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# Geometric thermodynamic fields and the generalized ensemble in colloidal physics

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The statistical geometry of hard-sphere mixtures, as defined by Speedy and Reiss, is found to lead to a sum rule that is identical in form to the fundamental equation of the generalized ensemble. This leads one to conjecture the specific form of a set of thermodynamic fields entirely defined by ensemble averages of geometric properties of the configurations. The potential for a direct physical understanding of these quantities is discussed and it is noted that they could, therefore, be of crucial significance to our future understanding of colloidal physics. In the presence of an ideal wall, an analogous sum rule is obtained in terms of interfacial geometric properties (the available surface area for insertions at the wall). For this case, which generalizes beyond hard-sphere models, there exists an obvious physical interpretation involving complete wetting at the ideal wall.

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Colloidal science is a large area that includes significant interest in nanoscience, biophysics, and fluid interfacial phenomena. The aspect of this science which one might define as "colloidal physics" is focused on the phase behavior of model colloidal systems. Solvated mixtures of hard spheres have played a key role in the definition of physical phenomena such as the phase behavior of polydisperse systems, and the depletion interaction of solvated colloidal particles (both with each other and with bounding surfaces). The seminal model is the hard-sphere fluid, for which there are strong arguments implying that it undergoes a first-order transition from liquid to solid at a particular density, for purely geometric reasons ("free volume").

The first step towards an understanding of the phase behavior is to identify the thermodynamic fields appropriate to the model. A thermodynamic field is an intensive property that is always identical amongst different phases that are in statistical-mechanical equilibrium; temperature $T$, pressure $p$, and chemical potentials $\mu_\nu$ are the standard thermodynamic fields of bulk matter. A thermodynamic field must remain fixed throughout a region of phase coexistence belonging to a first-order phase transition. For each field, there is an associated extensive variable (energy, volume, and particle number) and the different ensembles of statistical mechanics are distinguished by the different choices of fields versus extensive variables that are deemed to be fixed. The ensemble of preference for describing a macroscopic subsystem of a complex fluid, such as an interfacial region, is the grand ensemble, where the subvolume is the only specified extensive variable. The remaining specified variables, are therefore, a set of independent thermodynamic fields; their independence in the grand ensemble being equivalent to the Gibbs phase rule. However, as proposed by Guggenheim [1] and discussed in detail by Hill [2], one can go further and define a generalized ensemble, whose free energy is specified in terms of an overdetermined set of thermodynamic fields alone. For a single-component system, the free-energy of the generalized ensemble is treated as a function of $T, p, \mu$, and no extensive variable. Hill regards the generalized ensemble as the prototype of all others, the subsystem in thermal, mechanical, and chemical equilibrium. Its use is limited by problems arising from the specification of one more thermodynamic field than is allowed by the Gibbs phase rule. In particular, it would appear that one must first identify the fundamental equation of the generalized ensemble, expressing the relationship between the thermodynamic fields implied by the Gibbs phase rule, before one can then extract the average extensive properties from sum rules [2].

Founding the subject of "statistical geometry," Speedy [3] and Reiss [4] have given geometric interpretations of the thermodynamic fields of the hard-sphere model; as was apparently understood by Boltzmann [5]. This model has effectively one less thermodynamic field than general, with the temperature appearing only as a factor $\beta \equiv 1/k_B T$ ($k_B$ denotes Boltzmann's constant) of the relevant fields $\beta p$, $\beta\mu$. The extension of statistical geometry to hard-sphere mixtures has been discussed by Corti and Bowles [6,7]. With reference to Fig. 1, interpreted for three-dimensional space $D=3$, let us define the geometric quantity

$$\zeta_\nu \equiv (6V_o^\nu + \sigma_\nu S_o^\nu)/6V, \tag{1}$$

where $V$ is the system volume and $\sigma_\nu$ is the diameter of the spheres of component $\nu$. The probability of insertion of a test sphere of component $\nu$, namely $V_o^\nu/V$, defines the chemical potential of this component through Widom's potential distribution theorem [8] or its even earlier appearance in scaled-particle-theory [9]:

$$\rho_\nu \Lambda_\nu^3 e^{-\beta\mu_\nu} = \frac{V_o^\nu}{V}, \tag{2}$$

where $\rho_\nu$ and $\Lambda_\nu$ are the number density and thermal deBroglie wavelength of component $\nu$, respectively. This insertion probability must also be the Boltzmann factor of the work done on the system to insert the test sphere, which can be readily calculated in the grand ensemble via the functional derivative $\delta\Omega/\delta v_{\nu'}^{ext}(\mathbf{r}) = \rho_{\nu'}(\mathbf{r})$, where $v_{\nu'}^{ext}$ denotes the external field generated by an inserted $\nu$-sphere on species $\nu'$, [10]. In particular, one can use this to evaluate the derivative of $V_o^\nu$ with respect to the radius of the test sphere, which from Fig. 1 is simply $-S_o^\nu$. Thus, one arrives at the following geo-

