, \tag{153}$$

$$\overline{\Delta E \Delta T} = \left(\frac{\partial E}{\partial S} \right)_{V,N} \overline{\Delta S \Delta T} = kT_0^2, \tag{154}$$

$$\overline{\Delta E \Delta p} = \left(\frac{\partial E}{\partial V} \right)_{S,N} \overline{\Delta V \Delta p} = kT_0 p_0, \tag{155}$$

$$\overline{\Delta E \Delta \mu} = \left(\frac{\partial E}{\partial S} \right)_{V,N} \left(\frac{\partial \mu}{\partial T} \right)_p \overline{\Delta S \Delta T} + \left(\frac{\partial E}{\partial V} \right)_{S,N} \left(\frac{\partial \mu}{\partial p} \right)_T \overline{\Delta V \Delta p} = kT_0 (p_0 v_0 - T_0 s_0), \tag{156}$$

$$\overline{\Delta V \Delta \mu} = \left(\frac{\partial \mu}{\partial p} \right)_T \overline{\Delta V \Delta p} = -kT_0 v_0. \tag{157}$$

The fluctuation relations for the NpT ensemble are summarized in [Table 2](#).

Table 2
Complete set of fluctuation relations for a simple fluid in the NpT ensemble.

$\overline{(\Delta S)^2} = Nk c_v - kT_0 \left(\frac{\partial V}{\partial p} \right)_{T,N} \left(\frac{\partial p}{\partial T} \right)_\rho^2$	$\overline{\Delta \mu \Delta p} = -kT_0 v_0 \left(\frac{\partial p}{\partial V} \right)_{T,N}$ $+ \frac{kT_0^2}{Nc_v} \left(\frac{\partial p}{\partial T} \right)_\rho \left[v_0 \left(\frac{\partial p}{\partial T} \right)_\rho - s_0 \right]$
$\overline{\Delta S \Delta V} = kT_0 \left(\frac{\partial V}{\partial T} \right)_{p,N}$	$\overline{\Delta S \Delta T} = kT_0$
$\overline{(\Delta V)^2} = -kT_0 \left(\frac{\partial V}{\partial p} \right)_{T,N}$	$\overline{\Delta V \Delta p} = -kT_0$
$\overline{(\Delta E)^2} = NkT_0^2 c_v$	$\overline{\Delta S \Delta p} = 0$
$-kT_0^3 \left(\frac{\partial V}{\partial p} \right)_{T,N} \left[\left(\frac{\partial p}{\partial T} \right)_\rho - \frac{p_0}{T_0} \right]^2$	$\overline{\Delta V \Delta T} = 0$
$\overline{\Delta E \Delta S} = NkT_0 c_v$	$\overline{\Delta S \Delta \mu} = -kT_0 s_0$
$-kT_0^2 \left(\frac{\partial V}{\partial p} \right)_{T,N} \left(\frac{\partial p}{\partial T} \right)_\rho \left[\left(\frac{\partial p}{\partial T} \right)_\rho - \frac{p_0}{T_0} \right]$	$\overline{\Delta E \Delta T} = kT_0^2$
$\overline{\Delta E \Delta V} = -kT_0^2 \left(\frac{\partial V}{\partial p} \right)_{T,N} \left[\left(\frac{\partial p}{\partial T} \right)_\rho - \frac{p_0}{T_0} \right]$	$\overline{\Delta E \Delta p} = kT_0 p_0$
$\overline{(\Delta T)^2} = \frac{kT_0^2}{Nc_v}$	$\overline{\Delta E \Delta \mu} = kT_0 (p_0 v_0 - T_0 s_0)$
$\overline{(\Delta p)^2} = -kT_0 \left[\left(\frac{\partial p}{\partial V} \right)_{T,N} - \frac{T_0}{Nc_v} \left(\frac{\partial p}{\partial T} \right)_\rho^2 \right]$	$\overline{\Delta V \Delta \mu} = -kT_0 v_0$
$\overline{\Delta T \Delta p} = \frac{kT_0^2}{Nc_v} \left(\frac{\partial p}{\partial T} \right)_\rho$	
$\overline{(\Delta \mu)^2} = \frac{kT_0^2}{Nc_v} \left[v_0 \left(\frac{\partial p}{\partial T} \right)_\rho - s_0 \right]^2 - kT_0 v_0^2 \left(\frac{\partial p}{\partial V} \right)_{T,N}$	
$\overline{\Delta \mu \Delta T} = \frac{kT_0^2}{Nc_v} \left[v_0 \left(\frac{\partial p}{\partial T} \right)_\rho - s_0 \right]$	

9.5.3. μVT ensemble

We now turn to the grand-canonical ensemble, in which the volume of the system is fixed while the energy and the number of particles can fluctuate. The equilibrium temperature T_0 and the chemical potential μ_0 are fixed by the reservoir. The independent fluctuating variables are S and N , with the conjugate thermodynamic forces $P_1 = T$, and $P_2 = \mu$. Energy is a dependent extensive parameter. The chemical potential and pressure are also dependent parameters treated as functions of T and ρ .

All fluctuation relations can be obtained from those for the NpT ensemble by simply swapping the variables $V \rightarrow N$, $p \rightarrow -\mu$. In particular, the derivative $(\partial p/\partial T)_\rho$ is replaced by $-(\partial \mu/\partial T)_\rho$ and $(\partial p/\partial V)_{T,N}$ by $-V^{-1}(\partial \mu/\partial \rho)_T$. Furthermore, it is easy to verify that s_0 is replaced by s_0/v_0 and v_0 by $1/v_0$. The stiffness matrix becomes

$$K = \frac{1}{N_0 k c_v} \begin{pmatrix} 1 & \left(\frac{\partial \mu}{\partial T} \right)_\rho \\ \left(\frac{\partial \mu}{\partial T} \right)_\rho & \left(\frac{\partial \mu}{\partial T} \right)_\rho^2 + \frac{\rho_0 c_v}{T_0} \left(\frac{\partial \mu}{\partial \rho} \right)_T \end{pmatrix} \tag{158}$$

with the inverse

$$K^{-1} = kT_0 V \begin{pmatrix} \left(\frac{\partial \mu}{\partial \rho} \right)_T & - \left(\frac{\partial \mu}{\partial T} \right)_\rho \\ \left(\frac{\partial \mu}{\partial T} \right)_\rho^{-1} \left(\left(\frac{\partial \mu}{\partial T} \right)_\rho^2 + \frac{\rho_0 c_v}{T_0} \left(\frac{\partial \mu}{\partial \rho} \right)_T \right) & 1 \end{pmatrix}. \tag{159}$$

The results of the calculations are summarized in [Table 3](#).

The following scaling properties of fluctuations are evident from [Tables 1–3](#):

- Covariances of extensive properties scale in proportion to the system size (N or V).
- Covariances of intensive properties scale as inverse of the system size (N^{-1} or V^{-1}).

Table 3

Complete set of fluctuation relations for a simple fluid in the μVT ensemble.

$\overline{(\Delta S)^2} = \rho_0 k c_v V + k T_0 \left(\frac{\partial \mu}{\partial \rho} \right)_T^{-1} \left(\frac{\partial \mu}{\partial T} \right)_\rho^2 V$	$\overline{\Delta \mu \Delta p} = \frac{k T_0}{\rho_0 v_0 V} \left(\frac{\partial \mu}{\partial \rho} \right)_T$ $+ \frac{k T_0^2}{\rho_0 c_v v_0 V} \left(\frac{\partial \mu}{\partial T} \right)_\rho \left[s_0 + \left(\frac{\partial \mu}{\partial T} \right)_\rho \right]$
$\overline{\Delta S \Delta N} = -k T_0 \left(\frac{\partial \mu}{\partial \rho} \right)_T^{-1} \left(\frac{\partial \mu}{\partial T} \right)_\rho V$	$\overline{\Delta S \Delta T} = k T_0$
$\overline{(\Delta N)^2} = k T_0 \left(\frac{\partial \mu}{\partial \rho} \right)_T^{-1} V$	$\overline{\Delta N \Delta \mu} = k T_0$
$\overline{(\Delta E)^2} = \rho_0 k T_0^2 c_v V$	$\overline{\Delta S \Delta \mu} = 0$
$+ k T_0^3 \left(\frac{\partial \mu}{\partial \rho} \right)_T^{-1} \left[\left(\frac{\partial \mu}{\partial T} \right)_\rho - \frac{\mu_0}{T_0} \right]^2 V$	$\overline{\Delta N \Delta T} = 0$
$\overline{\Delta E \Delta S} = \rho_0 k T_0 c_v V$	
$- k T_0^2 \left(\frac{\partial \mu}{\partial \rho} \right)_T^{-1} \left(\frac{\partial \mu}{\partial T} \right)_\rho \left[\left(\frac{\partial \mu}{\partial T} \right)_\rho - \frac{\mu_0}{T_0} \right] V$	
$\overline{\Delta E \Delta N} = -k T_0^2 \left(\frac{\partial \mu}{\partial \rho} \right)_T^{-1} \left[\left(\frac{\partial \mu}{\partial T} \right)_\rho - \frac{\mu_0}{T_0} \right] V$	$\overline{\Delta S \Delta p} = k T_0 \frac{s_0}{v_0}$
$\overline{(\Delta T)^2} = \frac{k T_0^2}{\rho_0 c_v V}$	$\overline{\Delta E \Delta T} = k T_0^2$
$\overline{(\Delta \mu)^2} = \frac{k T_0}{\rho_0 V} \left[\rho_0 \left(\frac{\partial \mu}{\partial \rho} \right)_T + \frac{T_0}{c_v} \left(\frac{\partial \mu}{\partial T} \right)_\rho^2 \right]$	$\overline{\Delta E \Delta \mu} = k T_0 \mu_0$
$\overline{\Delta T \Delta \mu} = \frac{k T_0^2}{\rho_0 c_v V} \left(\frac{\partial \mu}{\partial T} \right)_\rho$	$\overline{\Delta E \Delta p} = \frac{k T_0}{v_0} (\mu_0 + T_0 s_0)$
$\overline{(\Delta p)^2} = \frac{k T_0}{v_0^2 V} \left(\frac{\partial \mu}{\partial \rho} \right)_T + \frac{k T_0^2}{\rho_0 c_v v_0^2 V} \left[s_0 + \left(\frac{\partial \mu}{\partial T} \right)_\rho \right]^2$	$\overline{\Delta N \Delta p} = \frac{k T_0}{v_0}$
$\overline{\Delta p \Delta T} = \frac{k T_0^2}{\rho_0 c_v v_0 V} \left[s_0 + \left(\frac{\partial \mu}{\partial T} \right)_\rho \right]$	

- “Cross-fluctuations” between extensive and intensive properties are independent of the system size.

