

Local equilibrium of the Gibbs interface in two-phase systems

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Abstract – We analyze the local equilibrium assumption for interfaces from the perspective of gauge transformations, which are the small displacements of Gibbs' dividing surface. The gauge invariance of thermodynamic properties turns out to be equivalent to conditions for jumps of bulk densities across the interface. This insight strengthens the foundations of the local equilibrium assumption for interfaces and can be used to characterize nonequilibrium interfaces in a compact and consistent way, with a clear focus on gauge-invariant properties. Using the principle of gauge invariance, we show that the validity of Clapeyron equations can be extended to nonequilibrium interfaces, and an additional jump condition for the momentum density is recognized to be of the Clapeyron type.

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Introduction. – Interfaces possess interesting thermodynamic properties that do not exist in bulk phases. A typical interfacial effect with many observable consequences is the surface tension of a liquid-gas interface. Can the concept of surface tension be generalized from equilibrium to nonequilibrium situations? Since we would expect the surface tension to depend on temperature, what kind of temperature shall we assign to interfaces in nonequilibrium situations? Interestingly, interfaces possess thermodynamic properties that do not coincide with the corresponding properties in the surrounding bulk phases. In this regard, the most important thermodynamic property characterizing the state of an interface in a pure two-phase system is its temperature, which may not even lie between the temperatures of the adjacent bulk phases [1,2].

The classical approach to describe equilibrium interfacial thermodynamics in phase coexistence relies on the arguments of Gibbs [3], who considers the interface as a separate 2D thermodynamic system which can be characterized in terms of excess densities. A nonequilibrium thermodynamic description of interfaces based on Gibbs' approach has been developed by Bedeaux and coworkers [4–6]. The main challenge is to generalize the concept of

local equilibrium, which is known to be a key ingredient to the nonequilibrium thermodynamics of bulk systems [7,8], to interfaces [9,10]. Even when in contact with nonequilibrium bulk phases, interfaces quickly relax to states that can locally be described by the same set of variables as equilibrium interfaces, with the same thermodynamic relations between these variables. Interfaces are always controlled by their bulk environments so that intensive variables play an important role in understanding interfacial thermodynamics and statistical mechanics.

Several studies have investigated the validity of the local equilibrium hypothesis. For instance, the hypothesis has been supported by nonequilibrium molecular dynamics simulations [11–13] and by the van der Waals square-gradient model [1,2]. However, such tests are very subtle. From a practical point of view, it is not clear how to extract a meaningful nonequilibrium interfacial temperature from the transition behavior of the kinetic temperature, which is typically used in molecular dynamics simulations. More fundamentally, excess densities are known to depend on the precise choice for the location of the interface [6,7,14–17]. How can we deal with this ambiguity in going from global to local equilibrium? Is there a unique or convincing way to implement local equilibrium? What are the observable consequences of local equilibrium?

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Providing conceptually clear definitions of the interfacial temperature, chemical potential and other thermodynamic quantities is essential to understand and build a thermodynamically consistent description of interfacial phenomena. Further outlining rational and efficient ways to measure these quantities is equally important in view of the numerous instances of interfacial phenomena in engineering applications [18–24]. In heterogeneous catalysis, for example, the reaction occurs at interfaces, and one may want to quantify its efficiency as a function of the interfacial temperature. Also in the layers of fuel cells, typically operating at high current densities, the water density varies from a vapor to a condensed phase across the catalytic layer. In these truly nonequilibrium situations, could the density profiles, more easily quantified [25], be used to predict the interfacial temperature?

In this paper, we analyze the effect of small changes in the choice of the interface’s location in nonequilibrium situations. We refer to such small displacements of the interface as *gauge transformations*. Whereas excess densities may often change under gauge transformations, the *principle of gauge invariance* should be obeyed by all static and dynamic descriptions of equilibrium and nonequilibrium interfaces. We here employ the principle of gauge invariance to strengthen the conceptual clarity of the description of nonequilibrium interfaces and, in particular, of the local equilibrium hypothesis. In that sense, we separate the gauge-variant and -invariant aspects of the Gibbs-like approach also for nonequilibrium interfaces, and we draw a complete and consistent description of the gauge-invariant thermodynamic properties of the interface. We notably find that these properties are governed by the same relations whether the total system is at or away from global equilibrium.