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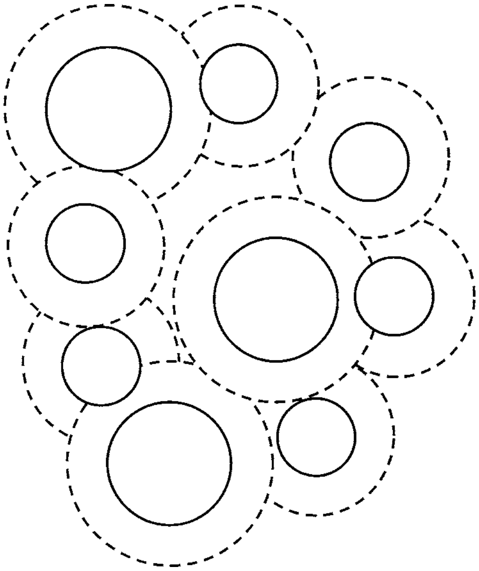

FIG. 1. Snapshot of a tiny region of a molecular or colloidal mixture. The solid circles (spheres, in three-dimensions) depict the basic colloidal model of a hard-sphere mixture. The dashed circles denote regions of phase space (for this instant in time) that are excluded to the center of a test sphere, that one imagines wishing to insert into the colloidal mixture (for the case drawn, the test sphere is identical to the smaller spheres). Within the region drawn one can readily distinguish an "accessible" volume in which such an insertion is possible, defined by that part not overlapped by the dashed circles (spheres, in three-dimensions). The ensemble averages of the total amount of accessible volume and its associated surface area, for insertion of component $\nu$, are denoted $V_o^\nu$ and $S_o^\nu$, respectively.

metric interpretation of the fundamental relation of scaled-particle-theory [11,6]:

$$\frac{S_o^\nu}{V_o^\nu} = 4\pi\sigma_\nu^2 \rho_\nu y_{\nu\nu} + 4\pi \sum_{\nu' \neq \nu} \left(\frac{\sigma_\nu + \sigma_{\nu'}}{2}\right)^2 \rho_{\nu'} y_{\nu\nu'}, \qquad (3)$$

where $y_{\nu\nu'}$ denotes the contact value of the radial-distribution function of a pair of hard-spheres $\nu\nu'$. This result is far more general than what we require below, because with a little thought one realizes that the above derivation does not require any specification of the interactions between the fluid molecules; only the hard-cavity interaction of each species with the test sphere is required. For example, if we replace the solid spheres drawn in Fig. 1 with just their centers, while keeping the dashed spheres (the cavities) in place, then these centers could label any part of a complex molecular structure. Thus, test cavities can be used to define a geometry of any molecular system, in whatever manner we wish to specify. However, in this paper, we require the test cavities to be, in turn, the species of the mixture, so that (2) defines the chemical potentials of the model. Furthermore, one can then introduce the pressure from the hard-sphere-mixture virial equation of state [12]:

$$\beta p = \sum_\nu \rho_\nu + \frac{2\pi}{3} \sum_\nu \sum_{\nu'} \left(\frac{\sigma_\nu + \sigma_{\nu'}}{2}\right)^3 \rho_\nu \rho_{\nu'} y_{\nu\nu'}. \qquad (4)$$

When (3) is then inserted into the virial equation to eliminate $\rho_\nu y_{\nu\nu}$ one sees trivially that the off-diagonal terms $\nu' \neq \nu$ cancel exactly, leaving the simple result [7]

$$\beta p = \sum_\nu \rho_\nu \left[1 + \frac{\sigma_\nu S_o^\nu}{6V_o^\nu}\right]. \qquad (5)$$

Finally, using (2) to eliminate the densities $\rho_\nu$ from Eq. (5), one arrives at a result of a remarkable character that in the grand ensemble is naturally written as [13]:

$$\beta p V = \ln \Xi = \sum_\nu \frac{e^{\beta\mu_\nu}}{\Lambda_\nu^3} \zeta_\nu V. \qquad (6)$$

Alternatively, this sum rule can be expressed in the form

$$\sum_\nu \zeta_\nu \frac{e^{\beta\mu_\nu}}{\beta p \Lambda_\nu^3} = 1, \qquad (7)$$

which is highly suggestive of the fundamental equation of the generalized ensemble [2]; in particular, this equivalence certainly applies in the ideal-gas limit $\zeta_\nu \rightarrow 1$.