The first of these properties explains why we could neglect the quadratic terms in the expansion for the reservoir entropy, justifying the reservoir approximation (66) discussed in Section 9.1.

Knowing the fluctuations of the extensive and intensive parameters, density fluctuations can also be calculated. For example, knowing $\overline{(\Delta N)^2}$ in the μVT ensemble, we obtain the density fluctuation

$$\overline{(\Delta \rho)^2} = \frac{k T_0}{V} \left(\frac{\partial \mu}{\partial \rho} \right)_T^{-1}. \tag{160}$$

10. Finite-reservoir ensembles

10.1. General considerations

We now revisit the system coupled to a reservoir discussed in Section 9.1 (Fig. 4). The system and the reservoir are described by extensive parameters X_1, \dots, X_n and X_1^r, \dots, X_n^r , respectively, with fixed total amounts $\tilde{X}_i = X_i + X_i^r$. Suppose m of these parameters are allowed to flow back and forth between the system and the reservoir, whereas the remaining $(n - m)$ parameters are fixed. Both the system and the reservoir are assumed to be single-phase substances with different fundamental equations $S = S(X_1, \dots, X_n)$ and $S_r = S_r(X_1^r, \dots, X_n^r)$, respectively. The probability distribution of the fluctuating parameters of the system is given by Eq. (64), which is repeated here for convenience:

$$W(X_1, \dots, X_m) = W_m \exp \left[\frac{S(X_1, \dots, X_m) - S(X_1^0, \dots, X_m^0)}{k} \right] \\ \times \exp \left[\frac{S_r(\tilde{X}_1 - X_1, \dots, \tilde{X}_m - X_m) - S_r(\tilde{X}_1 - X_1^0, \dots, \tilde{X}_m - X_m^0)}{k} \right]. \quad (161)$$

In Section 9.1, the entropy of the reservoir was approximated by the linear expansion (66) at the equilibrium parameter set X_1^0, \dots, X_m^0 . This linear approximation was justified by the large size of the reservoir in comparison with the system. We will now lift this assumption and adopt a more general expansion, Eq. (65), which includes quadratic terms:

$$S_r(\tilde{X}_1 - X_1, \dots, \tilde{X}_m - X_m) - S_r(\tilde{X}_1 - X_1^0, \dots, \tilde{X}_m - X_m^0) = - \sum_{i=1}^m F_i^0 (X_i - X_i^0) \\ - \frac{1}{2} k \sum_{i,j=1}^m A_{ij}^r (X_i - X_i^0)(X_j - X_j^0), \quad (162)$$

where

$$A_{ij}^r \equiv - \frac{1}{k} \left(\frac{\partial^2 S_r}{\partial X_i^r \partial X_j^r} \right)_0 \quad (163)$$

is the stability matrix of the reservoir. As usual, the derivatives are taken at the equilibrium parameter set X_1^0, \dots, X_m^0 .

Before analyzing fluctuations, let us examine the micro-state probability distribution $P(X_1, \dots, X_m)$. Recall that the latter is obtained from $W(X_1, \dots, X_m)$ by dropping $S(X_1, \dots, X_m)$ in the first line of Eq. (161) [see Eq. (70) in Section 9.2]. Thus,

$$P = W_m \exp \left[\frac{-S(X_1^0, \dots, X_m^0) + S_r(\tilde{X}_1 - X_1, \dots, \tilde{X}_m - X_m) - S_r(\tilde{X}_1 - X_1^0, \dots, \tilde{X}_m - X_m^0)}{k} \right] \\ = A \exp \left[- \frac{1}{k} \sum_{i=1}^m F_i^0 X_i - \frac{1}{2} \sum_{i,j=1}^m A_{ij}^r (X_i - X_i^0)(X_j - X_j^0) \right], \quad (164)$$

where A is a constant that can be found from the probability normalization condition. Thus, in addition to the usual linear terms $F_i^0 X_i$ appearing in the generalized canonical distribution (72), we now have a quadratic form representing the effect of the finite reservoir on the micro-state probability of the system.

The matrix elements A_{ij}^r scale as $1/N_r$. When the size of the reservoir increases to infinity, the quadratic terms in Eq. (164) vanish and we return to the generalized canonical distribution (72). In the opposite limit when the reservoir becomes extremely small in comparison with our system, the probability distribution is dominated by the quadratic terms. The distribution becomes a very sharp Gaussian peak. Accordingly, all micro-states whose X_i are even slightly deviated from X_i^0 become extremely improbable. The system behaves as if isolated and Eq. (164) approaches the micro-canonical distribution. In other words, Eq. (164) interpolates between the generalized canonical and micro-canonical distributions; we can smoothly transition from one distribution to the other by varying the reservoir size and thus scaling the reservoir stability matrix (163).

We now return to the parameter distribution function $W(X_1, \dots, X_m)$ and expand the entropy of our system in a manner similar to Eq. (162):

$$S(X_1, \dots, X_m) - S(X_1^0, \dots, X_m^0) = \sum_{i=1}^m F_i^0 (X_i - X_i^0) - \frac{1}{2} k \sum_{i,j=1}^m A_{ij} (X_i - X_i^0)(X_j - X_j^0), \quad (165)$$

with the usual stability matrix

$$A_{ij} \equiv -\frac{1}{k} \left(\frac{\partial^2 S}{\partial X_i \partial X_j} \right)_0. \tag{166}$$

Inserting the expansions (162) and (165) in Eq. (161), we obtain the multi-variable Gaussian distribution

$$W(X_1, \dots, X_m) = W_m \exp \left[-\frac{1}{2} \sum_{i,j=1}^m \tilde{\Lambda}_{ij} (X_i - X_i^0)(X_j - X_j^0) \right], \tag{167}$$

with the stability matrix

$$\tilde{\Lambda}_{ij} = A_{ij} + \Lambda_{ij}^r. \tag{168}$$

We thus arrive at the remarkable result that the finite size of the reservoir does not change the Gaussian form of the parameter distribution of the system. However, the reservoir does contribute to the matrix elements of the Gaussian distribution in an additive manner. We can, therefore, easily compute the mean-square fluctuations and covariances of the parameters X_1, \dots, X_m using the known Eqs. (81) and (82) with A_{ij} replaced by the full stability matrix $\tilde{\Lambda}_{ij}$:

$$\overline{\Delta X_i \Delta X_j} = \tilde{\Lambda}_{ij}^{-1}, \quad i, j = 1, \dots, m, \tag{169}$$

$$\overline{(\Delta X_i)^2} = \tilde{\Lambda}_{ii}^{-1}, \quad i = 1, \dots, m. \tag{170}$$

A number of other interesting relations can be derived. It follows from Eqs. (162) and (165) that

$$F_i = \frac{\partial S}{\partial X_i} = F_i^0 - k \sum_{j=1}^m A_{ij} (X_j - X_j^0), \tag{171}$$

$$F_i^r = \frac{\partial S_r}{\partial X_i^r} = F_i^0 + k \sum_{j=1}^m \Lambda_{ij}^r (X_j - X_j^0). \tag{172}$$

Averaging these equations over the distribution and using the fact that for a Gaussian distribution $\overline{X_j} = X_j^0$, we obtain

$$\overline{F_i^r} = \overline{F_i} = F_i^0. \tag{173}$$

In other words, not only the most probable but also average values of the thermodynamic forces are the same in the system and in the reservoir. Furthermore, subtracting Eq. (171) from Eq. (172) we have

$$F_i^r - F_i = k \sum_{l=1}^m \tilde{\Lambda}_{il} (X_l - X_l^0). \tag{174}$$

Starting from this equation, we can generate a set of fluctuation relations involving the difference $(F_i^r - F_i)$. For example, multiplying Eq. (174) by ΔX_j and averaging over the parameter distribution, we have

$$\overline{(F_i^r - F_i) \Delta X_j} = k \delta_{ij}, \quad i, j = 1, \dots, m, \tag{175}$$

where we used Eq. (169). Likewise, multiplying Eq. (174) by $(F_j^r - F_j)$ and averaging over the distribution, we obtain

$$\overline{(F_i^r - F_i)(F_j^r - F_j)} = k^2 \tilde{\Lambda}_{ij}, \quad i, j = 1, \dots, m, \tag{176}$$

where we used Eq. (175). In particular,

$$\overline{(F_i^r - F_i)^2} = k^2 \tilde{\Lambda}_{ii}, \quad i = 1, \dots, m. \tag{177}$$

These equations describe fluctuations of the differences between the values of the intensive parameters inside our system and in the reservoir.

We can also compute fluctuations inside our system. To this end, we rewrite Eq. (171) as

$$\Delta F_i = -k \sum_{p=1}^m \Lambda_{ip} \Delta X_p. \quad (178)$$

Multiplying this equation by ΔX_j and averaging over the distribution, we obtain the covariances

$$\overline{\Delta F_i \Delta X_j} = -k \sum_{p=1}^m \Lambda_{ip} \tilde{\Lambda}_{pj}^{-1}, \quad i, j = 1, \dots, m. \quad (179)$$

Similarly, multiplying Eq. (178) by ΔF_j and averaging over the distribution, we have

$$\overline{\Delta F_i \Delta F_j} = k^2 \sum_{p,q=1}^m \Lambda_{ip} \Lambda_{pq} \tilde{\Lambda}_{qj}^{-1}, \quad i, j = 1, \dots, m, \quad (180)$$

$$\overline{(\Delta F_i)^2} = k^2 \sum_{p,q=1}^m \Lambda_{ip} \Lambda_{pq} \tilde{\Lambda}_{qi}^{-1}, \quad i = 1, \dots, m. \quad (181)$$

As expected, in the limit of an infinitely large reservoir when $\tilde{\Lambda}_{ij}$ becomes identical to Λ_{ij} , Eqs. (179), (180) and (181) reduce to Eqs. (85), (86) and (87) for the generalized canonical ensemble.

10.2. Application to a simple fluid

To demonstrate the finite-ensemble formalism, consider a fixed volume V of a simple fluid embedded in another (generally, different) simple fluid serving as a reservoir. This situation was already discussed in Section 9.5.3 in the context of the grand-canonical ensemble. This time, however, the reservoir will be treated as an infinite source of heat (thermostat) but a *finite* source of particles. We thus have two fluctuating extensive properties, $X_1 = E$ and $X_2 = N$, with the conjugate thermodynamic forces $F_1 = 1/T$ and $F_2 = -\mu/T$.

