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Adsorbate Interactions and Surface Excess Entropy

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Using the Gibbs definition of surface excess properties and classical statistics of the adsorbed molecules, it is shown that interactions between these molecules can in some cases increase the surface excess entropy. This is in contradistinction to the classical result for a field-free bulk phase gas, but similar to effects which are possible for quantum gases.

KEY WORDS: Surface; entropy; interactions; virial expansion.

1. INTRODUCTION

The entropy of a thermodynamic system is a convenient measure of the degree of order in the system. In the classical case the absolute entropy of a noninteracting collection of molecules is given by the Sackur–Tetrode equation and it becomes possible to relate departures from the ideal entropy to the intermolecular interactions. A well known result for the slightly imperfect classical gas is that any interaction between molecules—whether attractive, repulsive, or both—reduces the entropy of the gas, relative always to the entropy it would have at the same temperature and density but with no interactions.

In the case of a quantum gas more care is required to determine the effect on entropy of interactions between particles, since first the one-particle states and the symmetry requirements must be analyzed. If the entropy is developed in a power series in the particle density, each of the terms (beyond the first) typically contains both statistics effects and interaction effects.

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Recently Callaway[1] has pursued this question with regard to a high-temperature, low-density collection of electrons in a solid, with the electron interaction described by the Hubbard Hamiltonian. The resulting equations for the interaction effect on the entropy depend on band structure, but it was shown that for certain model band structures the leading term could be positive. If an interpretation in terms of order is forced, it would be necessary—under these conditions—to admit that the effect of the electron interactions is to increase the disorder in the system.

This somewhat surprising result raises the question of whether it is peculiar to the quantum system. One purpose of this report is to point out that there are, in a sense, classical analogs—strictly classical systems in which the low-density effect of interparticle interaction is an increase in system entropy. The clue is in the dependence of the quoted electron result on the one-particle band structure. The classical case mentioned at the outset refers to field-free particles restricted in their motion only to remain inside some volume V. If there were a more profound ordering effect on the single particles—analogous to the combined effects of quantum statistics and crystal lattice potentials—then it is conceivable that particle interaction could in part break up the order induced by the external field.

We present here the analysis of such a situation, and one of interest in its own right: the classical statistics of particles "adsorbed on" a surface. In this case it is the surface which provides the external field; there are undoubtedly other examples. In the following section we summarize the statistical thermodynamics of the surface phase, after Gibbs, and subsequently we specialize to a classical treatment of the entropy of the surface phase.

2. THERMODYNAMICS

The Gibbs approach to the concept of the surface phase is based on the comparison of an actual system (parameters T, V, μ, $\mathscr{A}$) with a hypothetical system which is identical to the actual one except that the surface interaction has been "switched off."[2] The (grand canonical) parameters of the hypothetical system are thus only T, V, and μ (temperature, volume, and chemical potential). The area $\mathscr{A}$ does not occur here. Extensive thermodynamic properties of the hypothetical reference system are identified by a superscript zero, while those of the actual system are unadorned with superscripts. In general these extensive properties differ; an exception is the independent variable $V = V^0$, and another special case is $\mathscr{A}^0 = 0$. For other extensive properties the difference defines the *surface excess property* and are identified by superscript σ. For example, the surface excess number of molecules and the surface excess entropy are given by

$$N^\sigma = N - N^0, \qquad S^\sigma = S - S^0 \tag{1}$$

It is traditional to denote by Γ (with no σ) the surface excess concentration,

$$\Gamma = N^{\sigma}/\mathcal{A} \tag{2}$$

In this approach Γ can be either positive or negative, depending on the interaction with the surface.