Thermodynamic description of interfaces. – To prepare our efforts to develop a thermodynamic characterization of interfaces that can be used in dynamic theories of multiphase systems in nonequilibrium situations, we first recall Gibbs’ classical description of interfaces at equilibrium [3]. We then discuss some possible issues related to the idea of local equilibrium of interfaces, and we finally resolve these issues by means of the gauge transformations associated with atomistic displacements of interfaces. In particular, we obtain a compact characterization of the gauge-invariant thermodynamic properties of local equilibrium interfaces. For reasons of clarity, we restrict ourselves in this section on the conceptual foundations to single-component systems. The more relevant case of multicomponent multiphase systems will be discussed in the next section.

Equilibrium. Consider a system consisting of two coexisting bulk phases α and β , separated by an interface of area A , in global equilibrium. An increase in the internal energy of the system dU is then expressed as $dU = TdS - pdV + \gamma dA + m\mu dN$, which defines temperature T , pressure p , surface tension γ and chemical potential μ

in terms of the changes of U associated with changes in entropy S , volume V , surface area A , and number of particles N , each of mass m . Assuming global equilibrium and a planar separating surface, p , T and μ are constant throughout the two-phase system and the surface tension γ is uniform over the interface. We thus “do not need to ask what the values of p , T and μ at the interface are” [26]. Making proper use of the extensivity of U , S , V , A and N , we further obtain the Euler equation for the entire system at equilibrium, $U = TS - pV + \gamma A + m\mu N$. The total extensive properties of the system can be written as $U = U^\alpha + U^\beta + U^s$, $S = S^\alpha + S^\beta + S^s$, $N = N^\alpha + N^\beta + N^s$, and $V = V^\alpha + V^\beta$, where the superscripts α , β and s indicate the two bulk phases and the surface respectively. For example, the sum of the internal energy of the bulk phases, $U^\alpha + U^\beta$ differs from U by an interfacial term U^s . These splittings of the extensive quantities will in general depend on the precise position chosen for the dividing interface, as we will later discuss in detail. The thermodynamics for each equilibrium bulk phase leads to $dU^i = TdS^i - pdV^i + m\mu dN^i$ and $U^i = TS^i - pV^i + m\mu N^i$ for $i = \alpha, \beta$. Using the above expressions, one obtains the Euler and Gibbs-Duhem equations for the interface in global equilibrium,

$$u^s = T s^s + \gamma + \mu \rho^s, \quad (1a)$$

$$0 = s^s dT + d\gamma + \rho^s d\mu, \quad (1b)$$

where the excess surface densities are defined by $u^s = U^s/A$, $s^s = S^s/A$ and $\rho^s = mN^s/A$.

According to the Gibbs phase rule for two-phase coexistence of a single-component system, μ depends on T and hence also γ is a unique function of T . Therefore, the temperature T , the chemical potential $\mu(T)$, and the interfacial tension $\gamma(T)$ in eqs. (1) are well-defined thermodynamic properties of the interface, whereas the excess densities u^s , s^s , and ρ^s depend on the choice of the dividing surface. It is quite remarkable that the ambiguous (later called “gauge variant”) excess densities and the well-defined (later called “gauge invariant”) properties T , μ , and γ are related by the Euler and Gibbs-Duhem equations in very much the same way as the unambiguously defined, observable densities and intensive properties of bulk systems. The loss of one thermodynamic degree of freedom for phase coexistence according to the Gibbs phase rule is reflected in a one-parameter family of gauge transformations associated with small displacements of the interface. It would be desirable to have a thermodynamic characterization of interfaces that focuses on the gauge-invariant properties.