Because the reservoir has an infinite heat capacity, we have $\Lambda_{11}^r = 0$. Assuming for simplicity that the chemical potential of the reservoir μ_r is temperature-independent, we additionally have $\Lambda_{12}^r = \Lambda_{21}^r = 0$. Thus, the reservoir stability matrix is

$$\Lambda_{ij}^r = \begin{pmatrix} 0 & 0 \\ 0 & \Lambda_{22}^r \end{pmatrix} \quad (182)$$

with a single nonzero parameter Λ_{22}^r .

The micro-state probability distribution for our system can be found from Eq. (164):

$$P = A \exp \left[-\frac{E - \mu_0 N}{kT_0} - \frac{1}{2} \Lambda_{22}^r (N - N_0)^2 \right]. \quad (183)$$

As a side note, a similar equation can be obtained for a closed system coupled to a thermostat with a finite heat capacity. In this case, the role of the number of particles is played by the energy, so that the additional term contributed by the thermostat is quadratic in $(E - E_0)$:

$$P = A \exp \left[-\frac{E}{kT_0} - \frac{1}{2} \Lambda_{11}^r (E - E_0)^2 \right]. \quad (184)$$

This situation is known in the literature as the Gaussian ensemble [51,54]. By analogy, formula (183) can also be referred to as the Gaussian ensemble distribution.

Eq. (183) can be rewritten in the form

$$P = A \exp \left(-\frac{E - \hat{\mu}N}{kT_0} \right), \quad (185)$$

where

$$\hat{\mu} \equiv a - bN \quad (186)$$

with

$$a = \mu_0 + \Lambda_{22}^r kT_0 N_0, \quad (187)$$

$$b = \frac{1}{2} \Lambda_{22}^r kT_0. \quad (188)$$

Eq. (185) looks similar to the grand-canonical distribution, except that the fixed chemical potential of the reservoir μ_0 is replaced an “effective” chemical potential $\hat{\mu}$ linearly dependent on the current number of particles N . In the limit of $\Lambda_{22}^r \rightarrow 0$ (infinitely large reservoir), this dependence disappears and we return to the standard grand-canonical distribution with the chemical potential μ_0 .

Eq. (185)–(188) can be implemented in Monte Carlo computer simulations using an algorithm similar to that of the grand-canonical ensemble [1] but with a chemical potential adjustable “on the fly”. For binary mixtures, this approach was implemented in the semi-grand canonical mode as “variance-constrained” Monte Carlo [58,59]. A similar semi-grand canonical Monte Carlo method, called feedback Monte Carlo, was recently employed for interface free energy calculations by the capillary fluctuation approach [21]. Related Monte Carlo algorithms were earlier developed for closed systems coupled to a finite-capacity thermostat. The initially proposed “dynamical ensemble” method [68] developed for such systems later evolved into more sophisticated and computationally more efficient iterative Monte Carlo schemes based on Eq. (184) [56,57].

We now return to the analysis of fluctuations. To simplify the calculations, we will neglect the temperature dependence of the chemical potential, treating it solely as a function of the particle density ρ . Following the calculation methods presented in Section 9.5, it is easy to obtain the stability matrix of the fluid in the entropy scheme,

$$\Lambda_{ij} = \frac{1}{\rho_0 c_v kT_0^2 V} \begin{pmatrix} 1 & -\mu_0 \\ -\mu_0 & \rho_0 c_v T_0 \left(\frac{\partial \mu}{\partial \rho} \right)_T + \mu_0^2 \end{pmatrix} \quad (189)$$

and its inverse

$$\Lambda_{ij}^{-1} = kT_0 V \begin{pmatrix} \left(\frac{\partial \mu}{\partial \rho} \right)_T^{-1} & \mu_0 \\ \mu_0 & 1 \end{pmatrix} \begin{pmatrix} \rho_0 c_v T_0 \left(\frac{\partial \mu}{\partial \rho} \right)_T + \mu_0^2 & \\ & \mu_0 \end{pmatrix}. \quad (190)$$

Accordingly,

$$\tilde{\Lambda}_{ij} = \frac{1}{\rho_0 c_v kT_0^2 V} \begin{pmatrix} 1 & -\mu_0 \\ -\mu_0 & \rho_0 c_v T_0 \left(\frac{\partial \mu}{\partial \rho} \right)_T + \mu_0^2 + \rho_0 c_v kT_0^2 \Lambda_{22}^r V \end{pmatrix} \quad (191)$$

and

$$\tilde{\Lambda}_{ij}^{-1} = \frac{kT_0 V}{\left(\frac{\partial \mu}{\partial \rho} \right)_T + kT_0 V \Lambda_{22}^r} \begin{pmatrix} \rho_0 c_v T_0 \left(\frac{\partial \mu}{\partial \rho} \right)_T + \mu_0^2 + \rho_0 c_v kT_0^2 \Lambda_{22}^r V & \mu_0 \\ \mu_0 & 1 \end{pmatrix}. \quad (192)$$

We can now compute the mean-square fluctuations of the energy and the number of particles:

$$\overline{(\Delta E)^2} = \tilde{\Lambda}_{11}^{-1} = \frac{\rho_0 c_v kT_0^2 V \left(\frac{\partial \mu}{\partial \rho} \right)_T + kT_0 V (\mu_0^2 + \rho_0 c_v kT_0^2 \Lambda_{22}^r V)}{\left(\frac{\partial \mu}{\partial \rho} \right)_T + kT_0 V \Lambda_{22}^r}, \quad (193)$$

$$\overline{(\Delta N)^2} = \tilde{\Lambda}_{22}^{-1} = \frac{kT_0 V}{\left(\frac{\partial \mu}{\partial \rho} \right)_T + kT_0 V \Lambda_{22}^r}. \quad (194)$$

Similarly, for the covariance $\overline{\Delta E \Delta N}$ we have

$$\overline{\Delta E \Delta N} = \tilde{\Lambda}_{12}^{-1} = \frac{kT_0 \mu_0 V}{\left(\frac{\partial \mu}{\partial \rho}\right)_T + kT_0 V \Lambda_{22}^r}. \quad (195)$$

Fluctuations of the chemical potential could be found directly from Eq. (181). Instead, we will take a shortcut by taking advantage of the fact that $\mu = \mu(\rho)$ and therefore

$$\Delta \mu = \left(\frac{\partial \mu}{\partial \rho}\right)_T \frac{\Delta N}{V}. \quad (196)$$

Taking a square of this equation and averaging over the distribution, we obtain

$$\overline{(\Delta \mu)^2} = \left(\frac{\partial \mu}{\partial \rho}\right)_T^2 \frac{\overline{(\Delta N)^2}}{V^2} = \frac{\frac{kT_0}{V} \left(\frac{\partial \mu}{\partial \rho}\right)_T^2}{\left(\frac{\partial \mu}{\partial \rho}\right)_T + kT_0 V \Lambda_{22}^r}, \quad (197)$$

where we used Eq. (194). Applying the same method,

$$\overline{\Delta \mu \Delta N} = \left(\frac{\partial \mu}{\partial \rho}\right)_T \frac{\overline{(\Delta N)^2}}{V} = \frac{kT_0 \left(\frac{\partial \mu}{\partial \rho}\right)_T}{\left(\frac{\partial \mu}{\partial \rho}\right)_T + kT_0 V \Lambda_{22}^r}, \quad (198)$$

$$\overline{\Delta \mu \Delta E} = \left(\frac{\partial \mu}{\partial \rho}\right)_T \frac{\overline{\Delta E \Delta N}}{V} = \frac{\mu_0 kT_0 \left(\frac{\partial \mu}{\partial \rho}\right)_T}{\left(\frac{\partial \mu}{\partial \rho}\right)_T + kT_0 V \Lambda_{22}^r}. \quad (199)$$

Continuing along this line, all other covariances can be readily calculated.

Consider limiting cases of the above relations. When $\Lambda_{22}^r \rightarrow 0$ (the reservoir is an infinite source of particles), we exactly recover all results for the grand-canonical ensemble listed in Table 3. When $\Lambda_{22}^r \rightarrow \infty$ (the reservoir cannot supply or absorb particles), the system behaves as virtually closed (NVT). Accordingly, the energy fluctuation (193) reduces to

$$\overline{(\Delta E)^2} = \rho_0 kT_0^2 c_v V \quad (200)$$

in agreement with the NVT result (Table 1). All other mean-square fluctuations and covariances appearing in Eqs. (194)–(199) tend to zero as $1/\Lambda_{22}^r$. As evident from Table 1, in the NVT ensemble they are proportional to $(\partial \mu / \partial T)_\rho$ and thus generally not zero. In the present calculations, they vanished because we neglected the temperature dependence of μ for the sake of simplicity. More accurate but rather tedious calculations taking into account the temperature dependence of μ exactly recover the fluctuation relations from Table 1 when $\Lambda_{22}^r \rightarrow \infty$.

It is interesting to note that at the limit of normal thermodynamic stability when $(\partial \mu / \partial \rho)_T \rightarrow 0$, the canonical fluctuation $\overline{(\Delta N)^2}$ diverges to infinity (Table 3). However, when the system is coupled to a finite-size reservoir with a positive coefficient $\Lambda_{22}^r > 0$, the latter stabilizes the fluid and its compositional fluctuations remain finite and equal to $1/\Lambda_{22}^r$, see Eq. (194). The finite size of the reservoir smooths the singularity.

11. Fluctuations of grain boundary properties

GBs are interfaces separating regions of the same crystalline solid phase (called grains) with different crystallographic orientations. GBs can strongly impact physical and mechanical properties of crystalline materials, especially in nano-structured systems. While thermodynamics and kinetics of GBs has been studied extensively for several decades [69], it is only recently that fluctuations of GB properties have become the subject of dedicated research, primarily by atomistic computer simulations [15–22].

In preparation for the discussion of GB fluctuations, we will give a brief account of GB thermodynamics focusing on a plane GB in a binary substitutional solid solution.

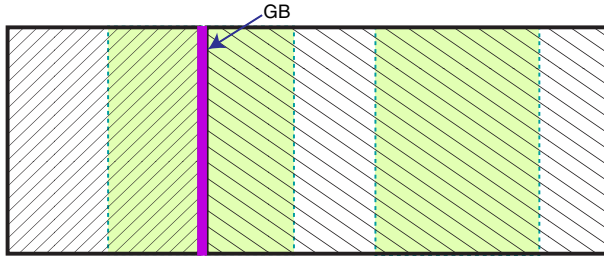


Fig. 5. Two grains with different crystallographic orientations separated by a plane grain boundary (GB). The shaded areas bounded by dashed lines mark a region containing the GB and a comparison region inside one of the grains containing the same total number of atoms. These two regions are selected for calculations of GB excess quantities.

