

How to think about the $N = 1$ convention and other dimensionless numbers in SCFT

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1 Overview

The SCFT equations implemented in PSCF are not in any preferred set of units. For comparison to experiments, this is very straightforward. You can use a good set of units (e.g., nm for length scales) and follow the usual methods to convert from experimental parameters (molecular weight, density, etc.) to SCFT parameters via a reference volume that you need for Flory-Huggins theory, which is usually something that looks like the size of one of the chemical monomers.

But the situation is more confusing when you are working on a theory problem since there are no obvious set of units to use. I think a good way to think about the problem is to define a reference polymer with statistical segment length b_0 , degree of polymerization N_0 , and corresponding unperturbed, root-mean-squared end-to-end size of $R_0^2 = N_0 b_0^2$. It then follows (I will show why below) that the values in `kuhn`, `block_length`, `chi` and `cell_param` blocks of the input file are the values of these quantities for your actual polymer relative to the values b_0 , N_0 and R_0 for the reference chain. Once this correspondence is made, then it is straightforward to understand how to interpret the segregation strength, free energy, and unit cell parameters.

2 Dimensionless formulation

Consider the set of equations that you are solving in the canonical ensemble SCFT. Let us use k to denote the species and i to denote a monomer chemistry, such that b_i is the statistical segment length of a chain of monomer i , $\omega_i(\mathbf{r})$ is the chemical potential field acting on monomer i , and χ_{ij} is the Flory-Huggins parameter between monomer i and monomer j . The overall degree of polymerization of each species is N_k and the overall volume fraction of that block is ϕ_k . The problem is solved in a total volume V with monomer volume ν . The unit cell size is quantified by the trio of lattice parameters (a, b, c) , where the absence of a subscript for the lattice parameter b distinguishes it from the reference statistical segment length b_0 or the statistical segment length of monomer i , b_i .

The equations we need to solve are the propagators and partition functions for each species k ,

$$\frac{\partial q_k(\mathbf{r}, s)}{\partial s} = \left[\frac{b_i^2}{6} \nabla^2 - \omega_i(\mathbf{r}) \right] q_k(\mathbf{r}, s), \quad q_k(\mathbf{r}, 0) = 1 \quad (1)$$

$$-\frac{\partial q_k^\dagger(\mathbf{r}, s)}{\partial s} = \left[\frac{b_i^2}{6} \nabla^2 - \omega_i(\mathbf{r}) \right] q_k^\dagger(\mathbf{r}, s), \quad q_k^\dagger(\mathbf{r}, N_k) = 1 \quad (2)$$

$$Q_k = \frac{1}{V} \int d\mathbf{r} q_k(\mathbf{r}, s = N_k) \quad (3)$$

which are then used to compute the densities and fields for each monomer type i ,

$$\rho_i(\mathbf{r}) = \sum_k \frac{\phi_k}{Q_k N_k} \int_i ds q_k(\mathbf{r}, s) q_k^\dagger(\mathbf{r}, s) \quad (4)$$

$$\omega_i(\mathbf{r}) = \sum_j \chi_{ij} \rho_j(\mathbf{r}) + \xi(\mathbf{r}) \quad (5)$$

$$1 = \sum_i \rho_i(\mathbf{r}) \quad (6)$$

All of these are the “dimensional” quantities describing the polymer (recognizing that N has no dimensions, hence the quotation marks). The important point is that these are neither the inputs nor the outputs of PSCF in the formalism that I am describing here. Let us work through these equations one-by-one to see what happens if we define all length scales to be relative to R_0 .

2.1 Forward propagator

If we define the dimensionless length

$$\tilde{\mathbf{r}} \equiv \mathbf{r}/R_0 \quad (7)$$

and dimensionless gradient operator

$$\tilde{\nabla} \equiv R_0 \nabla \quad (8)$$

the forward propagator can be written as

$$\frac{\partial q_k(\tilde{\mathbf{r}}, s)}{\partial s} = \left[\frac{b_i^2}{6R_0^2} \tilde{\nabla}^2 - \omega_i(\tilde{\mathbf{r}}) \right] q_k(\tilde{\mathbf{r}}, s) \quad (9)$$