According to the Clapeyron equations [26], the functional form of $\mu(T)$ contains important information about the “jump ratios” at two-phase coexistence. Calling $\Delta\rho = \rho^\alpha - \rho^\beta$, $\Delta s = s^\alpha - s^\beta$, and $\Delta u = u^\alpha - u^\beta$ the jumps of the bulk densities $\rho^i = mN^i/V^i$, $s^i = S^i/V^i$, and $u^i = U^i/V^i$

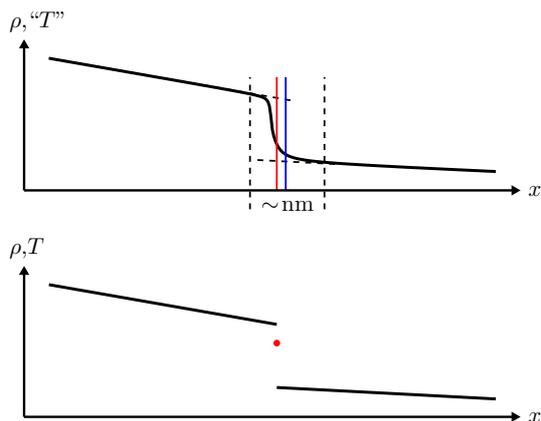


Fig. 1: (Colour on-line) Hypothetical nonequilibrium profile of mass density, or temperature, in the diffuse interface model (top) and in the sharp interface model (bottom). In the diffuse model, the transition between two bulk phases occurs over a very small length scale (in numerical calculations, one often chooses length scales much larger than the physical nanometer scale indicated in the figure). Defining a unique temperature of the interface with true thermodynamic significance is a challenge. In this article, we adopt the sharp interface approach, considering the interface as a 2D system with its own density, temperature,

(for $i = \alpha, \beta$) across the interface, we calculate

$$\frac{d\mu(T)}{dT} = -\frac{\Delta s}{\Delta\rho}, \quad (2a)$$

$$\mu(T) - T \frac{d\mu(T)}{dT} = \frac{\Delta u}{\Delta\rho}. \quad (2b)$$

In other words, the jump ratios can be readily calculated from the chemical potential $\mu(T)$ at phase coexistence; hence they are predictable functions of the interfacial temperature.

Local equilibrium. The fact that the temperature T and the chemical potential μ are uniform throughout a heterogeneous equilibrium system is a central point to the approach of Gibbs recalled above [26]. In nonequilibrium situations, these quantities are not constant, and thermodynamic relationships must be established in a local form, using densities of the extensive properties, like in eqs. (1), and adopting equilibrium at a local scale. Using this assumption of local equilibrium, the interface possesses its own thermodynamic properties, such as temperature T^s and chemical potential μ^s , governed by equilibrium equations of state while not being conditioned by an equilibrium environment. Across the interface, we do not assume the continuity of the intensive quantities: their value in the interface can, under nonequilibrium conditions, differ from the values in the adjacent bulk phases. For example, one usually has $T^s \neq T^\alpha, T^\beta$, even if T^α, T^β are evaluated in the vicinity of the interface, as illustrated in fig. 1; the interfacial temperature T^s may not even lie between the bulk temperatures T^α and T^β .

In nonequilibrium situations, one can still define¹ the interfacial excess densities of the energy, u^s , entropy, s^s , and mass, ρ^s per unit area, as well as the excess parallel pressure $p_{\parallel}^s = -\gamma$. Similar to the equilibrium case, u^s , s^s , and ρ^s may depend on the location of the dividing surface. However, the definitions of T^s , μ^s , γ , and of the interfacial velocity \mathbf{v}^s , which are measurable quantities, should not depend on the chosen position of the dividing surface. References [1,2,23] present definitions of the interfacial quantities that fulfill these requirements. But how should we implement the local equilibrium assumption in a full dynamic theory for nonequilibrium systems? Can we postulate the validity of all equilibrium equations of state relating, with no distinction, gauge-variant and gauge-invariant properties without violating the principle of gauge invariance for a dynamic theory? This would be equivalent to assuming eqs. (1). Should we expect only the equilibrium relationships between gauge-invariant properties to be valid? Or should even the Clapeyron equations (2) remain valid in nonequilibrium situations? The latter go beyond eqs. (1) because they express relationships between interfacial and bulk variables rather than relationships between interfacial variables only. Should the Clapeyron equations be modified, say by velocity differences? Or should there be an additional Clapeyron-type equation for the jump in the momentum density? All these questions are answered in the following section.