11.1. Grain boundary thermodynamics

Consider a bicrystal (i.e., a system of two grains) enclosed in a rectangular box with rigid impermeable walls (Fig. 5). Since the system is closed, the total number of particles N is fixed. We will assume that the grains possess appropriate crystallographic symmetries such that the mechanical stresses existing in the bicrystal do not create a difference in strain energy densities in the grains that would cause GB migration.

Before discussing GB thermodynamics, we will first specify thermodynamic properties of the homogeneous single-crystalline solid solution forming the grains. We postulate the following fundamental equation of this solution in the energy representation¹⁶:

$$E_g = E_g(S_g, V_g, N_s^g, N_2^g). \quad (201)$$

Here, the suffix g indicates that the properties refer to a region in one of the grains, such as the shaded layer shown in Fig. 5, N_2^g is the number of atoms of species 2 and N_s^g is the number of lattice sites in the region. Vacancies are neglected, so that the number of atoms of species 1 is $N_1^g = N_s^g - N_2^g$. The differential of Eq. (201) is

$$dE_g = TdS_g - pdV_g + \varphi dN_s^g + Mn_2^g, \quad (202)$$

where $T = \partial E_g / \partial S_g$ is temperature, $p = -\partial E_g / \partial V_g$ is pressure (negative of the stress component normal to the GB plane), $M = \partial E_g / \partial N_2^g$ is the diffusion potential of species 2 relative to species 1 [72–74], and $\varphi = \partial E_g / \partial N_s^g$ is a thermodynamic potential conjugate to the number of sites N_s^g . On the other hand, the energy defined by Eq. (201) is a homogeneous function of first degree in all four arguments. Using the Euler theorem for homogeneous functions [75] we have

$$E_g = TE_g - pV_g + \varphi N_s^g + MN_2^g. \quad (203)$$

Combining Eqs. (202) and (203) we obtain the Gibbs–Duhem equation

$$-S_g dT + V_g dp - N_s^g d\varphi - N_2^g dM = 0. \quad (204)$$

To develop GB thermodynamics, we define the GB excess of any extensive property X by

$$\tilde{X} \equiv X - X_g, \quad (205)$$

where X is the value of the property for a bicrystalline layer containing the GB and X_g is the value of the same property for a homogeneous grain layer containing the same total number of atoms. Examples

¹⁶ Generally, the fundamental equation of a stressed solid depends on the deformation gradient relative to a chosen reference state [25,70,71]. In the particular case considered here, the cross-section of the solid is fixed and only deformation in the normal direction is permitted. Under such conditions, only the normal component of the deformation gradient is relevant and varies as a linear function of the volume. It is convenient to represent this component by the volume itself.

of such layers are shown by shaded regions in Fig. 5. The choice of these layers is totally arbitrary and does not affect \tilde{X} as long as their boundaries are unaffected by the GB or the walls. According to this definition of excess, a bicrystalline layer can be thought of as composed of two subsystems: (1) the reference grain layer containing the same total number of atoms and (2) the excess system representing the GB and described by the excess properties $\tilde{S}, \tilde{E}, \tilde{V}$, etc.

Just as the grain thermodynamics has been formulated above starting from a postulated fundamental equation (201), we will postulate a fundamental equation of the GB in the form

$$\tilde{E} = \tilde{E}(\tilde{S}, \tilde{V}, \tilde{N}_2, A). \quad (206)$$

Note that \tilde{N}_1 is not an independent variable because

$$\tilde{N}_1 + \tilde{N}_2 = 0 \quad (207)$$

by our definition of excesses. The excess energy (206) is a homogeneous function of first degree in all four arguments. Applying the Euler theorem [75] we have

$$\tilde{E} = \frac{\partial \tilde{E}}{\partial \tilde{S}} \tilde{S} + \frac{\partial \tilde{E}}{\partial \tilde{V}} \tilde{V} + \frac{\partial \tilde{E}}{\partial \tilde{N}_2} \tilde{N}_2 + \frac{\partial \tilde{E}}{\partial A} A. \quad (208)$$

On the other hand, the differential of Eq. (206) is

$$d\tilde{E} = \frac{\partial \tilde{E}}{\partial \tilde{S}} d\tilde{S} + \frac{\partial \tilde{E}}{\partial \tilde{V}} d\tilde{V} + \frac{\partial \tilde{E}}{\partial \tilde{N}_2} d\tilde{N}_2 + \frac{\partial \tilde{E}}{\partial A} dA. \quad (209)$$

Combining Eqs. (208) and (209) we obtain the GB version of the Gibbs–Duhem equation:

$$\tilde{S} d\frac{\partial \tilde{E}}{\partial \tilde{S}} + \tilde{V} d\frac{\partial \tilde{E}}{\partial \tilde{V}} + \tilde{N}_2 d\frac{\partial \tilde{E}}{\partial \tilde{N}_2} + A d\frac{\partial \tilde{E}}{\partial A} = 0. \quad (210)$$

Next, we find the conditions of thermodynamic equilibrium between the GB and the grains. To this end, we consider a variation of the total energy ($\tilde{E} + E_g$) of a bicrystalline layer at a fixed composition, volume and entropy. In equilibrium, this variation ($d\tilde{E} + dE_g$) must be zero [25]. Here, dE_g is given by Eq. (202) and $d\tilde{E}$ by Eq. (209). The variation is subject to the following constraints:

$$d\tilde{N}_1 + dN_1^g = 0, \quad (211)$$

$$d\tilde{N}_2 + dN_2^g = 0, \quad (212)$$

$$d\tilde{V} + dV_g = 0, \quad (213)$$

$$d\tilde{S} + dS_g = 0, \quad (214)$$

as well as $dA = 0$. Furthermore, by adding Eqs. (211) and (212) and taking into account Eq. (207), it follows that the number of sites in the reference grain region is conserved: $dN_3^g = dN_1^g + dN_2^g = 0$. Inserting these constraints into the total energy variation, we arrive at the equilibrium condition

$$\left(\frac{\partial \tilde{E}}{\partial \tilde{S}} - T \right) d\tilde{S} + \left(\frac{\partial \tilde{E}}{\partial \tilde{V}} + p \right) d\tilde{V} + \left(\frac{\partial \tilde{E}}{\partial \tilde{N}_2} - M \right) d\tilde{N}_2 = 0. \quad (215)$$

Because the variations $d\tilde{S}$, $d\tilde{V}$ and $d\tilde{N}_2$ are independent and can be positive or negative, the coefficients multiplying them must be zero. We thus obtain the equilibrium values of the derivatives of \tilde{E} :

$$\left(\frac{\partial \tilde{E}}{\partial \tilde{S}} \right)_0 = T_0, \quad (216)$$

$$\left(\frac{\partial \tilde{E}}{\partial \tilde{N}_2}\right)_0 = M_0, \quad (217)$$

$$\left(\frac{\partial \tilde{E}}{\partial \tilde{V}}\right)_0 = -p_0. \quad (218)$$

As usual, the subscript 0 labels the equilibrium state.

The remaining derivative

$$\gamma_0 \equiv \left(\frac{\partial \tilde{E}}{\partial A}\right)_0 \quad (219)$$

is called the equilibrium GB free energy. The precise thermodynamic meaning of this property will be discussed later.

11.2. Quasi-equilibrium grain boundary states

So far, we have only specified the derivatives of \tilde{E} with respect to \tilde{S} , \tilde{N}_2 , \tilde{V} and A for equilibrium states of the system. Namely, such derivatives are equal to the equilibrium temperature, diffusion potential, negative of pressure in the grains and the equilibrium GB free energy, respectively. For the analysis of GB fluctuations, we must consider these derivatives without assuming equilibrium between the GB and the grains. Such derivatives form a new set of variables T , p , M and γ defined as follows:

$$\frac{\partial \tilde{E}}{\partial \tilde{S}} \equiv T, \quad (220)$$

$$\frac{\partial \tilde{E}}{\partial \tilde{N}_2} \equiv M, \quad (221)$$

$$\frac{\partial \tilde{E}}{\partial \tilde{V}} \equiv -p, \quad (222)$$

$$\frac{\partial \tilde{E}}{\partial A} \equiv \gamma. \quad (223)$$

These new variables can be interpreted as, respectively, the local temperature, negative of local pressure, local diffusion potential and the GB free energy when the GB is *not* in equilibrium with the grains. Indeed, by postulating the fundamental equation (206) we implicitly assumed that the GB follows this equation even in the absence of equilibrium with the grains. One can think of such GB states as being disconnected from the actual grains and equilibrated with imaginary grains with a different set of intensive parameters T , M and p . In terms of the variables (220)–(223), the differential form of the fundamental equation (206) becomes

$$d\tilde{E} = Td\tilde{S} - pd\tilde{V} + Md\tilde{N}_2 + \gamma dA. \quad (224)$$

The existence of quasi-equilibrium states in which the GB obeys a fundamental equation without being in equilibrium with the grains is an important supposition of the interface fluctuation theory. As discussed in Sections 4 and 5, the entire thermodynamic theory of equilibrium fluctuations is built on the assumption that all fluctuated states are states of quasi-equilibrium. The theory discussed here is an application of this principle to GBs.

Suppose the bicrystal has been initially equilibrated and then the GB deviates from this initial equilibrium to a nearby quasi-equilibrium state where it is no longer in equilibrium with the grains.

Denoting the equilibrium excess entropy, volume and number of atoms \tilde{S}_0 , \tilde{V}_0 and \tilde{N}_2^0 , respectively, the Gibbs–Duhem Eq. (210) for this variations becomes

$$\tilde{S}_0 d\frac{\partial\tilde{E}}{\partial\tilde{S}} + \tilde{V}_0 d\frac{\partial\tilde{E}}{\partial\tilde{V}} + \tilde{N}_2^0 d\frac{\partial\tilde{E}}{\partial\tilde{N}_2} + Ad\frac{\partial\tilde{E}}{\partial A} = \tilde{S}_0 dT - \tilde{V}_0 dp + \tilde{N}_2^0 dM + Ad\gamma = 0. \quad (225)$$

This equation can be rewritten in the form

$$d\gamma = -\frac{\tilde{S}_0}{A} dT + \frac{\tilde{V}_0}{A} dp - \frac{\tilde{N}_2^0}{A} dM, \quad (226)$$

which will be used later.

In the particular case when the states of the grains also vary in such a manner that the entire system undergoes an equilibrium process, Eq. (226) becomes

$$d\gamma_0 = -\frac{\tilde{S}_0}{A} dT_0 + \frac{\tilde{V}_0}{A} dp_0 - \frac{\tilde{N}_2^0}{A} dM_0. \quad (227)$$

This is one of the forms of the Gibbs adsorption equation for a fixed GB area. This equilibrium equation should not be confused with Eq. (226) describing fluctuations in which the GB deviates from equilibrium with the grains.