Substitute $R_0^2 = b_0^2 N$ while defining a dimensionless statistical segment length

$$\tilde{b}_i \equiv b_i/b_0 \quad (10)$$

to get

$$\frac{\partial q_k(\tilde{\mathbf{r}}, s)}{\partial s} = \left[\frac{\tilde{b}_i^2}{6N_0} \tilde{\nabla}^2 - \omega_i(\tilde{\mathbf{r}}) \right] q_k(\tilde{\mathbf{r}}, s) \quad (11)$$

If we then multiply by N_0

$$N_0 \frac{\partial q_k(\tilde{\mathbf{r}}, s)}{\partial s} = \left[\frac{\tilde{b}_i^2}{6} \tilde{\nabla}^2 - N_0 \omega_i(\tilde{\mathbf{r}}) \right] q_k(\tilde{\mathbf{r}}, s) \quad (12)$$

it makes sense to define a rescaled contour variable

$$\tilde{s} \equiv s/N_0 \quad (13)$$

and a new field

$$\tilde{\omega}_i \equiv N_0 \omega_i \quad (14)$$

to give

$$\frac{\partial q_k(\tilde{\mathbf{r}}, \tilde{s})}{\partial \tilde{s}} = \left[\frac{\tilde{b}_i^2}{6} \tilde{\nabla}^2 - \tilde{\omega}_i(\tilde{\mathbf{r}}) \right] q_k(\tilde{\mathbf{r}}, \tilde{s}) \quad (15)$$

The reason I did not call the contour s “dimensionless” is because N is a pure number. Likewise, the $\tilde{\omega}$ field is not “dimensionless” because the potential was already made dimensionless with $k_B T$ in formulating the equations. But this difference between “rescaled” and “dimensionless” is just a minor point and it’s OK if you think about \tilde{s} and $\tilde{\omega}_i$ as dimensionless too. I will probably confuse this notation later but did not do a careful check.

Every term is linear in q_k , so there is no need to introduce a dimensionless propagator.

2.2 Backwards propagator

Clearly, all the same operations apply to the backwards propagator, so I feel comfortable just writing down the answer:

$$-\frac{\partial q_k^\dagger(\tilde{\mathbf{r}}, \tilde{s})}{\partial \tilde{s}} = \left[\frac{\tilde{b}_i^2}{6} \tilde{\nabla}^2 - \tilde{\omega}_i(\tilde{\mathbf{r}}) \right] q_k^\dagger(\tilde{\mathbf{r}}, \tilde{s}) \quad (16)$$

2.3 Partition function

For the partition function, we can define a dimensionless volume $\tilde{V} = V/R_0^3$ that will cancel the R_0^3 term that comes from making the three dimensional differential $d\mathbf{r}$ dimensionless too. We then get

$$Q_k = \frac{1}{\tilde{V}} \int d\tilde{\mathbf{r}} q_k(\tilde{\mathbf{r}}, \tilde{s} = \tilde{N}_k) \quad (17)$$

where

$$\tilde{N}_k \equiv N_k/N_0 \quad (18)$$

is the scaled degree of polymerization. Nothing happens to Q_k through this process, so we do not need a tilde notation here.

2.4 Monomer density

For the densities, changing from s to \tilde{s} produces

$$\rho_i(\tilde{\mathbf{r}}) = \sum_k \frac{\phi_k}{Q_k \tilde{N}_k} \int_i d\tilde{s} q_k(\tilde{\mathbf{r}}, \tilde{s}) q_k^\dagger(\tilde{\mathbf{r}}, \tilde{s}) \quad (19)$$

where the factor of N_0 that came from \tilde{s} was absorbed into N_k to convert it to \tilde{N}_k . Similar to Q_k , the densities ρ_i are not affected by the change of variable.