Gauge transformations. Both in equilibrium and in nonequilibrium systems, the calculation of excess densities starts by choosing a dividing surface. As this choice is essentially a mathematical construct, measurable properties of the interface, like for instance the reflection of light [27], the velocity and the temperature, must be independent of this choice. It is therefore appropriate to call the change from one dividing surface to another one a “gauge transformation.” Choosing a particular dividing surface is like fixing the gauge. A shift of the dividing surface over an atomistic distance ℓ toward the phase α will change, for instance, the excess momentum density \mathbf{M}^s and the excess mass density ρ^s of the interface to other values $\mathbf{M}^{s'}$ and $\rho^{s'}$ given by [28]

$$\mathbf{M}^{s'} = \mathbf{M}^s + \ell \Delta \mathbf{M}, \quad (3a)$$

$$\rho^{s'} = \rho^s + \ell \Delta \rho. \quad (3b)$$

Here $\Delta \mathbf{M} = \mathbf{M}^\alpha - \mathbf{M}^\beta$ and $\Delta \rho = \rho^\alpha - \rho^\beta$ are the jumps of bulk densities across the interface in equilibrium or nonequilibrium situations. Similar transformations are obtained for the other excess densities. The quantities \mathbf{M}^s , ρ^s , u^s and s^s are thus called *gauge variant*. For the excess parallel pressure $p_{\parallel}^s = -\gamma$ of a planar interface, we find that γ is independent of the position of the interface, that is, *gauge invariant*. Other examples of gauge-invariant properties are the velocity, the temperature and the chemical

¹Note that we will not explicitly indicate here the possible spatial and temporal dependency of the nonequilibrium thermodynamic quantities.

potential of the interface. From the gauge invariance of $\mathbf{v}^s = \mathbf{M}^s/\rho^s$, we first conclude that $\rho^s = 0$ implies $\mathbf{M}^s = \mathbf{0}$. Starting from a gauge with $\rho^s = 0$ and making use of the transformation rules (3), we find

$$\mathbf{v}^s = \frac{\mathbf{M}^{s'}}{\rho^{s'}} = \frac{\Delta \mathbf{M}}{\Delta \rho}. \quad (4)$$

We thus arrive at a Clapeyron-type relation involving the jump of the momentum density from one bulk phase to the other. Note that the principle of gauge invariance requires the identity (4) for nonequilibrium jumps; at equilibrium, this identity becomes trivial.

More generally, ratios of jumps in the densities of the bulk extensive quantities from one phase to the other play a crucial role for gauge invariance. Indeed, by characterizing different gauges in terms of the excess mass density ρ^s rather than the position of the Gibbs surface, we can, for example, rewrite gauge transformations of the type (3) for the excess entropy and energy densities as

$$s^s(T^s, \rho^s) = s^s(T^s, 0) + \frac{\Delta s}{\Delta \rho} \rho^s, \quad (5a)$$

$$u^s(T^s, \rho^s) = u^s(T^s, 0) + \frac{\Delta u}{\Delta \rho} \rho^s, \quad (5b)$$

both for equilibrium and for nonequilibrium interfaces. The local equilibrium assumption states that the relationships $s^s(T^s, \rho^s)$ and $u^s(T^s, \rho^s)$ are given by the equilibrium equations of state and it hence implies that also the jump ratios $\Delta s/\Delta \rho$ and $\Delta u/\Delta \rho$ in eqs. (5) must be given by their equilibrium values, that is, by the Clapeyron equations (2) in terms of $\mu^s(T^s)$. The occurrence of jump ratios in eqs. (5) and also their values at equilibrium follow as a consequence of gauge invariance². Whereas the usual derivation of Clapeyron equations is based on a direct comparison of coexisting bulk phases, gauge invariance focuses on the interfacial properties and their dependence on the precise location of Gibbs' dividing surface. Following the idea that local equilibrium is a consequence of fast relaxation of the interface, we expect that not only jump ratios but even the jumps themselves are given by the proper equilibrium values. This conjecture has been verified for the van der Waals square-gradient model [1,2].