We can now understand the meaning of the parameter γ . Let us rewrite Eq. (208) in the form

$$\tilde{E} = T\tilde{S} - p\tilde{V} + M\tilde{N}_2 + \gamma A, \quad (228)$$

from which

$$\gamma = \frac{\tilde{E} - T\tilde{S} + p\tilde{V} - M\tilde{N}_2}{A}. \quad (229)$$

As was shown by Gibbs [25], an expression of the form $E - TS + pV - \sum_i \mu_i N_i$ is the reversible work required for the creation of a new system with extensive properties E , S , V and N_i by drawing the energy and matter from an infinite reservoir with a temperature T , pressure p and chemical potentials μ_i . Thus, the numerator in Eq. (229) can be interpreted as the reversible work of GB formation from an imaginary infinite reservoir with the intensive parameters T , p and M . In the present case, the term $\mu_1 \tilde{N}_1 + \mu_2 \tilde{N}_2$ reduces to $M\tilde{N}_2$ due to the constraint imposed by Eq. (207). In short, γ is the reversible work of GB formation per unit area. Accordingly, the equilibrium GB free energy γ_0 is the reversible work of GB formation per unit area from a reservoir with the same intensive parameters T_0 , p_0 and M_0 as in the actual grains:

$$\gamma_0 = \frac{\tilde{E} - T_0\tilde{S} + p_0\tilde{V} - M_0\tilde{N}_2}{A}. \quad (230)$$

In other words, this is the reversible work of GB formation between two infinitely large grains.

11.3. Grain boundary fluctuations

We are now in a position to analyze GB fluctuations. We will compute generalized canonical fluctuations of GB properties treating the grains as an infinite reservoir coupled to the GB. Although the foregoing discussion utilized the energy scheme, the latter is impractical for GB fluctuations.¹⁷ Instead, we will now switch to the entropy scheme in which the independent additive invariants fluctuating between the GB and the grains are $X_1 = \tilde{E}$, $X_2 = \tilde{V}$ and $X_3 = \tilde{N}_2$. The conjugate thermodynamic forces

¹⁷ The energy scheme involves fluctuations of the excess entropy \tilde{S} , which is not accessible by experiments or atomistic simulations. In the entropy scheme, \tilde{S} is replaced by the more accessible excess energy \tilde{E} .

are readily found from Eq. (224): $F_1 = 1/T$, $F_2 = p/T$ and $F_3 = -M/T$. We can also rewrite Eq. (226) in terms of the new variables:

$$d\gamma = \sum_{i=1}^3 B_i dF_i, \tag{231}$$

with the coefficients

$$B_1 \equiv \frac{T_0(\tilde{E}_0 - \gamma_0 A)}{A}, \tag{232}$$

$$B_2 \equiv \frac{T_0 \tilde{V}_0}{A}, \tag{233}$$

$$B_3 \equiv -\frac{T_0 \tilde{N}_2^0}{A}. \tag{234}$$

In the Gaussian approximation to fluctuations, the distribution of the excess parameters X_i is given by Eq. (79) with the stability matrix

$$A_{ij} = -\frac{1}{k} \begin{pmatrix} \left(\frac{\partial^2 \tilde{S}}{\partial \tilde{E}^2} \right)_0 & \left(\frac{\partial^2 \tilde{S}}{\partial \tilde{E} \partial \tilde{V}} \right)_0 & \left(\frac{\partial^2 \tilde{S}}{\partial \tilde{E} \partial \tilde{N}_2} \right)_0 \\ \left(\frac{\partial^2 \tilde{S}}{\partial \tilde{E} \partial \tilde{V}} \right)_0 & \left(\frac{\partial^2 \tilde{S}}{\partial \tilde{V}^2} \right)_0 & \left(\frac{\partial^2 \tilde{S}}{\partial \tilde{V} \partial \tilde{N}_2} \right)_0 \\ \left(\frac{\partial^2 \tilde{S}}{\partial \tilde{E} \partial \tilde{N}_2} \right)_0 & \left(\frac{\partial^2 \tilde{S}}{\partial \tilde{V} \partial \tilde{N}_2} \right)_0 & \left(\frac{\partial^2 \tilde{S}}{\partial \tilde{N}_2^2} \right)_0 \end{pmatrix}. \tag{235}$$

The elements of this matrix represent equilibrium excess properties of the GB. For example,

$$\left(\frac{\partial^2 \tilde{S}}{\partial \tilde{E}^2} \right)_0 = \left(\frac{\partial}{\partial \tilde{E}} \left(\frac{1}{T} \right) \right)_0 = -\frac{1}{T_0^2 A \tilde{c}_v}, \tag{236}$$

where

$$\tilde{c}_v \equiv \frac{1}{A} \left(\frac{\partial \tilde{E}}{\partial T} \right)_0 \tag{237}$$

is the GB heat capacity (more accurately, the excess heat capacity per unit GB area computed at fixed \tilde{V}/A and \tilde{N}_2/A). Similarly,

$$\left(\frac{\partial^2 \tilde{S}}{\partial \tilde{V}^2} \right)_0 = \left(\frac{\partial}{\partial \tilde{V}} \left(\frac{p}{T} \right) \right)_0 = -\frac{1}{T_0 \tilde{V}_0 \tilde{\kappa}_T} - \frac{p_0}{T_0^2 \tilde{V}_0 \tilde{\alpha}}, \tag{238}$$

where

$$\tilde{\kappa}_T \equiv -\frac{1}{\tilde{V}_0} \left(\frac{\partial \tilde{V}}{\partial p} \right)_0 \tag{239}$$

is the isothermal compressibility of the GB and

$$\tilde{\alpha} \equiv \frac{1}{\tilde{V}_0} \left(\frac{\partial \tilde{V}}{\partial T} \right)_0 \tag{240}$$

is the GB thermal expansion coefficient.

Equilibrium GB properties can be computed directly by atomistic simulations. For example, $\tilde{\kappa}_T$ can be found by computing the excess GB volume as a function of pressure at a fixed temperature followed by numerical differentiation [76]. However, analysis of GB fluctuations offers a more efficient approach in which the entire set of equilibrium GB properties can be extracted from a single simulation run using fluctuation relations. Indeed, the excess properties \tilde{E} , \tilde{V} and \tilde{N}_2 are readily accessible by atomistic simulations. By computing their covariances, the inverse stability matrix can be found from the fluctuation relation

$$\overline{\Delta X_i \Delta X_j} = \Lambda_{ij}^{-1}, \quad i, j = 1, 2, 3. \quad (241)$$

The latter can be then inverted to obtain the stability matrix Λ_{ij} and thus the equilibrium GB properties such as \tilde{c}_v , $\tilde{\kappa}_T$, $\tilde{\alpha}$, etc. Furthermore, knowing the stability matrix, fluctuations of thermodynamic forces can be predicted from the fluctuation relations

$$\overline{\Delta F_i \Delta F_j} = k^2 \Lambda_{ij}, \quad i, j = 1, \dots, 3. \quad (242)$$

Knowing these covariances, straightforward algebraic manipulations can be applied to find $\overline{(\Delta M)^2}$, $\overline{(\Delta T)^2}$ and $\overline{(\Delta p)^2}$, as well as the covariances $\overline{\Delta M \Delta T}$, $\overline{\Delta M \Delta p}$ and $\overline{\Delta p \Delta T}$. As a general rule,

$$\overline{\Delta P_i \Delta P_j} = \sum_{m,n=1}^3 k^2 \left(\frac{\partial P_i}{\partial F_m} \right)_0 \left(\frac{\partial P_j}{\partial F_n} \right)_0 \Lambda_{nm}, \quad i, j = 1, \dots, 3, \quad (243)$$

where the transformation matrix $\partial P_i / \partial F_m$ is

$$\left(\frac{\partial P_i}{\partial F_m} \right)_0 = \begin{pmatrix} -T_0^2 & p_0 T_0 & -M_0 T_0 \\ 0 & -T_0 & 0 \\ 0 & 0 & -T_0 \end{pmatrix}. \quad (244)$$

To our knowledge, the proposed calculation scheme has not been implemented.

As an interesting application, one can predict the equilibrium mean-square fluctuation $\overline{(\Delta \gamma)^2}$ of the GB free energy, where $\Delta \gamma \equiv \gamma - \gamma_0$. The fluctuation form of Eq. (231) is

$$\Delta \gamma = \sum_{i=1}^3 B_i \Delta F_i. \quad (245)$$

Taking a square of this equation and averaging over the distribution, we obtain

$$\overline{(\Delta \gamma)^2} = \sum_{i,j=1}^3 B_i B_j \overline{\Delta F_i \Delta F_j}. \quad (246)$$

Applying Eq. (242) for $\overline{\Delta F_i \Delta F_j}$, this equation finally becomes

$$\overline{(\Delta \gamma)^2} = k^2 \sum_{i,j=1}^3 B_i B_j \Lambda_{ij}. \quad (247)$$

This calculation requires the knowledge of Λ_{ij} and the equilibrium values of the excess GB energy, volume and segregation as ingredients for the parameters B_i . The GB free energy is usually treated as a static property. An estimate of its fluctuation $\overline{(\Delta \gamma)^2}$ would provide a critical assessment of this approximation.

12. Fluctuations in pre-melted grain boundaries

In this section we address another fluctuation topic associated with GBs. At high temperatures approaching the melting point of the solid, many GBs become atomically disordered and can develop a liquid-like structure reminiscent of a thin liquid film [69]. Our goal is to describe equilibrium thermodynamic properties of this film and derive the distribution function of its width. The analysis is based on the sharp interface model of pre-melting (Fig. 6). The grains are formed by the same binary solid solution phase as discussed in Section 11.

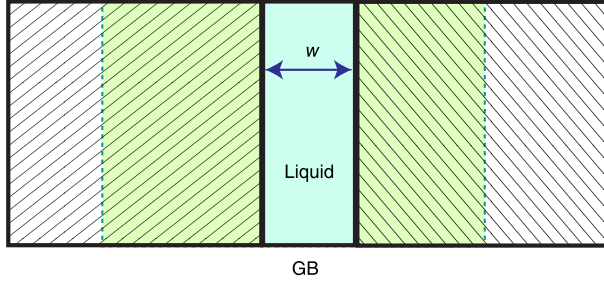


Fig. 6. Sharp interface model of GB pre-melting. The pre-melted GB is modeled by a liquid layer of a width w bounded by two sharp interfaces endowed with thermodynamic properties of actual solid–liquid interfaces between bulk phases.

12.1. Thermodynamic background

12.1.1. Equilibrium state of pre-melted grain boundary

We will consider the same bicrystal in a rigid box as discussed in Section 11, but this time we will adopt a particular model of GB structure, namely, a liquid layer of a certain width w bounded by two solid–liquid interfaces (Fig. 6). We start by describing equilibrium thermodynamic properties of this boundary.