In the presence of the surface a new term must be incorporated into the basic equation for the differential of E, the internal energy:

$$dE = T\,dS - p\,dV - \varphi\,d\mathcal{A} + \mu\,dN \tag{3}$$

where p is the bulk phase pressure and φ is the "spreading pressure." Similarly we have for the Hemholtz free energy A and the Gibbs free energy G

$$\begin{aligned} dA &= -S\,dT - p\,dV - \varphi\,d\mathcal{A} + \mu\,dN \\ dG &= -S\,dT + V\,dp - \varphi\,d\mathcal{A} + \mu\,dN \end{aligned} \tag{4}$$

Integrating Eq. (3) at constant intensive variables gives

$$E = TS - pV - \varphi\mathcal{A} + \mu N \tag{5}$$

and consequently

$$G = N\mu - \varphi\mathcal{A} \tag{6}$$

It is important to recognize that the chemical potential is no longer just the Gibbs free energy per molecule.

We introduce statistical theory through the grand canonical ensemble:

$$\Xi(T, V, \mathcal{A}, \mu) = \sum_{N} Q_N(T, V, \mathcal{A})\,\lambda^N \tag{7}$$

where $Q_N = e^{-A/kT}$ is the canonical partition function and $\lambda = e^{\mu/kT}$. Through standard techniques—most easily by the maximum term method—it is found that the connection between Ξ and the thermodynamics is

$$\ln \Xi = (pV + \varphi\mathcal{A})/kT \tag{8}$$

The working equation for the surface-containing system is then

$$d(kT \ln \Xi) = S\,dT + p\,dV + \varphi\,d\mathcal{A} + N\,d\mu \tag{9}$$

The reference system—with the surface interaction switched off—is similarly described by

$$\ln \Xi^0 = pV/kT \tag{10a}$$

$$d(kT \ln \Xi^0) = S^0\,dT + p\,dV + N^0\,d\mu \tag{10b}$$

where the surface term is absent. With the view of obtaining virial expansions we introduce the activity series

$$V^{-1} \ln \Xi = \sum b_j \lambda^j \tag{11}$$

which parallels the usual expansion

$$V^{-1} \ln \Xi^0 = \sum b_j^0 \lambda^j \tag{12}$$

The coefficients b_j are functionally related to the canonical partition functions $Q_j(T, V, \mathcal{A})$ in exactly the same way the reference coefficients are related to surface-free canonical functions $Q_j^0(T, V)$.

By subtracting Eq. (12) from (11) and using Eqs. (8) and (10a), we have the activity expansion of the spreading pressure

$$\varphi/kT = (V/\mathcal{A}) \sum \hat{b}_j \lambda^j \tag{13}$$

where $\hat{b}_j \equiv b_j - b_j^0$. Similarly we find the activity expansion of Γ,

$$\Gamma = (V/\mathcal{A}) \sum j \hat{b}_j \lambda^j \tag{14}$$

In the usual way the activity λ is eliminated from Eqs. (13) and (14) to produce the virial expansion

$$\varphi/kT = \Gamma + \hat{B}_2(T)\,\Gamma^2 + \cdots \tag{15}$$

where

$$\hat{B}_2 = -(\mathcal{A}/V)\,\hat{b}_2/\hat{b}_1^2 \tag{16}$$

Higher order terms could also be obtained, but we stop with the first nonideal term. We have been following the notation and technique of Hill(2) thus far in this section.

In the following section we will employ these relationships to study the entropy of the "surface phase"—more correctly, the surface excess entropy. Here, however, we wish to show the basis for the statements made earlier about the entropy of the slightly imperfect bulk phase gas. Standard thermodynamic arguments show that for any gas the entropy is given by see, e.g., Ref. 3)

$$S(T, V, N) = S(T, V, N)_{\text{ideal}} + \int_V^\infty \left[\frac{Nk}{V'} - \left(\frac{\partial p}{\partial T}\right)_{V,N}\right] dV' \tag{17}$$

(We are suppressing the superscript zero since the remainder of this section is devoted entirely to the surface free case.)