2.5 Chemical potential fields

This the most illuminating of the cases. Recall that, for the propagator, we had to define a scaled chemical potential field in Eq. 14. So we need to multiply Eq. 6 by N_0 to get

$$\tilde{\omega}_i(\tilde{\mathbf{r}}) = \sum_j \chi_{ij} N_0 \rho_j(\tilde{\mathbf{r}}) + N_0 \xi(\tilde{\mathbf{r}}) \quad (20)$$

To keep everything consistent, let's define

$$\tilde{\xi} \equiv N_0 \xi \quad (21)$$

such that

$$\tilde{\omega}_i(\tilde{\mathbf{r}}) = \sum_j (\chi_{ij} N_0) \rho_j(\tilde{\mathbf{r}}) + \tilde{\xi}(\tilde{\mathbf{r}}) \quad (22)$$

This suggests that we should make a rescaled χ value

$$\tilde{\chi}_{ij} = \chi_{ij} N_0 \quad (23)$$

such that the field is now

$$\tilde{\omega}_i(\tilde{\mathbf{r}}) = \sum_j \tilde{\chi}_{ij} \rho_j(\tilde{\mathbf{r}}) + \tilde{\xi}(\tilde{\mathbf{r}}) \quad (24)$$

Note that there is nothing to do for the sum of the densities in Eq. 6 other than convert the position to dimensionless form.

2.6 Dimensionless equation set

The end result of making the equations dimensionless (or, perhaps better put, rescaled to the reference chain) requires the solution of

$$\frac{\partial q_k(\tilde{\mathbf{r}}, \tilde{s})}{\partial \tilde{s}} = \left[\frac{\tilde{b}_i^2}{6} \tilde{\nabla}^2 - \tilde{\omega}_i(\tilde{\mathbf{r}}) \right] q_k(\tilde{\mathbf{r}}, \tilde{s}) \quad (25)$$

$$-\frac{\partial q_k^\dagger(\tilde{\mathbf{r}}, \tilde{s})}{\partial \tilde{s}} = \left[\frac{\tilde{b}_i^2}{6} \tilde{\nabla}^2 - \tilde{\omega}_i(\tilde{\mathbf{r}}) \right] q_k^\dagger(\tilde{\mathbf{r}}, \tilde{s}) \quad (26)$$

$$Q_k = \frac{1}{\tilde{V}} \int d\tilde{\mathbf{r}} q_k(\tilde{\mathbf{r}}, \tilde{s} = \tilde{N}_k) \quad (27)$$

$$\rho_i(\tilde{\mathbf{r}}) = \sum_k \frac{\phi_k}{Q_k \tilde{N}_k} \int_i d\tilde{s} q_k(\tilde{\mathbf{r}}, \tilde{s}) q_k^\dagger(\tilde{\mathbf{r}}, \tilde{s}) \quad (28)$$

$$\tilde{\omega}_i(\tilde{\mathbf{r}}) = \sum_j \tilde{\chi}_{ij} \rho_j(\tilde{\mathbf{r}}) + \tilde{\xi}(\tilde{\mathbf{r}}) \quad (29)$$

$$1 = \sum_i \rho_i(\tilde{\mathbf{r}}) \quad (30)$$

These are the equations solved by PSCF for this problem. As a result, the inputs are

- `kuhn` $\leftarrow b_i/b_0$
- `block_length` $\leftarrow N_{i,k}/N_0$
- `chi` $\leftarrow \chi_{ij} N_0$
- `cell_param` $\leftarrow (a, b, c)/R_0$

where $N_{i,k}$ is the degree of polymerization of block i in species k .

3 Implications for analysis of the results

Once we recognize how this rescaling works, then the ($N = 1$, $b = 1$) convention makes a lot of sense — it means that your SCFT calculation is being computed in terms of that chain because what you are inputting is $\tilde{N} = 1$ and $\tilde{b} = 1$, not $N = 1$ and $b = 1$. In many cases, though, we need to set these parameters to non-zero values. For a blend, for example, you can have two different N_i values. Even for a neat melt, we have done lots of work with conformationally asymmetric chains where $\tilde{b}_i \neq 1$.

3.1 Segregation strength

From the form for $\tilde{\omega}_i$ in Eq. 24, the calculation is defined with a rescaled segregation strength $\tilde{\chi}_{ij} = \chi_{ij} N_0$, where you have input a numerical value for χ_{ij} but we have left N_0 unspecified. If you want to convert this into something that is related to your problem, it makes sense to multiply the value of χ_{ij} use in the input by one of the values of \tilde{N}_k from the input,

$$\tilde{\chi}_{ij} \tilde{N}_k = \chi_{ij} N_0 \left(\frac{N_k}{N_0} \right) = \chi_{ij} N_k \quad (31)$$

If you set one of the input $\tilde{N}_k = 1$, then there is nothing to do here; you are already computing in terms of $\chi_{ij} N_k$.