As in Section 11, thermodynamic properties of the solid solution forming the grains are fully described by the fundamental equation (201) in the energy representation. The binary liquid solution (index L) is described by its own fundamental equation

$$E_L = E_L(S_L, V_L, N_1^L, N_2^L) \quad (248)$$

with the differential form

$$dE_L = T_L dS_L - p_L dV_L + \mu_1 dN_1^L + \mu_2 dN_2^L. \quad (249)$$

Here, T_L and p_L are the temperature and pressure of the liquid and μ_1 and μ_2 are the chemical potentials of the components.

To describe thermodynamics of the solid–liquid interfaces bounding the liquid layer, we will first take a detour and consider a single plane interface between the bulk solid and liquid phases. We can choose an arbitrary geometric dividing surface partitioning our system in two parts with volumes V_g and V_L . We then compute the excess of any extensive property X by

$$\tilde{X} = X - X_g - X_L, \quad (250)$$

where X is the value of the property for the solid–liquid system with a volume ($V_g + V_L$) and X_g and X_L are properties of the phases computed as if the volumes V_g and V_L remained homogeneous all the way to the dividing surface [25]. By this definition, $\tilde{V} = 0$. Because the densities of all properties are generally different on either side of the interface, the excess defined by Eq. (250) depends on the exact position of the dividing surface within the interface region. We will adopt the rule by which we always place the dividing surface in such a manner that the excess of the total number of atoms N vanishes: $\tilde{N} = 0$. The fundamental equation of the solid–liquid interface is formulated in the form

$$\tilde{E} = \tilde{E}(\tilde{S}, \tilde{N}_2, A), \quad (251)$$

with the differential form

$$d\tilde{E} = \frac{\partial \tilde{E}}{\partial \tilde{S}} d\tilde{S} + \frac{\partial \tilde{E}}{\partial \tilde{N}_2} d\tilde{N}_2 + \frac{\partial \tilde{E}}{\partial A} dA. \quad (252)$$

Returning to the pre-melted GB modeled by a thin layer of the liquid phase (Fig. 6), we will assume that the solid–liquid interfaces bounding this layer follow the same fundamental Eq. (251)

as if they were interfaces between two bulk phases. This is, of course, an approximation. In reality, the liquid layer width is on the order of a nanometer and its thermodynamic properties in this narrow confinement are different from properties of bulk liquid. In addition, the solid–liquid interfaces separated by such a short distance can interact with each other due to their finite thickness comparable with the width of the layer. The difference between the actual GB structure and this highly idealized liquid-layer structure is accounted for by introducing an interaction between the two solid–liquid interfaces called the “disjoining” interaction. The disjoining interaction (index d) is included in the model by adding an extra energy term E_d and an associated entropy S_d , and postulating the following fundamental equation of the disjoining interaction:

$$E_d = E_d(S_d, V_L). \quad (253)$$

The dependence on V_L has been added to make the disjoining interaction a function of the distance between the solid–liquid interfaces, which for a fixed cross-section considered here, is proportional to V_L . Both E_d and S_d are proportional to the GB area and have the same dimensions as the excess quantities \tilde{E} and \tilde{S} , respectively. Both E_d and S_d tend to zero if the width of the liquid layer increases to infinity (bulk solid–liquid system).

To summarize the model, the GB is represented by a homogeneous liquid layer separated from the grains by two geometrically sharp solid–liquid interfaces to which we assign thermodynamic properties of actual solid–liquid interfaces between bulk phases (Fig. 6). These sharp interfaces coincide with the dividing surfaces separated by a distance w and interact with each other by disjoining forces that follow the fundamental equation (253).

We will next derive the conditions of thermodynamic equilibrium by considering a variation of state of a bicrystalline layer indicated in Fig. 6 by a shaded region with dashed boundaries. During this variation, the layer remains isolated from the rest of the system and keeps a constant value of its entropy. Under these constraints, the variation of the total energy

$$\hat{E} = E_g + E_L + \tilde{E} + E_d \quad (254)$$

must be zero [25]. The terms of this equation are represented by the fundamental equations (201), (248), (251) and (253), respectively. Accordingly,

$$\begin{aligned} d\hat{E} = & TdS_g - p_g dV_g + \varphi dN_s^g + MdN_2^g + T_L dS_L - p_L dV_L + \mu_1 dN_1^L + \mu_2 dN_2^L \\ & + \frac{\partial \tilde{E}}{\partial \tilde{S}} d\tilde{S} + \frac{\partial \tilde{E}}{\partial \tilde{N}_2} d\tilde{N}_2 + \frac{\partial \tilde{E}}{\partial A} dA + \frac{\partial E_d}{\partial S_d} dS_d + \frac{\partial E_d}{\partial V_L} dV_L = 0 \end{aligned} \quad (255)$$

subject to the following constraints:

$$dS_g + dS_L + d\tilde{S} + dS_d = 0, \quad (256)$$

$$dV_g + dV_L = 0, \quad (257)$$

$$dN_1^g + dN_1^L + d\tilde{N}_1 = 0, \quad (258)$$

$$dN_2^g + dN_2^L + d\tilde{N}_2 = 0, \quad (259)$$

$$d\tilde{N}_1 + d\tilde{N}_2 = 0, \quad (260)$$

$$dN_1^g + dN_2^g - dN_s^g = 0, \quad (261)$$

as well as $dA = 0$. Here, $-p_g$ is the component of the mechanical stress in the grains normal to the GB.

Out of 14 differentials appearing on the right-hand sides of Eqs. (255)–(261), 7 are eliminated by the constraints, leaving 7 independent variations:

$$d\hat{E} = (T_L - T) dS_L + \left(\frac{\partial \tilde{E}}{\partial \tilde{S}} - T \right) d\tilde{S} + \left(\frac{\partial E_d}{\partial S_d} - T \right) dS_d$$

$$\begin{aligned}
& + \left(\frac{\partial E_d}{\partial V_L} - p_L + p_g \right) dV_L + (\varphi - \mu_1) dN_1^g \\
& + (\varphi - \mu_2 + M) dN_2^g + \left(\frac{\partial \tilde{E}}{\partial \tilde{N}_2} + \mu_1 - \mu_2 \right) d\tilde{N}_2 = 0.
\end{aligned} \tag{262}$$

Equating the differential coefficients to zero, we obtain the following equilibrium conditions:

$$T = T_L = \left(\frac{\partial \tilde{E}}{\partial \tilde{S}} \right)_0 = \left(\frac{\partial E_d}{\partial S_d} \right)_0 \equiv T_0, \tag{263}$$

$$p_L^0 = p_g^0 + \left(\frac{\partial E_d}{\partial V_L} \right)_0, \tag{264}$$

$$\left(\frac{\partial \tilde{E}}{\partial \tilde{N}_2} \right)_0 = M_0 = \mu_2^0 - \mu_1^0, \tag{265}$$

$$\varphi_0 = \mu_1^0, \tag{266}$$

where T_0 is the uniform temperature throughout the equilibrium system. As usual, the superscript 0 marks the equilibrium state.

Eq. (264) is the mechanical equilibrium condition, which can be written in the form

$$p_L^0 = p_g^0 + p_d^0, \tag{267}$$

where p_d^0 is the equilibrium value of the *disjoining pressure* defined by

$$p_d \equiv \frac{\partial E_d}{\partial V_L}. \tag{268}$$

Thus, the liquid phase within the GB layer is subject to an additional pressure p_d on top of the pressure p_g existing in the grains.

12.1.2. Calculation of the disjoining pressure

Calculation of the equilibrium disjoining pressure p_d^0 can be simplified by reformulation of the equilibrium conditions in the density form. The fundamental equation (201) of the solid solution can be rewritten in the density form

$$\varepsilon_g = \varepsilon_g(s_g, v_g, c_g), \tag{269}$$

where ε_g , s_g and v_g are, respectively, the energy, entropy and volume per lattice site (which is same as per atom since we neglect vacancies), and c_g is the site (atomic) fraction of species 2. Accordingly, $T = \partial \varepsilon_g / \partial s_g$, $p_g = -\partial \varepsilon_g / \partial v_g$ and $M = \partial \varepsilon_g / \partial c_g$. From Eq. (203) we have

$$\varphi = \varepsilon_g - Ts_g + p_g v_g - Mc_g, \tag{270}$$

while the Gibbs–Duhem equation (204) becomes

$$s_g dT - v_g dp_g + d\varphi + c_g dM = 0. \tag{271}$$

It is more convenient to express all properties of the grain as functions of the variable set (T, p_g, c_g) . The thermodynamic potential appropriate for these variables is

$$\omega(T, p_g, c_g) \equiv \varphi + Mc_g = \varepsilon_g - Ts_g + p_g v_g. \tag{272}$$

Its differential form is

$$d\omega = -s_g dT + v_g dp_g + M dc_g, \tag{273}$$

which is easily derivable from Eq. (271). Similarly, for the liquid solution we will use the variable set (T_L, p_L, c_L) and, accordingly, the Gibbs free energy

$$g(T_L, p_L, c_L) \equiv \varepsilon_L - T_L s_L + p_L v_L = (1 - c_L)\mu_1 + c_L\mu_2 \quad (274)$$

with the differential

$$dg = -s_L dT_L + v_L dp_L + (\mu_2 - \mu_1) dc_L, \quad (275)$$

where all densities are counted per atom.

We now reformulate the equilibrium conditions (265) and (266) in the form

$$M(T_0, p_g^0, c_g^0) = \mu_2(T_0, p_L^0, c_L^0) - \mu_1(T_0, p_L^0, c_L^0), \quad (276)$$

$$\omega(T_0, p_g^0, c_g^0) = g(T_0, p_L^0, c_L^0) + M(T_0, p_g^0, c_g^0)(c_g^0 - c_L^0), \quad (277)$$

respectively. This is a system of two non-linear equations with respect to five equilibrium parameters $(T_0, p_g^0, p_L^0, c_g^0, c_L^0)$. It follows that our solid–liquid system has three degrees of freedom. Let us choose the independent variable set (T_0, p_g^0, c_g^0) . For any given state of the grains defined by these parameters, we can solve Eqs. (276) and (277) to find the composition c_L^0 and pressure p_L^0 in the liquid layer, and thus the disjoining pressure $p_d^0 = p_L^0 - p_g^0$.