We now introduce the usual virial expansion for the bulk gas,

$$p/kT = \rho + B_2(T)\,\rho^2 + \cdots \tag{18}$$

which is analogous to Eq. (15). Here $\rho = N/V$ is the number density. If If $\Delta S = S - S_{\text{ideal}}$, we have from Eqs. (17) and (18)

$$\begin{aligned}\Delta S &= -\int_V^\infty [(N^2k/V'^2)(B_2 + T\,\partial B_2/\partial T) + \cdots]\,dV' \\ &= -(N^2k/V)(B_2 + T\,\partial B_2/\partial T) + \cdots \qquad (19)\end{aligned}$$

where the higher-order terms may be omitted if V is sufficiently large. Thus far the argument is general, but at this point we assume that the molecules may be described classically—at least insorfar as their relative motion is concerned. In that case the second virial coefficient has the form

$$B_2(T) = -(2\Omega)^{-1}\int f_{12}\,d\mathbf{R}_{12} \qquad (20)$$

where $\mathbf{R}_{12}$ stands for the position and orientation (if not monatomic) of molecule 2 relative to molecule 1. The factor Ω arises from the integration over the orientations of a single molecule. In any event, the integrand is

$$f_{12} = \exp[-U(\mathbf{R}_{12})/kT] - 1 \qquad (21)$$

where U is the interaction potential.

With Eqs. (20) and (21) we may evaluate the leading term in the series (19), since

$$B_2 + T\,\partial B_2/\partial T = -(2\Omega)^{-1}\int [e^{-y} - 1 + ye^{-y}]\,d\mathbf{R}_{12} \qquad (22)$$

where $y = U/kT$. But the integrand $e^{-y} - 1 + ye^{-y}$ is nowhere positive, so the integral is negative and so is ΔS, whether U is attractive, repulsive, or some combination of both.

3. SURFACE EXCESS ENTROPY

Our goal now is to obtain equations analogous to Eqs. (17) and (19) for the surface excess entropy S^σ, with ρ replaced by Γ. To this end, Eqs.((9)–(12) result in

$$\begin{aligned}S^\sigma &= (\partial/\partial T)(kTV \textstyle\sum \hat{b}_j\lambda^j) \\ &= kV \textstyle\sum [\hat{b}_j + T\hat{b}_j' - (\mu/kT)\,j\hat{b}_j]\,\lambda^j \\ &= kV \textstyle\sum (\hat{b}_j + T\hat{b}_j')\,\lambda^j - \alpha\Gamma\mu/T \qquad (23)\end{aligned}$$

where Eq. (14) has been used to effect the last step. The prime denotes the temperature derivative.

The next step is to invert Eq. (14) to obtain a Γ expansion of λ to insert in Eq. (23). Since also $\mu/T = k \ln \lambda$, it is possible to develop the entire right-hand side of Eq. (23) as a function of the surface concentration Γ. The result, through the second-order terms $j = 2$, is

$$S^{\sigma} = S^{\sigma}_{\text{ideal}} + (\mathscr{A}^2\Gamma^2 k/V)\mathscr{S} \tag{24}$$

where

$$S^{\sigma}_{\text{ideal}} = kV(\hat{b}_1 + T\hat{b}_1{}')(\mathscr{A}\Gamma/V\hat{b}_1) - \mathscr{A}\Gamma k \ln(\mathscr{A}\Gamma/V\hat{b}_1) \tag{25}$$

and

$$\mathscr{S} = (\hat{b}_1\hat{b}_2 - 2\hat{b}_2 T\hat{b}_1{}' + \hat{b}_1 T\hat{b}_2{}')/\hat{b}_1{}^3 \tag{26}$$

Equations (24)–(26) for the surface entropy are general and independent of the mechanics obeyed by the molecules, as are the relationships to canonical partition functions:

$$\begin{aligned} \hat{b}_1 &= (Q_1 - Q_1{}^0)/V \\ \hat{b}_2 &= \{(Q_2 - Q_1{}^2/2) - [Q_2{}^0 - (Q_1{}^0)^2/2]\}/V \end{aligned} \tag{27}$$

To proceed further, we make some simplifying assumptions. The first is that we are dealing with a monatomic gas which may be described classically. We assume furthermore that the potential energy of a configuration of molecules may be represented additively by a one-body interaction with the surface $[u^*(\mathbf{r}_i) \equiv u_i{}^*]$ and pair interactions between molecules $[u(\mathbf{r}_{ij}) \equiv u_{ij}]$. We will also need to assume that both potentials u^* and u vanish for large arguments sufficiently rapidly for certain integrals (of Mayer functions) to converge and be volume independent.