3.2 Free energy

The Helmholtz free energy per coarse-grained monomer is given by

$$\frac{F\nu}{k_{\text{B}}TV} = \sum_k \frac{\phi_k}{N_k} \left[\ln \left(\frac{\phi_k}{Q_k} \right) - 1 \right] - \frac{1}{V} \sum_i \int d\mathbf{r} \omega_i(\mathbf{r}) \rho_i(\mathbf{r}) + \frac{1}{2V} \sum_{ij} \chi_{ij} \int d\mathbf{r} \rho_i(\mathbf{r}) \rho_j(\mathbf{r}) \quad (32)$$

Making this equation into our dimensionless form requires first changing the V and $d\mathbf{r}$ variables to dimensionless form,

$$\frac{F\nu}{k_{\text{B}}TV} = \sum_k \frac{\phi_k}{N_k} \left[\ln \left(\frac{\phi_k}{Q_k} \right) - 1 \right] - \frac{1}{\tilde{V}} \sum_i \int d\tilde{\mathbf{r}} \omega_i(\tilde{\mathbf{r}}) \rho_i(\tilde{\mathbf{r}}) + \frac{1}{2\tilde{V}} \sum_{ij} \chi_{ij} \int d\tilde{\mathbf{r}} \rho_i(\tilde{\mathbf{r}}) \rho_j(\tilde{\mathbf{r}}) \quad (33)$$

and then multiplying by N_0 to convert N_k and ω_i to dimensionless forms

$$\frac{F\nu N_0}{k_{\text{B}}TV} = \sum_k \frac{\phi_k}{\tilde{N}_k} \left[\ln \left(\frac{\phi_k}{Q_k} \right) - 1 \right] - \frac{1}{\tilde{V}} \sum_i \int d\tilde{\mathbf{r}} \tilde{\omega}_i(\tilde{\mathbf{r}}) \rho_i(\tilde{\mathbf{r}}) + \frac{1}{2\tilde{V}} \sum_{ij} \tilde{\chi}_{ij} \int d\tilde{\mathbf{r}} \rho_i(\tilde{\mathbf{r}}) \rho_j(\tilde{\mathbf{r}}) \quad (34)$$

Recalling the previous section, it is good to see that the overlap integral (last term) involves $\chi_{ij}N_0$, which we have already identified as the segregation strength from the previous section.

It proves useful to break up left-hand side to

$$\frac{F\nu N_0}{k_{\text{B}}TV} = \left(\frac{F}{k_{\text{B}}T} \right) \left(\frac{\nu N_0}{V} \right) \quad (35)$$

We can then define

$$n_0 \equiv \frac{V}{\nu N_0} \quad (36)$$

as the number of chains of degree of polymerization N_0 , which is more satisfying than “per monomer”. As a result, the free energy in our dimensionless formulation is per chain of size N_0 ,

$$\frac{F}{n_0 k_{\text{B}}T} = \sum_k \frac{\phi_k}{\tilde{N}_k} \left[\ln \left(\frac{\phi_k}{Q_k} \right) - 1 \right] - \frac{1}{\tilde{V}} \sum_i \int d\tilde{\mathbf{r}} \tilde{\omega}_i(\tilde{\mathbf{r}}) \rho_i(\tilde{\mathbf{r}}) + \frac{1}{2\tilde{V}} \sum_{ij} (\chi_{ij} N_0) \int d\tilde{\mathbf{r}} \rho_i(\tilde{\mathbf{r}}) \rho_j(\tilde{\mathbf{r}}) \quad (37)$$

If you want to express the free energy in terms of any of the other chain lengths, you just need to multiply by the relevant value of \tilde{N}_k

$$\frac{F}{n_0 k_{\text{B}}T} \tilde{N}_k = \frac{F}{k_{\text{B}}T} \frac{N_k \nu}{V} = \frac{F}{n_k k_{\text{B}}T} \quad (38)$$

Likewise, if you picked one of the $\tilde{N}_k = 1$, then the free energy is already in terms of chains of that size.