Equations (5) express the interplay between gauge-invariant and gauge-variant properties. The gauge $\rho^s = 0$ is of particular importance. By choosing $\rho^s = 0$ in eqs. (1) we obtain

$$s^s(T^s, 0) = -\frac{d\gamma(T^s)}{dT^s}, \quad (6a)$$

$$u^s(T^s, 0) = \gamma(T^s) - T^s \frac{d\gamma(T^s)}{dT^s}. \quad (6b)$$

Equations (6) show that, if one separates the entropic and energetic contributions to the gauge-invariant interfacial tension γ by means of its temperature dependence, one

²Note that the gauge invariance of the Gibbs-Duhem equation (1b), $0 = \Delta s dT + \Delta \rho d\mu$, implies the Clapeyron equation (2a); the gauge invariance of the Euler equation (1a), $\Delta u = T \Delta s + \mu \Delta \rho$, further implies (2b).

obtains the excess densities of entropy and energy in the special gauge $\rho^s = 0$ occurring in eqs. (5). We are actually led to a characterization of the thermodynamics of local equilibrium interfaces that focuses on the gauge-invariant information and allows us to superimpose gauge-variant information in terms of the jump ratios governed by the Clapeyron equations (2). Local equilibrium can thus be fully and consistently implemented in nonequilibrium gauge theories, including the equilibrium Clapeyron equations and an additional one for the jump of the momentum density.

Multicomponent systems. – Multiphase systems of practical importance usually involve many components. Here we generalize the above arguments to multicomponent systems. For a n -component system, the state of a bulk phase can be characterized by the $n+1$ intensive variables μ_1, \dots, μ_n , and T , where μ_j is the chemical potential of the component j , and the corresponding mass density will be denoted by ρ_j . All information about the bulk equations of state is contained in the thermodynamic potential $p(T, \mu_1, \dots, \mu_n)$. According to the Gibbs phase rule, for two-phase coexistence we loose one degree of freedom. We choose to characterize the thermodynamic state of an interface in a n -component system by the intensive variables $\mu_1^s, \dots, \mu_{n-1}^s$, and T^s . The condition for phase coexistence is given by the relationship $\mu_n^s(T^s, \mu_1^s, \dots, \mu_{n-1}^s)$ and all the constitutive information is contained in the interfacial tension $\gamma(T^s, \mu_1^s, \dots, \mu_{n-1}^s)$. The role of the pressure-like quantity γ , given as a function of intensive variables, as a thermodynamic potential for interfaces is natural because interfaces are controlled by the surrounding bulk phases, thus acting as baths for the state of the interface.

Instead of characterizing the interface by falling back on the Euler and Gibbs-Duhem equations for nonequilibrium multicomponent interfaces, $u^s = T^s s^s + \gamma + \sum_{j=1}^n \mu_j^s \rho_j^s$ and $0 = s^s dT^s + d\gamma + \sum_{j=1}^n \rho_j^s d\mu_j^s$, we emphasize the interplay of gauge-invariant and -variant information in the same way as in eqs. (5), (6) by writing

$$s^s - \frac{\Delta s}{\Delta \rho_n} \rho_n^s = -\frac{\partial \gamma}{\partial T^s} \Big|_{\mu_{k \neq n}^s}, \quad (7a)$$

$$u^s - \frac{\Delta u}{\Delta \rho_n} \rho_n^s = \gamma - T^s \frac{\partial \gamma}{\partial T^s} \Big|_{\mu_{k \neq n}^s}, \quad (7b)$$

$$\rho_j^s - \frac{\Delta \rho_j}{\Delta \rho_n} \rho_n^s = -\frac{\partial \gamma}{\partial \mu_j^s} \Big|_{T^s, \mu_{k \neq j, n}^s}, \quad (7c)$$