For the single-component case, it follows directly from (7) that the geometric quantity $\zeta$ is a thermodynamic field; this result constitutes the "magic relation" of Reiss [4]. There exist strong arguments for believing that pure hard-sphere fluid undergoes a first-order phase transition to a solid, well before the random closed-packed jamming limit. For the general hard-sphere or colloidal mixture, fluid-fluid and solid-solid phase transitions are also anticipated. Key issues in colloidal science such as the role of the depletion interaction and the effects of polydispersity are contained within this class of models. It would therefore be of some importance if one could decide whether or not (7) in the case of mixtures is associated with every $\zeta_\nu$ being a thermodynamic field. This would have to follow if one could argue that (7) really was the fundamental relation of the generalized ensemble, since each term would have to contain nothing but thermodynamic fields (no extensive quantities are specified in this ensemble). If one then worked back down beyond (6) to the canonical ensemble then one would have identified the partition function of the canonical ensemble as (see the Appendix)

$$Q = \prod_\nu \frac{V^{N_\nu} \zeta_\nu^{N_\nu}}{N_\nu! \Lambda_\nu^{3N_\nu}}. \qquad (8)$$

In which case $\zeta_\nu$ are phase-space reduction factors. If the above discussion is generalized to arbitrary dimension $D$ then the factor 6 appearing in (1) is readily seen to be 2D in the general case [14]. Note that the reduction in available phase space is not simply the reduction in available space for insertion $V_o^\nu/V$, instead one must include an additional volume ratio $\sigma_\nu S_o^\nu/2DV$. One might hope to be able to identify a "physical" reason for this correction directly from (8) [15].

Let us now consider the statistical geometry in the presence of an ideal boundary; a semi-infinite planar hard wall.

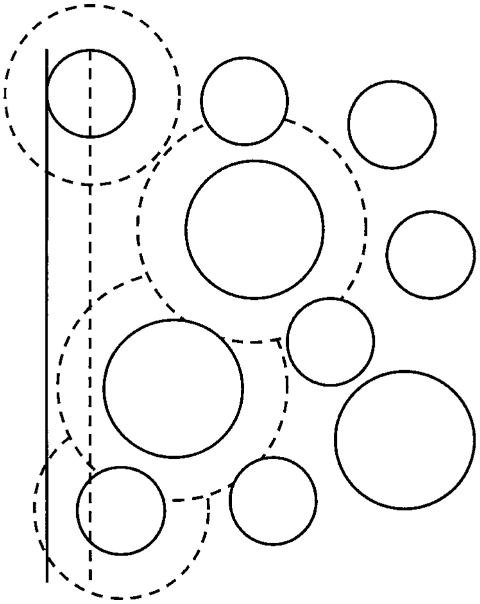

FIG. 2. Another snapshot of a tiny region of the system defined in Fig. 1, but this time in the vicinity of an ideal boundary wall (a hard wall). In this situation one is particularly interested in the insertion of a test sphere at the hard wall (compare with the top left sphere). Accordingly, the figure only shows the dashed exclusion zones (see caption to Fig. 1) formed from particles that are neighbors of the ideal wall. For this configuration one observes a region of an accessible wall area, just below the sphere at the wall. The ensemble average of the total amount of this accessible area, for the insertion of component $\nu$, is denoted $S_{ow}^{\nu}$.

In this situation one can re-express the virial equation for the pressure purely in terms of the density at the wall:

$$\beta p = \sum_{\nu} \rho_{\nu}^{w}, \tag{9}$$

where, hereafter, subscript or superscript $w$ will denote a property at the wall. From Fig. 2 it follows that the probability of a particle insertion at the wall is the geometric quantity

$$\zeta_{\nu}^{w} \equiv \frac{S_{ow}^{\nu}}{A}, \tag{10}$$

which must be equivalent to the lefthand-side of the potential distribution theorem (2), applied at the wall. Using this result to eliminate the densities $\rho_{\nu}^{w}$ from the wall virial, Eq. (9) leads directly to the sum rule

$$\sum_{\nu} \zeta_{\nu}^{w} \frac{e^{\beta\mu_{\nu}}}{\beta p \Lambda_{\nu}^{3}} = 1. \tag{11}$$