We do need to be a bit careful in the notation here. For example, if we have an AB/CD blend with $N_{\text{AB}} \neq N_{\text{CD}}$, we could multiply by \tilde{N}_{AB} to express the result “per AB diblock chain”. Perhaps a clearer way to write this out is “per chain of length N_{AB} ”. In our two most recent submissions, we used the first case in Ben’s paper and the second in Sojung’s paper; I suggest we modify the notation in Ben’s paper when it comes back from review.

3.3 Unit cell size

For me, the unit cell size has always been the hardest part to understand but this analysis should make it relatively straightforward. Since we used R_0 as the length scale for making space dimensionless, it means that the unit cell parameters (a, b, c) are being reported in dimensionless form. If we focus on a as the representative case (since it is the same logic for the other parameters), the input/output of the PSCF code is

$$\tilde{a} \equiv a/R_0 \quad (39)$$

If you picked one of the chains to have $\tilde{N}_k = 1$ and all of its statistical segment lengths to be $\tilde{b}_i = 1$, then the unit cell parameters are in terms of the end-to-end distance R_e of that chain. It is worthwhile to remember that these are unperturbed values of the rms end-to-end distance. So it would make sense to say that we are trying to report the results in units of the “unperturbed end-to-end distance.” When the chains are in the fields, they are perturbed from their relaxed state (either compressed or stretched). Indeed, this change in the average conformation of the chains is one of the key factors contributing to the free energy.

We often want to consider conformationally asymmetric chains in analysis (e.g., for Frank-Kasper phases or to model an experiment) and need the unit cell parameter in terms of R_e of the conformationally asymmetric chain. Let’s work through that example carefully for a diblock copolymer to see how to do it.

The actual values for this chain are a degree of polymerization N with volume fraction f_A and statistical segment lengths b_A and b_B . The unperturbed end-to-end distance is the sum of the two random walks

$$R_e^2 = N_A b_A^2 + N_B b_B^2 \quad (40)$$

As an aside, we often talk about an effective statistical segment length b_{eff} that is derived by factoring out the total degree of polymerization

$$R_e^2 = N(f_A b_A^2 + f_B b_B^2) = N b_{\text{eff}}^2 \quad (41)$$

If we want to express the unit cell parameter in terms of R_e , we would write Eq. 39 as

$$\frac{a}{R_e} = \tilde{a} \left(\frac{R_0}{R_e} \right) = \frac{\tilde{a}}{\tilde{R}_e} \quad (42)$$

The value of \tilde{a} is the output from PSCF. The factor \tilde{R}_e that we need to make the conversion is more easily manipulated as its square

$$\tilde{R}_e^2 = \left(\frac{R_e}{R_0} \right)^2 = \frac{N_A b_A^2 + N_B b_B^2}{N_0 b_0^2} = \tilde{N}_A \tilde{b}_A^2 + \tilde{N}_B \tilde{b}_B^2 \quad (43)$$

So, for this particular diblock problem, the unit cell parameter relative to the diblock chain’s unperturbed size is

$$\frac{a}{R_e} = \tilde{a} \left(\frac{R_0}{R_e} \right) = \frac{\tilde{a}}{\left(\tilde{N}_A \tilde{b}_A^2 + \tilde{N}_B \tilde{b}_B^2 \right)^{1/2}} \quad (44)$$

where we have now expressed everything in terms of inputs to PSCF.

In a “normal” calculation, we might define the conformational asymmetry as $\epsilon = b_A/b_B$. It is simplest to pick $\tilde{b}_B = 1$ so that you can just do a sweep in \tilde{b}_B to study different values of ϵ . If you also picked $N = N_0$, then you do need to remember that your unit cell parameters are being scaled with $b_B N^{1/2}$. You could set up your PSCF calculation so that the calculation is done in

terms of R_e for your chain by selecting \tilde{b}_A and \tilde{b}_B so that the unit cell parameters are scaled with R_e . However, this would require adjusting \tilde{b}_A and \tilde{b}_B for every value of f_A since b_{eff} is a function of both ϵ and f_A ,