for $j = 1, \dots, n-1$, where the gauge is now characterized by the value of the excess mass density ρ_n^s . The convenient reference gauge, for which the expressions for all other excess densities in eqs. (7) are particularly simple, is given by $\rho_n^s = 0$. Note that this choice may in some instance appear inappropriate, as it can lead to negative values for the surface excess density of other components. Choosing

another reference gauge can circumvent such problems (see sect. 4.2.3 of ref. [19]). To obtain the jump ratios occurring in eqs. (7), we can generalize the Clapeyron equations (2) as follows:

$$\frac{\Delta s}{\Delta \rho_n} = - \left. \frac{\partial \mu_n^s}{\partial T^s} \right|_{\mu_{k \neq n}^s}, \quad (8a)$$

$$\frac{\Delta u}{\Delta \rho_n} = \mu_n^s - T^s \left. \frac{\partial \mu_n^s}{\partial T^s} \right|_{\mu_{k \neq n}^s}, \quad (8b)$$

$$\frac{\Delta \rho_j}{\Delta \rho_n} = - \left. \frac{\partial \mu_n^s}{\partial \mu_j^s} \right|_{T^s, \mu_{k \neq j, n}^s}, \quad (8c)$$

for $j = 1, \dots, n-1$. As Gibbs already noticed [3], in multi-component systems, one may introduce gauge-invariant adsorptions Γ_{jk} of component j relative to component k defined by $m_j \Gamma_{jk} = \rho_j^s - \rho_k^s (\Delta \rho_j / \Delta \rho_k)$, where m_j is the mass of the particles of component j . The adsorptions relative to component n are given in eq. (7c).

Implications. – The proposed local equilibrium approach to describe interfaces in dynamic multiphase systems requires some typical practical procedures and implies a number of predictions which can be tested. In the thermodynamic characterization of interfaces of n -component systems, the two functions $\mu_n^s(T^s, \mu_1^s, \dots, \mu_{n-1}^s)$ and $\gamma(T^s, \mu_1^s, \dots, \mu_{n-1}^s)$ contain all the gauge-invariant thermodynamic information. Note that $\mu_n^s = \mu_n^s(T^s, \mu_1^s, \dots, \mu_{n-1}^s)$ is the condition for phase coexistence and does not contain any information about the structure of the interface. The gauge-invariant characterization of the interface structure is contained entirely in the pressure-like thermodynamic potential $\gamma(T^s, \mu_1^s, \dots, \mu_{n-1}^s)$ [24]. In experiments, the determination of the function $\mu_n^s(T^s, \mu_1^s, \dots, \mu_{n-1}^s)$ is a major challenge, but it can rely on decades of experience with the CALPHAD (CALculation of PHase Diagrams) method [29]. A number of experimental techniques for measuring the equilibrium interfacial tension $\gamma(T^s, \mu_1^s, \dots, \mu_{n-1}^s)$ exist. In Monte Carlo and molecular dynamics simulations [30,31], the calculation of chemical potentials can be based on the particle insertion method [32] in either of the bulk phases. The key equation of interfacial statistical mechanics provides the interfacial tension in the form of the anisotropic part of the stress tensor [14], $\gamma = -\frac{1}{4A} \sum_{i,j} (\mathbf{f}_{ij} \cdot \mathbf{r}_{ij} - 3\mathbf{n} \cdot \mathbf{f}_{ij} \mathbf{r}_{ij} \cdot \mathbf{n})$, where \mathbf{r}_{ij} gives the position of particle j with respect to the position of particle i , \mathbf{f}_{ij} is the force exerted by particle i on particle j , \mathbf{n} is a unit normal vector on the interface, and A is the area of the interface.

Once the functional forms of μ_n^s and γ are available, one needs to be able to identify the values of T^s , $\mu_1^s, \dots, \mu_{n-1}^s$ characterizing the state of an evolving interface at any time. For a single-component system, the local equilibrium interfacial tension $\gamma(T^s)$ can actually serve as a convenient thermometer to find T^s when calibrated with the equilibrium results for $\gamma(T)$. For multicomponent systems, the relationship between the excess densities needs to be

considered in addition. An unambiguous way of evaluating the chemical potentials is based on the invariant adsorptions $\Gamma_{jn}(T^s, \mu_1^s, \dots, \mu_{n-1}^s)$ relative to the n -th component [2], most conveniently calculated in the gauge $\rho_n^s = 0$.

