



## Maximal cell density predictions for compressible polymer foams

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### ABSTRACT

Thermodynamic upper bounds for polymer foam cell densities are predicted using compressible self-consistent field theory. It is found that the incompressible limit always gives the highest, and therefore ultimate, upper bound. Qualitative comparisons between the compressible and incompressible cases agree, indicating that low temperatures and high blowing agent content should be used to achieve high cell densities. The inhomogeneous bubble structure reveals deviations from the expected homogeneous Sanchez–Lacombe equation of state, consistent with some experimental results. A generalized Sanchez–Lacombe equation of state is discussed in the context of its suitability as a simple alternative to the Simha–Somcynsky equation of state.

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### 1. Introduction

Polymer foams have found many applications in fields such as transportation, packaging, construction, consumer goods and many other areas [1]. New applications continue to be found, and there is particular economic and technological interest in advanced, high quality foams. These typically have bubble sizes on the order of microns or nanometers and can have superior properties compared to conventional polymer foams. The creation of such advanced micro- or nano-cellular foams is, however, a non-trivial task and many different techniques and chemistries are being explored to this end. To rationalize and reduce the scope of this search, it is desirable to have a method of determining whether a given combination of polymer and blowing agent under particular thermodynamic conditions is likely to be able to produce a foam of a desired quality, independent of the technique used to generate the foam. Such a method would not guarantee that the desired foam could necessarily be achieved, but it could provide evidence that a foam of a prescribed cell density is at least thermodynamically possible for given choices of polymer and blowing agent.

Recently, we introduced a method of predicting the maximum cell density of foams based on self-consistent field theory (SCFT)

[2]. The method didn't predict an absolute cell density, but rather provided an upper bound that, from a thermodynamic perspective, real foams would be unlikely to exceed. One would expect that actual foams would in fact have cell densities significantly lower than the predicted maximum, due to important kinetic and processing issues. Polymer foaming is after all a non-equilibrium process and the SCFT method is an equilibrium model. Nonetheless, one can use SCFT for polymer foaming as has been argued in Refs. [3,4]. Our method was not quantitative however but rather provided only qualitative guidance such as finding that foaming should take place at as low a practical temperature as possible, that the maximum amount of blowing agent that doesn't cause spinodal decomposition should be used, and that polymer surface tension is not always an important factor in predicting cell densities [2]. The root of the qualitative nature of our predictions was that we used, for simplicity, an incompressible model of polymer foaming. This is far from realistic, but there is evidence that such an approach can be used to give reliable qualitative predictions [5–7].

In this paper, we drop the incompressible limitation in order to explore the extent to which compressibility affects our previous qualitative predictions. We find that all our previous predictions continue to be valid and, what's more, that the incompressible case does indeed set the thermodynamic upper bound on polymer foam cell densities. In addition, we are able to comment on the limitations of the Sanchez–Lacombe equation of state and we speculate on how it might be easily adapted to become competitive with the Simha–Somcynsky equation of state. The results we present in this

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work are a qualitative demonstration of the approach, but the methodology can be made quantitative under certain conditions.

## 2. Theory

We describe a compressible mixture of monodisperse polymer and either gas or super-critical fluid using a hole-based self-consistent field theory (SCFT). In hole theories, a compressible formalism is achieved by representing voids in the mixture as particles that occupy some space. These fictitious particles have no energetic interactions with any of the true chemical species but contribute only translational entropy to the problem. An appropriate choice of the volume for the hole particles allows this entropy to produce the experimentally expected equation of state (EOS) – more holes correspond to lower pressure and fewer holes correspond to higher pressure. The hole-based SCFT that we use in this work was first introduced by Hong and Noolandi [8]. As there are many very good reviews of SCFT, such as Refs. [9,10], we will not present the details of SCFT here but rather refer the reader to our previous works for incompressible [2,3] and compressible [6,11] polymer foams. The SCFT model for a compressible polymer solvent system can however be summarized by the free energy functional

$$\begin{aligned} \tilde{F} \equiv \frac{NF}{\rho_0 k_B T V} = & -\phi_p \ln \left( \frac{Q_p}{V \phi_p} \right) - \frac{\phi_s}{\alpha_s} \ln \left( \frac{Q_s}{V \phi_s} \right) - \frac{\phi_h}{\alpha_h} \ln \left( \frac{Q_h}{V \phi_h} \right) \\ & + \frac{1}{V} \int d\mathbf{r} \left[ \chi_{ps} N \phi_p(\mathbf{r}) \phi_s(\mathbf{r}) + \frac{1}{2} \chi_{pp} N \phi_p(\mathbf{r}) \phi_p(\mathbf{r}) \right. \\ & + \frac{1}{2} \chi_{ss} N \phi_s(\mathbf{r}) \phi_s(\mathbf{r}) - w_p(\mathbf{r}) \phi_p(\mathbf{r}) - w_s(\mathbf{r}) \phi_s(\mathbf{r}) \\ & \left. - w_h(\mathbf{r}) \phi_h(\mathbf{r}) \right]. \end{aligned} \quad (1)$$