$$b_{\text{eff}}^2 = b_B^2(f_A\epsilon^2 + f_B) \quad (45)$$

So if you choose $b_0 = b_{\text{eff}}$ to get your results in terms of R_e for your conformationally asymmetric chain, you would need to pick

$$\tilde{b}_A = \frac{b_A}{b_0} = \frac{b_A}{b_{\text{eff}}} = \frac{b_A}{b_B(f_A\epsilon^2 + f_B)^{1/2}} = \frac{\epsilon}{(f_A\epsilon^2 + f_B)^{1/2}} \quad (46)$$

and

$$\tilde{b}_B = \frac{b_B}{b_0} = \frac{b_B}{b_{\text{eff}}} = \frac{b_B}{b_B(f_A\epsilon^2 + f_B)^{1/2}} = \frac{1}{(f_A\epsilon^2 + f_B)^{1/2}} \quad (47)$$

This is annoying.

3.4 Accuracy of the contour integration

In our papers, we have generally reported the value of ds used for the integration over the chain contour. That value is meaningful only when also specifying N_k , which has generally been $N_k = 1$ but we did not specify. To preserve the accuracy, what is meaningful is ds/N_k ; in other words, you want to know how many integration steps we are using to represent the chain. Going forward, it would be helpful to specify something like ds/N_{AB} so that it's clear what was done.

3.5 Rescale function in PSCF

The **rescale** function in PSCF allows for changes in convention in PSCF. This analysis should make clear what was written in the 2016 Macromolecules paper. Imagine that we have entered values for \tilde{N}_k , \tilde{b}_k , $\tilde{\chi}_{ij}$ and \tilde{a} and the other unit cell parameters. They are all based on some value of N_0 that is connected to R_0 . Now imagine that we have made the change

$$N'_0 = N_0\lambda \quad (48)$$

and we want to do an equivalent set of calculations with this new convention for N'_0 . In other words, what do we do so that the calculation is for the same R_0 but now defined with a different reference volume so that the reference chain has a different value of N ?

For the chain contour, we need

$$\tilde{N}'_k = \frac{N_k}{N'_0} = \frac{N_k}{N'_0} \frac{N_0}{N_0} = \frac{N_k}{N_0} \frac{N_0}{N'_0} = \frac{\tilde{N}_k}{\lambda} \quad (49)$$

For the statistical segment lengths, we need

$$\tilde{b}'_i = \frac{b_i}{b'_0} = \frac{b_i}{b'_0} \frac{b_0}{b_0} = \frac{b_i}{b_0} \frac{b_0}{b'_0} = \tilde{b}_i \left(\frac{b_0}{b'_0} \right) \quad (50)$$

In order for both calculations to correspond to a chain with the same unperturbed size R_0 , we further require that

$$N_0 b_0^2 = N'_0 (b'_0)^2 \quad (51)$$

Reorganizing the terms gives

$$\frac{b_0}{b'_0} = \left(\frac{N'_0}{N_0} \right)^{1/2} \quad (52)$$

Using Eq. 48 then leads to

$$\frac{b_0}{b'_0} = \lambda^{1/2} \quad (53)$$

and thus

$$\tilde{b}'_i = \tilde{b}_i \lambda^{1/2} \quad (54)$$

For the χ parameters, we need

$$\tilde{\chi}' = \chi N'_0 = \chi N'_0 \frac{N_0}{N_0} = (\chi N_0) \frac{N'_0}{N_0} = \tilde{\chi} \frac{N'_0}{N_0} = \tilde{\chi} \lambda \quad (55)$$

Finally, for the unit cell parameters, no rescaling is needed because

$$\tilde{a}' = \frac{a}{R_0} = \tilde{a} \quad (56)$$

The unit cell parameters were made dimensionless with the invariant, R_0 , which is not affected by the choice of N_0 .

Note that, within the code, there is also the need to change the fields because the convention for N_0 has changed. The rescaled form is identical to what we did with χ , i.e. multiplication by N_0 , so the result is the same,

$$\tilde{\omega}' = \tilde{\omega} \lambda \quad (57)$$

While I have been focusing on what has to be done for the param file here, you would need to implement this rescaling in the input guess for the fields.