Once again we appear to have arrived at the fundamental equation of the generalized ensemble, in which case each $\zeta_{\nu}^{w}$ is a thermodynamic field. In contrast to (7) there is an obvious, although startling, physical interpretation of this conjecture. Namely, if any one of a set of coexisting phases completely wets the ideal wall, then in the approach to a first-order bulk transition one would find the growth of a macroscopic amount of this wetting phase appearing at the wall. It is trivial from Fig. 2 that each $\zeta_{\nu}^{w}$ cannot then vary across the bulk phase-coexistence region of phase space. Considering the multitude of potential phases present in a polydisperse mixture, the conclusion that one of them must completely wet the wall is far from obvious [16]. Furthermore, one need not restrict this conjecture to hard-sphere mixtures; for example, adding sphere-sphere (but not wall-sphere) attractions to the model only results in an additional factor $\langle \exp(-\beta\psi_{att}) \rangle_{w\nu}$ to $\zeta_{\nu}^{w}$. Here, the subscript denotes the presence of a hard cavity on the wall, $\psi_{att}$ is the attractive energy that a particle of type $\nu$ would experience if inserted into this cavity, and the angular brackets denote an ensemble average in the presence of the cavity, [8,10]. Similarly, note that each $\rho_{\nu}^{w}$ is a field whenever $\zeta_{\nu}^{w}$ is, since $\zeta_{\nu}^{w} = \rho_{\nu}^{w} \Lambda_{\nu}^{3} e^{-\beta\mu_{\nu}}$. Again, if at phase coexistence one of the phases must always completely wet the ideal wall, then any interfacial geometric quantity such as $\zeta_{\nu}^{w}$ or $\rho_{\nu}^{w}$ must be a thermodynamic field at bulk phase transitions. For single-component systems, this extreme conclusion is supported by the little evidence available. For phase coexistence involving a vapor it is most likely that the vapor will always completely wet (i.e., dry) the hard wall; see (9) and note that the second virial coefficient of the pressure will be negative for coexistence with a vapor [17]. Also, there is numerical evidence for concluding that hard-sphere solid completely wets a hard wall in the presence of its melt [18]. In such cases, ideal walls, often assumed to be the boundary condition of choice for a canonical ensemble, are a special case demanding careful handling in the presence of bulk phase coexistence.

In conclusion, for bulk hard-sphere fluid and any pure fluid at a planar ideal wall, statistical geometry provides us with fascinating examples of geometric thermodynamic fields. This paper has proved that the analogous extensions to multicomponent systems take an identical form to the fundamental equation of the generalized ensemble in the ideal-gas limit. The conjecture that this correspondence is general should be equivalent to the conjecture that each geometric quantity $\zeta_{\nu}$ or $\zeta_{\nu}^{w}$ is a thermodynamic field. If so, the implications for geometric constraints that must hold at phase transitions in colloidal systems is remarkable. Notwithstanding, until a proof of this interpretation of (7) and (11) can be supplied, geometric thermodynamic fields and indeed the generalized ensemble, remain enigmatic topics of equilibrium statistical mechanics that on the one hand appear to promise much but on the other hand have yet to deliver this promise.

## APPENDIX

Provided each $\zeta_{\nu}$ is a thermodynamic field and hence independent of the number densities at fixed temperature and chemical potentials, one can transform Eq. (6) as follows:

$$\Xi = \prod_{\nu} \exp\left\{ \frac{e^{\beta\mu_{\nu}} V \zeta_{\nu}}{\Lambda_{\nu}^{3}} \right\}, \tag{A1}$$

$$= \prod_{\nu} \sum_{N_{\nu}} \frac{1}{N_{\nu}!} \frac{e^{\beta N_{\nu}\mu_{\nu}} V^{N_{\nu}} \zeta_{\nu}^{N_{\nu}}}{\Lambda_{\nu}^{3N_{\nu}}}, \tag{A2}$$

$$=\sum \cdots \sum_{\{N_\nu\}} \cdots \sum e^{\beta \Sigma_\nu N_\nu \mu_\nu} Q. \tag{A3}$$

This identification of the canonical ensemble partition function $Q$ is rigorous only for the single-component limit; for mixtures we have had to conjecture that each $\zeta_\nu$ is a thermodynamic field. Note that Eq. (8) is still not a product of independent terms since each $\zeta_\nu$ is a function of all the others; i.e., a function of all of the chemical potentials not just $\beta\mu_\nu$. Similarly, from Fig. 1 one notes that each $\zeta_\nu$ is a geometric property of the total mixture, not of an individual component.

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[14] This result comes entirely from the virial equation for the pressure (4); the factor $D$ arises from the $L^D$ scaling in the volume ($DpV$ on the left of the virial equation) while factor 2 arises from the pair-potential form of the configurational virial.

[15] Reiss [4] notes that $\sigma_\nu/2D$ is also the ratio of the volume to the surface area of $D$-sphere $\nu$, which, in fact, is his justification for ascribing "magic" to the relationship with thermodynamic fields.

[16] In fact, the "curious" layering transitions of the Asakura-Oosawa-Vrij model at a hard wall would appear to be a different class altogether; see J. M. Brader, R. Evans, and M. Schmidt, Mol. Phys. **101**, 3349 (2003); M. Dijkstra and R. van Roij, J. Phys.: Condens. Matter **17**, S3507 (2005). If so, it is still possible to conjecture that each $\zeta_\nu^w$ is a thermodynamic field, but only at the expense of declaring them magic relations applicable to interfacial phase transitions.

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