After clarifying how the local equilibrium description of an interface can be handled and how the values of T^s , $\mu_1^s, \dots, \mu_{n-1}^s$ characterizing an evolving interface can be found, we can look at the observable predictions of assuming local equilibrium. The most impressive prediction is that the jump ratios in a nonequilibrium environment must be the same as in the corresponding equilibrium state of the interface. These jump ratios are actually given in eqs. (8). A test of the jump ratio relationships corresponds to a test of gauge invariance. We can further test the expressions for the excess densities in eqs. (7) in a particular gauge, most conveniently $\rho_n^s = 0$. Note that only eqs. (7a) and (7b) have predictive power because eq. (7c) has already been used to identify the values of the chemical potentials characterizing the state of the interface. In a computer simulation, the excess energy density is directly available so that eq. (7b) is tested most conveniently.

Conclusions. – The local equilibrium assumption for interfaces is an important ingredient to a transport theory of multiphase systems. Many aspects and implications of the implementation of local equilibrium for interfaces have been elaborated in the literature. In the present paper, we have strengthened the foundations of the local equilibrium assumption by using the principle of gauge invariance. The gauge transformations appearing naturally in a macroscopic theory of interfaces are the microscopic displacements of the interface, which change the excess densities in the interface but should not affect any thermodynamic properties. Gauge invariance suggests that the jumps of bulk densities across an interface are central to understanding local equilibrium of the interface.

We have compiled a number of consequences of the local equilibrium assumption which can be used to test its validity. Such tests are important because local equilibrium for interfaces is far from obvious for dynamic nonequilibrium systems. Particularly alarming is the existence of nonintegrable long-time tails in the velocity autocorrelation function for two-dimensional flows so that the regularization provided by the bulk environment is essential for avoiding singular interfacial transport properties (the interface would then be a so-called “quasi-two-dimensional” fluid; see ref. [33] and references therein). Using the property of local equilibrium for the interface between two bulk phases, we have seen that, in a single-component system, the knowledge of the interfacial tension and of the chemical potential as functions of the temperature gives a complete description of the thermodynamic properties of the interface in equilibrium as well as away from equilibrium. We have also given the generalization to multicomponent systems. Whereas the complete thermodynamic information about a bulk phase of a n -component system is contained in a single thermodynamic potential depending

on $n + 1$ variables, the complete gauge-invariant thermodynamic information about an interface is contained in two functions of n variables. The transparent combination of gauge-variant and -invariant thermodynamic information is given in eqs. (7), (8).

It lies in the nature of interfaces that they cannot be studied as isolated objects, so that experimental investigations of interfaces are difficult. Even the conceptually clear identification of purely interfacial properties is difficult. As interfacial properties are often measured under nonequilibrium conditions, the local equilibrium assumption can be extremely useful to extract valid equilibrium properties and to separate static and dynamic material properties in a meaningful way. For instance, according to the present results, there is no need to invoke a concept like a dynamic surface tension, different from the equilibrium one [34,35]. An apparent dynamic interface tension arises merely because the state variables of the interface depend on time.

One objective of this paper has been to show which set of experimental data is sufficient for a complete thermodynamic description of an interface both in equilibrium and in nonequilibrium situations. We also expect that our observations will be useful for studying transport phenomena into and through membranes [23]. Indeed, nonequilibrium interfacial thermodynamics will help to construct proper boundary conditions for such transport problems.

It is important to realize that at no instance in our arguments, the temperature or the chemical potentials of the interface are considered to be equal to either of the values in the adjacent phases when the system is not in equilibrium. Neither are the temperature and chemical potentials left and right of the interface equal to each other in nonequilibrium systems. The assumption that these properties are continuous through a nonequilibrium interface is very common. However, this paradigm is fundamentally incorrect.

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