For practical applications, we will replace this exact calculation scheme by a simple approximation. At given temperature T_0 and pressure p_g^0 , let c_g^* and c_L^* be the solid and liquid compositions corresponding to the bulk solid–liquid coexistence ($p_d^0 = 0$). These two compositions must satisfy the equations¹⁸

$$M(T_0, p_g^0, c_g^*) = \mu_2(T_0, p_g^0, c_L^*) - \mu_1(T_0, p_g^0, c_L^*), \quad (278)$$

$$\omega(T_0, p_g^0, c_g^*) = g(T_0, p_g^0, c_L^*) + M(T_0, p_g^0, c_g^*)(c_g^* - c_L^*). \quad (279)$$

Note that the pressure continuity condition $p_L^0 = p_g^0$ valid for a two-phase bulk system with a plane interface eliminates one degree of freedom, leaving our system with two degrees of freedom in compliance with the Gibbs phase rule. For a fixed pressure p_g^0 , Eqs. (278) and (279) define the solidus and liquidus lines, $c_g^*(T_0)$ and $c_L^*(T_0)$, on the phase diagram of the system.

We seek an approximate form of Eqs. (276) and (277) in the vicinity of the solidus line. As a measure of proximity of the grains to the solidus line at given T_0 and p_g^0 , we choose the diffusion potential deviation

$$\Delta M \equiv M(T_0, p_g^0, c_g^0) - M(T_0, p_g^0, c_g^*) \quad (280)$$

from its solidus value $M(T_0, p_g^0, c_g^*)$. All functions appearing in Eqs. (276) and (277) can be then approximated by linear expansions in the small parameters ΔM , $(c_g^0 - c_g^*)$, $(c_L^0 - c_L^*)$ and $(p_L^0 - p_g^0)$. The linearized form of these equations becomes

$$\Delta M = \left(\frac{\partial(\mu_2 - \mu_1)}{\partial c_L} \right)_* (c_L^0 - c_L^*) + \left(\frac{\partial(\mu_2 - \mu_1)}{\partial p_L} \right)_* p_d^0, \quad (281)$$

$$\left(\frac{\partial \omega}{\partial c_g} \right)_* (c_g^0 - c_g^*) = \left(\frac{\partial g}{\partial c_L} \right)_* (c_L^0 - c_L^*) + \left(\frac{\partial g}{\partial p_L} \right)_* p_d^0 + M(T_0, p_g^0, c_g^*)(c_g^0 - c_L^0 - c_g^* + c_L^*) + (c_g^* - c_L^*) \Delta M, \quad (282)$$

¹⁸ We will not go into details, but Eqs. (278) and (279) can be given a geometric interpretation of a common tangent construction. M being the slope of the common tangent to the curves $\omega(T_0, p_g^0, c)$ and $g(T_0, p_g^0, c)$ as functions of composition c at fixed T_0 and p_g^0 .

where the asterisk indicates that the derivatives are taken in the bulk-coexistence state ($\Delta M = 0$). All zero-order terms have canceled out by Eqs. (278) and (279). The equations obtained are simplified by utilizing the relations

$$\left(\frac{\partial \omega}{\partial c_g}\right)_* = \left(\frac{\partial g}{\partial c_l}\right)_* = M(T_0, p_g^0, c_g^*), \quad (283)$$

$$\left(\frac{\partial g}{\partial p_L}\right)_* = v_L^*, \quad (284)$$

$$\left(\frac{\partial(\mu_2 - \mu_1)}{\partial p_L}\right)_* = \bar{v}_L^{2*} - \bar{v}_L^{1*}, \quad (285)$$

where $\bar{v}_L^i = \partial \mu_i / \partial p_L$ are partial molar volumes of the components in the liquid phase, with the asterisk indicating that these volumes refer to the bulk-coexistence state. Using these relations, Eqs. (281) and (282) become, respectively,

$$\Delta M = \left(\frac{\partial(\mu_2 - \mu_1)}{\partial c_l}\right)_* (c_L^0 - c_L^*) + (\bar{v}_L^{2*} - \bar{v}_L^{1*}) p_d^0, \quad (286)$$

$$0 = v_L^* p_d^0 + (c_g^* - c_L^*) \Delta M. \quad (287)$$

Eq. (287) immediately gives us the equilibrium disjoining pressure,

$$p_d^0 = \frac{c_L^* - c_g^*}{v_L^*} \Delta M, \quad (288)$$

while Eq. (286) can be solved for the deviation of the liquid-layer composition c_L^0 from the liquidus composition c_L^* :

$$c_L^0 - c_L^* = \frac{\Delta M - (v_L^{2*} - v_L^{1*}) p_d^0}{\left(\frac{\partial(\mu_2 - \mu_1)}{\partial c_l}\right)_*} = \frac{1 - \frac{v_L^{2*} - v_L^{1*}}{v_L^*} (c_L^* - c_g^*)}{\left(\frac{\partial(\mu_2 - \mu_1)}{\partial c_l}\right)_*} \Delta M. \quad (289)$$

In many systems, the difference between the partial molar volumes of the components is small in comparison with v_L^* and the latter equation can be simplified to

$$c_L^0 - c_L^* = \frac{1}{\left(\frac{\partial(\mu_2 - \mu_1)}{\partial c_l}\right)_*} \Delta M. \quad (290)$$

For a single-component system, ΔM loses its significance. The appropriate measure of proximity of the system to bulk melting is then the difference ($T_0 - T_m$) between the temperature of the bicrystal and the bulk melting point T_m at a given pressure p_g^0 . The equilibrium conditions (276) and (277) reduce to one equation,

$$\omega(T_0, p_g^0, 0) = g(T_0, p_L^0, 0), \quad (291)$$

which for bulk equilibrium becomes

$$\omega(T_m, p_g^0, 0) = g(T_m, p_g^0, 0). \quad (292)$$

Linearizing Eq. (291) in the small parameters ($T_0 - T_m$) and p_d^0 we have

$$\left(\frac{\partial \omega}{\partial T}\right)_* (T_0 - T_m) = \left(\frac{\partial g}{\partial T}\right)_* (T_0 - T_m) + \left(\frac{\partial g}{\partial p_L}\right)_* p_d^0, \quad (293)$$

from which

$$p_d^0 = \frac{s_L^* - s_g^*}{v_L^*} (T_0 - T_m) = \frac{H_m}{T_m v_L^*} (T_0 - T_m), \quad (294)$$

where $H_m = (s_L^* - s_g^*) T_m$ is the enthalpy of melting per atom.

12.2. Analysis of fluctuations

To describe fluctuations in the pre-melted GB, we treat the grains as an infinite reservoir and apply the canonical fluctuation relation (98). The system coupled to the reservoir is the GB possessing the energy

$$E_{GB} \equiv E_L + \tilde{E} + E_d. \quad (295)$$

We will initially consider the full set of fluctuating parameters, which will later be reduced to a smaller set. Namely, we will initially treat all arguments of the fundamental equations (248), (251) and (253), except for the fixed GB area, as the fluctuating parameters. In the energy scheme, the fluctuating parameter set is

$$Z = (S_L, \tilde{S}, S_d, V_L, N_1^L, N_2^L, \tilde{N}_2). \quad (296)$$

The thermodynamic forces conjugate to these parameters are

$$P = \left(T_L, \frac{\partial \tilde{E}}{\partial \tilde{S}}, \frac{\partial E_d}{\partial S_d}, -p_L + \frac{\partial E_d}{\partial V_L}, \mu_1, \mu_2, \frac{\partial \tilde{E}}{\partial \tilde{N}_2} \right). \quad (297)$$

The reversible work of GB formation (99) takes the form

$$\mathcal{R} = E_{GB} - E_{GB}^0 - \sum_{i=1}^7 P_i^0 (Z_i - Z_i^0), \quad (298)$$

where the thermodynamic forces are taken in the state of equilibrium. Using the equilibrium conditions (263)–(265), we obtain

$$\begin{aligned} \mathcal{R} = & (E_L - E_L^0) + (\tilde{E} - \tilde{E}_0) + (E_d - E_d^0) - T_0(S_L - S_L^0) - T_0(\tilde{S} - \tilde{S}_0) - T_0(S_d - S_d^0) \\ & + p_L^0(V_L - V_L^0) - p_d^0(V_L - V_L^0) - \mu_1^0(N_1^L - N_1^{L0}) - \mu_2^0(N_2^L - N_2^{L0}) - M_0(\tilde{N}_2 - \tilde{N}_2^0). \end{aligned} \quad (299)$$

Next, we will make some approximations that will reduce the number of fluctuating parameters. The difference $(E_L - E_L^0)$ appearing in Eq. (299) will be approximated by its linear expansion around equilibrium:

$$E_L - E_L^0 = T_0(S_L - S_L^0) - p_L^0(V_L - V_L^0) + \mu_1^0(N_1^L - N_1^{L0}) + \mu_2^0(N_2^L - N_2^{L0}). \quad (300)$$

Likewise, $(\tilde{E} - \tilde{E}_0)$ will also be evaluated in the linear approximation:

$$\tilde{E} - \tilde{E}_0 = T_0(\tilde{S} - \tilde{S}_0) + M_0(\tilde{N}_2 - \tilde{N}_2^0). \quad (301)$$

The terms related to the disjoining interaction will remain intact. Inserting the linear expansions (300) and (301) in Eq. (299), several terms cancel out and we are left with

$$\mathcal{R} = (E_d - E_d^0) - T_0(S_d - S_d^0) - p_d^0(V_L - V_L^0). \quad (302)$$

Although Eq. (302) contains variations of three variables, only one fluctuating parameter is independent. To see this, we apply the Legendre transformation with respect to the disjoining entropy to obtain the thermodynamic potential

$$\Psi(T, V_L) = E_d(S_d, V_L) - TS_d. \quad (303)$$

This thermodynamic potential is called the *disjoining potential* and its differential form is

$$d\Psi = -S_d dT + p_d dV_L. \quad (304)$$

The latter equation suggests another definition of the disjoining pressure:

$$p_d = \left(\frac{\partial \Psi}{\partial V_L} \right)_T. \quad (305)$$

Thus, Eq. (302) can be rewritten in the form

$$\mathcal{R} = \Psi(T_0, V_L) - \Psi(T_0, V_L^0) - p_d^0(V_L - V_L^0), \quad (306)$$

showing that, at a given temperature T_0 , \mathcal{R} is solely a function of V_L . In other words, V_L is the only independent fluctuating parameter. By neglecting higher-order terms in Eqs. (300) and (301), we have suppressed fluctuations of all other independent parameters.