Under these assumptions the momentum contributions to the interaction term $\mathscr{S}$ all cancel and will henceforth be suppressed altogether. The remaining (configurational) factors are readily found to be

$$\begin{aligned} \hat{b}_1 &= V^{-1} \int f_1{}^* \, d\mathbf{r}_1 \\ \hat{b}_2 &= (2V)^{-1} \iint f_{12} f_{12}^* \, d\mathbf{r}_1 \, d\mathbf{r}_2 \end{aligned} \tag{28}$$

where $f_1{}^* = \exp(-\beta u_1{}^*) - 1$, $f_{12}^* = \exp[-\beta(u_1{}^* + u_2{}^*] - 1$, and $f_{12} = \exp(-\beta u_{12}) - 1$, with $\beta = 1/kT$. Additionally the temperature derivatives are given by

$$\begin{aligned} T\hat{b}_1{}' &= V^{-1} \int \beta u_1{}^*(f_1{}^* + 1) \, d\mathbf{r}_1 \\ T\hat{b}_2{}' &= (2V)^{-1} \iint [\beta u_{12}(f_{12} + 1) f_{12}^* \\ &\qquad + \beta u_{12}^* f_{12}(f_{12}^* + 1)] \, d\mathbf{r}_1 \, d\mathbf{r}_2 \end{aligned} \tag{29}$$

where $u_{12}^* = u_1{}^* + u_2{}^*$.

If Eqs. (28) and (29) are inserted in Eq. (26), the result is the desired analog of the bulk phase formulas (19) and (22). It is, however, considerably more complex and no obvious statements about the sign of the interaction term $\mathscr{S}$ present themselves. We can, in fact, see that $\mathscr{S}$ can have either sign by considering the high-temperature, weak-interaction limit. That is, we suppose that $\beta u_1{}^* \ll 1$ and $\beta u_{ij} \ll 1$, so that $f_i{}^* \approx \beta u_i{}^*, f_{ij}^* \approx \beta u_{ij}^*$, and $f_{ij} \approx \beta u_{ij}$. Making these substitutions in the preceding equations leads in a straightforward way to the simple result

$$\mathscr{S} = \tfrac{1}{2} \iint u_{12}(u_1{}^* + u_2{}^*)\, d\mathbf{r}_1\, d\mathbf{r}_2\, V\Big(\int u_1{}^*\, d\mathbf{r}_1\Big)^2 \tag{30}$$

Supposing $u_i{}^*$ to be negative everywhere (so that $\Gamma > 0$), it is clear that $\mathscr{S}$ is positive if u_{12} is everywhere—or predominantly—negative.

4. DISCUSSION

We have shown that it is possible for the interaction entropy to be positive for a classical gas in the vicinity of an attracting surface. To obtain this result, it is necessary to approach the surface excess properties from the Gibbs point of view. If the surface phase were described in an *ad hoc* fashion as a two-dimensional system,(2) this conclusion could not be reached. The earlier discussion of the three-dimensional bulk phase gas would apply equally well and the two-dimensional interaction entropy would necessarily be negative. It may be true that physically reasonable forms of the potentials $u_i{}^*$ and u_{ij} would produce negative values for $\mathscr{S}$. On the other hand, a heuristic explanation of the positive $\mathscr{S}$ for attractive interactions seems valid: The "accessible" volume near the surface available to molecule 2 is extended to include the region near molecule 1, if the interactions are predominantly attractive. This greater "accessible" region of favorable energy is tantamount to increased entropy.

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NOTE ADDED IN PROOF

Professor H. S. Leff has kindly pointed out that he has proved more generally [*Am. J. Phys.* **37**, 548 (1969)] the negative effect of interactions on entropy, in the field-free case. Classical mechanics is assumed, but not low density.

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