In Equation (1),  $\phi_p(\mathbf{r})$ ,  $\phi_s(\mathbf{r})$  and  $\phi_h(\mathbf{r})$  are the local (position dependent) volume fractions of polymer, gas (or fluid), and holes, respectively. The subscript “s” is used for the gas volume fraction since it is customary in SCFT to refer to molecules lacking polymeric internal degrees of freedom as “solvent” molecules. We will continue to use this term in this paper. The total system volume fractions for polymer, solvent and holes are  $\phi_p$ ,  $\phi_s$  and  $\phi_h$ , respectively, and single molecule partition functions are given by  $Q_p$ ,  $Q_s$  and  $Q_h$ , respectively. The ratio of the volume of a solvent molecule to a polymer molecule is denoted by  $\alpha_s$  and that of a hole to a polymer molecule is  $\alpha_h$ . The volume of one polymer segment is designated as  $\rho_0^{-1}$  and the degree of polymerization is  $N$ . The segregation between polymer segments, solvent molecules and holes would normally be specified using Flory–Huggins parameters  $\chi_{ps}$ ,  $\chi_{ph}$  and  $\chi_{sh}$ , but we find this misleading as the holes don’t actually interact with polymer or solvent. Instead, we follow our previous convention [11] and use the parameters  $\chi_{ps}$ ,  $\chi_{pp}$  and  $\chi_{ss}$  for polymer–solvent, polymer–polymer and solvent–solvent interactions, respectively. These parameters are related to the chemistry of the polymer and solvent molecules and are also inversely proportional to temperature  $T$ . Following Ref. [11], we assume a dimensionless temperature dependence for each  $\chi$  (or more conveniently, the product  $\chi N$ ) of

$$\chi N = \frac{A}{T} + B \quad (2)$$

where we chose  $A_{ps} = 270$ ,  $A_{pp} = -12$ ,  $A_{ss} = 0$  and all  $B$ ’s as zero. The mean fields felt by each polymer segment, solvent molecule or hole due to interactions with all other segments, molecules and holes in

the system are given by  $w(\mathbf{r})_{p, s \text{ or } h}$ . The left hand side of Equation (1) is the system free energy ( $F$ ) per system volume ( $V$ ), made dimensionless using appropriate factors. In this work, all lengths are phrased in terms of the radius of gyration of a polymer,  $R_g$ . Variation of Equation (1) with respect to all functions yields a set of coupled, non-linear equations to be solved self-consistently. The hole formalism allows one to complete the set of equations with the expression

$$\phi_p(\mathbf{r}) + \phi_s(\mathbf{r}) + \phi_h(\mathbf{r}) = 1. \quad (3)$$

The SCFT equations are solved numerically as described in previous work [3,6,7,11]. For any given hole volume fraction and box size, the sample pressure can be calculated using the formula

$$P = - \left( \frac{\partial F}{\partial V} \right)_{n_p, n_s, T} \quad (4)$$

where  $n_p$  and  $n_s$ , the number of polymer and solvent molecules in the volume  $V$ , are held constant.

The formalism is used in a way that parallels Ref. [2]. We choose close-packed polymer and solvent volume fractions for the incompressible case,  $\phi_p^0$  and  $\phi_s^0$ , and change the size of the calculational volume  $V$  to find the maximum cell density. The definition of the cell density is given in the next paragraph. We then add holes by increasing the hole volume fraction  $\phi_h$  from zero. This means that  $\phi_p$  and  $\phi_s$  will have to change for Equation (3) to be satisfied, but the ratio of  $\phi_p$  to  $\phi_s$  must remain the same as the ratio  $\phi_p^0$  to  $\phi_s^0$ . The volume  $V$  is varied again to find the maximum cell density for this choice of  $\phi_h$ . This procedure is repeated for a range of hole volume fractions, in other words, for a range of sample volumes.

The calculation is done in spherical coordinates with only one bubble in the volume  $V$ , so the bubble will naturally centre itself within the spherical coordinates in order to minimize the free energy [12]. This is depicted schematically in Fig. 1(a) with a data plot of a radial cross section of the system shown in Fig. 1(b). The volume  $V$  is then the average volume per bubble. The typical cell number density is thus the inverse of  $V$ , at least in principle. One can choose to define the cell density as the number of cells per unit volume or the number of cells per unit volume of polymer [13]. We chose the latter in Ref. [2] and we follow this convention again in this work. Therefore the cell density is defined as the inverse of the product of the calculational box volume times the overall polymer volume fraction. This gives us the best possible cell density for a given amount of solvent and holes. Our method is not able to account for kinetic phenomena, bubble polydispersity and other experimental realities, so our predictions must be viewed as upper limits on possible cell densities. The maximum cell density will typically be found at the smallest possible bubble radius for any given  $\phi_s$  and  $\phi_h$ , that is, at the critical radius. Paralleling our previous article however, one can also find maximum cell densities for other criteria such as the cell density corresponding to the maximum amount of bubble surface area per volume of foam or to the smallest radius cell that completely excludes polymer from its interior. Specifically, the first of these cases, the critical radius of the bubble, is considered to be the smallest radius that our SCFT computation predicts is stable. Smaller than this radius, the bubble structure will collapse during computation and a uniform mixture is predicted. For the second case, the surface area of a bubble can be found given the bubble radius. We give an SCFT definition of bubble radius in a previous work [3], and this allows us to predict the bubble area for a given calculation volume, specifically, the bubble area to volume ratio. The radius of this maximum is, surprisingly, not necessarily the critical radius. Thirdly, the local volume fractions of each chemical species are outputs of the SCFT, so it is

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