The probability distribution of the liquid volume V_L is given by Eq. (98), which becomes

$$W(V_L) = W_m \exp\left(-\frac{\mathcal{R}}{kT_0}\right) = W_m \exp\left[-\frac{\Psi(T_0, V_L) - \Psi(T_0, V_L^0) - p_d^0(V_L - V_L^0)}{kT_0}\right]. \quad (307)$$

Remembering that the cross-section of the bicrystal is fixed, we finally arrive at the distribution function of the liquid-layer width w :

$$W(w) = W_m \exp\left[-A \frac{\psi(T_0, w) - \psi(T_0, w_0) - p_d^0(w - w_0)}{kT_0}\right], \quad (308)$$

where $w_0 = V_L^0/A$ is the equilibrium width of the layer and $\psi = \Psi/A$ is the disjoining potential per unit area. Note that this distribution depends on the GB area A : the larger the area, the sharper is the peak of the distribution around w_0 . The disjoining pressure can be rewritten as $p_d = (\partial\psi/\partial w)_T$. Its equilibrium value p_d^0 appearing in Eq. (308) can be found from the bulk thermodynamic properties using Eq. (288) for a binary alloy and Eq. (294) for a single-component system. Knowing p_d^0 and the distribution of w at a given temperature T_0 , one can invert Eq. (308) and extract the disjoining potential $\psi(T_0, w)$.

The GB width distribution (308) in conjunction with Eqs. (288) and (294) for the equilibrium disjoining pressure answers the goal of this section. For single-component systems, an equation similar to (308) was derived in previous work [16–18,77] and utilized for calculations of disjoining interactions in Ni GBs by atomistic simulations [16–18]. In the present paper, this distribution has been extended to binary systems.

As a further approximation, we can expand $\psi(T_0, w)$ around the equilibrium width keeping only linear and quadratic terms:

$$\psi(T_0, w) = \psi(T_0, w_0) + p_d^0(w - w_0) + \frac{1}{2} \left(\frac{\partial^2\psi}{\partial w^2}\right)_0 (w - w_0)^2, \quad (309)$$

where the second derivative is taken at equilibrium. This results in the Gaussian distribution

$$W(w) = W_m \exp\left[-\frac{A}{2kT_0} \left(\frac{\partial^2\psi}{\partial w^2}\right)_0 (w - w_0)^2\right], \quad (310)$$

from which the mean-square fluctuation of the GB width is

$$\overline{(w - w_0)^2} = \frac{kT_0}{A(\partial^2\psi/\partial w^2)_0}. \quad (311)$$

This estimate shows that the root-mean-square fluctuation of the liquid-layer width scales with the GB area as $1/\sqrt{A}$.

According to the foregoing derivation, the GB width w appearing in the sharp-interface model of GB premelting (Fig. 6) has the meaning of the distance between two dividing surfaces of the solid–liquid

interfaces. Such dividing surfaces are characterized by a zero excess of the total number of particles [$\tilde{V} = 0$, $\tilde{N} = 0$, see excess definition (250)]. It should be, therefore, understood that the alternate definitions of w adopted in atomistic simulations [16–18] constitute approximations to the strict definition.

13. Concluding remarks

The thermodynamic theory of fluctuations presented here expands the postulational basis of the traditional classical thermodynamics by incorporating equilibrium fluctuations. The main additional element of the expanded theory is the fluctuation postulate expressed by Eq. (15) [or equivalently, Eq. (19)]. Due to its statistical nature, this postulate signifies a break with the determinism of classical thermodynamics. The statistical component introduced by this postulate propagates through the entire logical structure of thermodynamics. The equilibrium state of a system is no longer a state but a distribution over states. Thermodynamic properties become distributions around the average values which are measured by macroscopic experiments. Similar expansions of classical thermodynamics were previously discussed by Tisza and Quay [40] and Callen [27,28,39] and can be traced back to Einstein [41]. The fluctuation postulate formulated in this paper describes fluctuations in an isolated system and stems from the microcanonical distribution in statistical mechanics. In this sense, our approach is different from that of Tisza and Quay [40] and Callen [27,28,39] and is more aligned with Einstein's proposal [41].

The fluctuation postulate relies on the concept of non-equilibrium entropy. Without a proper definition of non-equilibrium entropy, we cannot talk about its increase during equilibration or behavior during fluctuations. In some sense, non-equilibrium entropy is defined already in classical thermodynamics. The thermodynamic equilibrium conditions of classical thermodynamics are formulated through the entropy maximum principle [25,27–29]. In this principle, the actual equilibrium state of the system is compared with possible *virtual* states in which the system is *imagined* to be partitioned into isolated equilibrium subsystems; their entropies are then summed up and compared with the equilibrium entropy of the actual system. The expanded thermodynamics goes one step further: it assumes that such states are *actually implemented* during spontaneous fluctuations away from the equilibrium state. The term “quasi-equilibrium” introduced in this paper captures three defining properties of such fluctuated states: (1) non-equilibrium, (2) real (as opposed to virtual states of classical thermodynamics), and (3) composed of subsystems that can be treated as isolated (on a certain time scale) and each described by a fundamental equation. The quasi-equilibrium states are characterized by a set of internal parameters λ_i . The fluctuation postulate specifies the distribution function of these parameters for an isolated system.

The second law of thermodynamics is re-formulated to include fluctuations. In the refined formulation, it is only the entropy \bar{S} averaged over the fluctuations that monotonically increases and reaches a maximum at equilibrium. On shorter time scales, the non-equilibrium entropy \hat{S} incessantly fluctuates around its average value and can never accede a certain maximum value S (Figs. 2 and 3). Thus, the average entropy \bar{S} obtained by macroscopic measurements (performed on the time scale t_{TD}) is always somewhat smaller than S .

In classical thermodynamics, a central role is played by the fundamental equation which encapsulates all equilibrium thermodynamic properties of the system. This equation, first discovered by Gibbs [25], looks exactly like our Eq. (4) but has a subtly different meaning. In the classical fundamental equation, the entropy S is a static property defined through the maximum-entropy principle (e.g., Callen's Postulate II [27,28] or Tisza's Postulate *Pb1* [29]) and measured experimentally. In the expanded theory, S appearing in Eq. (4) has the statistical-mechanical meaning of the maximum micro-canonical entropy of an isolated system. As noted in the previous paragraph, this entropy is slightly larger than the measured entropy \bar{S} . In other words, the measured entropy \bar{S} does not exactly satisfy the fundamental equation (4) of the present theory. This fact, of course, does not create any problems. It only reflects the possibility of different definitions of the fundamental equation for a fluctuating system. Since both S and \bar{S} are well-defined for any given set of conserved parameters X_1, \dots, X_n , $S(X_1, \dots, X_n)$ could also be taken as the fundamental equation [27,28,38,39]. We would then have to re-define the temperature, pressure and all other intensities, and to modify many other

equations of the theory. In the end, taking the fundamental equation $\bar{S}(X_1, \dots, X_n)$ as the point of departure would not lead to a logically consistent thermodynamic fluctuation theory consistent with statistical mechanics.¹⁹ The advantage of our Eq. (4) with the entropy defined as above is that it leads to a simple and complete logical structure fully consistent with statistical mechanics. In the limit of an infinite large system, the fluctuations vanish and S and \bar{S} become numerically equal. Accordingly, Eq. (4) becomes the fundamental equation in the sense of classical thermodynamics.

Similar considerations apply to canonical fluctuations. If the average values $\bar{X}_1, \dots, \bar{X}_m$ of the fluctuating extensive parameters X_1, \dots, X_m are formally inserted in the fundamental Eq. (4), we do not obtain the canonical entropy \bar{S} . However, in the limit of a large system, all canonical averages do satisfy (4) and the latter becomes the classical fundamental equation.

For the sake of simplicity, we have only considered a particular class of thermodynamic systems for which all arguments of the fundamental equation are additive invariants. In the future, the theory can be generalized to include pseudo-thermodynamic and quasi-thermodynamic variables [29]. Pseudo-thermodynamic variables are neither additive nor conserved; an example is furnished by long-range order parameters in atomically ordered compounds. Quasi-thermodynamic variables can be additive but need not be conserved. They give rise to additional work terms in the total energy variation. However, the conjugate thermodynamic forces do not become spatially homogeneous when the system reaches equilibrium and thus cannot be considered as intensities. Examples include the total magnetic or electric-dipole moment of the system, the conjugate variables for which are, respectively, the magnetic and electric field. Elastic strains and stresses in inhomogeneously deformed crystalline solids belong to the same category. All such cases require a separate treatment.

To facilitate practical applications of the theory, we have presented a regular procedure for calculations of equilibrium fluctuations of extensive parameters, intensive parameters and densities in systems with any number of parameters. The proposed formalism has been demonstrated by deriving the complete set of fluctuation relations for a simple fluid in three different ensembles. The results are summarized in Tables 1–3 and may present a reference value. It should be noted that these calculations treat all fluctuations in the Gaussian approximation. Greene and Callen [27,38] proposed a more general method that does not rely on the Gaussian approximation and enables calculations of higher-order correlation moments such as $\Delta X_i \Delta X_j \Delta X_k$, $\Delta X_i \Delta X_j \Delta X_k \Delta X_l$, etc. Such moments are rarely important and were not discussed in this paper.

The proposed fluctuation formalism has been applied to solve two problems related to GBs in binary solid solutions. First, we developed a set of equations relating the fluctuations of excess GB properties, readily accessible by atomistic simulations, to equilibrium GB characteristics such as the excess elastic modulus, excess heat capacity and others. These equations offer a computationally efficient approach to computing the entire set of such properties from a single simulation run. Furthermore, the covariances between the fluctuations generate a set of thermodynamic relations that can be tested by simulations to verify the fundamental understanding of GB thermodynamics. Implementation of this program is presently underway.

Second, we have extended the sharp interface model of GB pre-melting to binary alloys and derived the distribution of the fluctuating liquid-layer width w . This distribution has recently been applied to calculate the disjoining potential for several GBs in Cu–Ag alloys [24]. The disjoining potential is a key GB property allowing predictions of different pre-melting scenarios, such as the continuous melting, thin-to-thick transitions or abrupt melting after over-heating [78,79]. In the version of the pre-melting model considered here, we essentially treat the grains, the liquid layer and the solid–liquid interfaces as parts of the same infinite reservoir. We only account for fluctuations of w due to disjoining interaction. All thermodynamic relations are in place to develop a more general model that would include fluctuations of intensive properties of the liquid layer and/or the solid–liquid interface properties. This generalization could be the subject of future work.

¹⁹ As already mentioned, Greene and Callen [38] resolved these difficulties by making an additional approximation that essentially identifies the canonical and micro-canonical entropies. This identification is not satisfying for a rigorous fluctuation theory. The distinction between the two entropies was discussed in Section 9.3.

Finally, the approach demonstrated here for GBs can be readily extended to other interfaces. It would be interesting to study the fluctuations of excess properties of solid–liquid and especially solid–solid interfaces to determine their excess elastic and thermal properties and test some of the basic equations of interface thermodynamics.

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