

the SPM

$$f(m) = \begin{cases} \lambda, & n = 0 \\ 1, & \text{otherwise} \end{cases}. \quad (2.7)$$

Thus, for finite  $\lambda$

$$\frac{f(m)}{f(m-1)} = 1, \forall m > 2, \quad (2.8)$$

which remains bounded as  $m \rightarrow \infty$ , therefore this model does not exhibit explosive condensation, again by using [1].

## 2.2.4 Calculation of the Partition Function of the SPM on a Closed Ring

Whilst we are on the subject of the duality between the SPM and the Misanthrope Process, we can observe that the probability weighting of any configuration is proportional to  $\lambda^{-k}$ , where  $k$  is the number of particle-particle adjacencies in the SPM and the number of empty slots in the Misanthrope Process. This begs the question: if we know the weightings, can we calculate the partition function, and therefore other quantities such as the free energy or chemical potential, for the SPM on a closed ring with particle density  $\rho$ ?

In order to attempt this, we must first make two observations from the field of combinatorics:

- The number of possible ways to select, without ordering or replacement,  $M$  objects from  $N$  is

$$\binom{M}{N} = \frac{N!}{M!(N-M)!}. \quad (2.9)$$

- The number of ways to insert  $M$  unlabelled balls into  $N$  boxes is

$$\binom{N+M-1}{M-1} = \frac{(N+M-1)!}{N!(M-1)!}. \quad (2.10)$$

Now let us consider a Misanthrope Process on a closed ring of  $N$  slots, into which we wish to distribute  $L - N$  particles; this corresponds to the SPM on a ring with  $L$  slots containing  $N$  particles. Say we wish to distribute the particles so that only  $M$  of the slots contain any particles at all; then the above two combinatorial results suggest that there are  $\frac{N!}{M!(N-M)!}$  ways to choose which  $M$  slots, into which

we insert one particle each, leaving  $\frac{(L-N-1)!}{(L-N)!(M-1)!}$  ways to insert the remainder. Thus, the overall number of possible ways to distribute the particles so that only  $M$  slots contain any at all is

$$C_M = \frac{N!(L-N-1)!}{M!(N-M)!(L-N)!(M-1)!}. \quad (2.11)$$

As we know, the weighting of a configuration in which only  $M$  of the slots are nonempty is  $\lambda^{-(N-M)}$ ; therefore, the partition function  $Z_L(\lambda, N)$  for a system of size  $L$  is

$$Z_L(\lambda, N) = \sum_{M=1}^{M=\min\{N-1, L-N\}} \left[ \frac{N!(L-N-1)!}{M!(N-M)!(L-N)!(M-1)!} \lambda^{-(N-M)} \right]. \quad (2.12)$$

For statistical mechanics, we are really interested in the situation where the system size is very large. Therefore, let us define  $\rho, m \in (0, 1)$  so that  $N = \rho L$  and  $M = mL$ , and invoke the Stirling approximation  $\log x! \sim x \log x$  for large  $x$ . Regarding  $L$  as a large constant, and keeping only leading order behaviour in  $L$ , we find that

$$Z_L(\lambda, \rho) \sim \int_0^{\min\{\rho, 1-\rho\}} dm \exp L [-2m \log m + (1-\rho) \log (1-\rho) + \rho \log \rho - (1-\rho-m) \log (1-\rho-m) - (\rho-m) \log (\rho-m) - (\rho-m) \log \lambda]. \quad (2.13)$$

This integral looks quite intractable, but recall that in the limit  $L \rightarrow \infty$  we can evaluate it asymptotically using the Laplace's Method. This requires finding the location of extrema of the exponentiated term as a function of  $m$ ; these occur when

$$\lambda(1-m-\rho)(\rho-m) = m^2. \quad (2.14)$$

One of the solutions occurs in  $(0, \min\{\rho, 1-\rho\})$ , at

$$m_+ = \frac{\lambda + \sqrt{\lambda^2 + 4\lambda(1-\lambda)\rho(1-\rho)}}{2(1-\lambda)}, \quad (2.15)$$

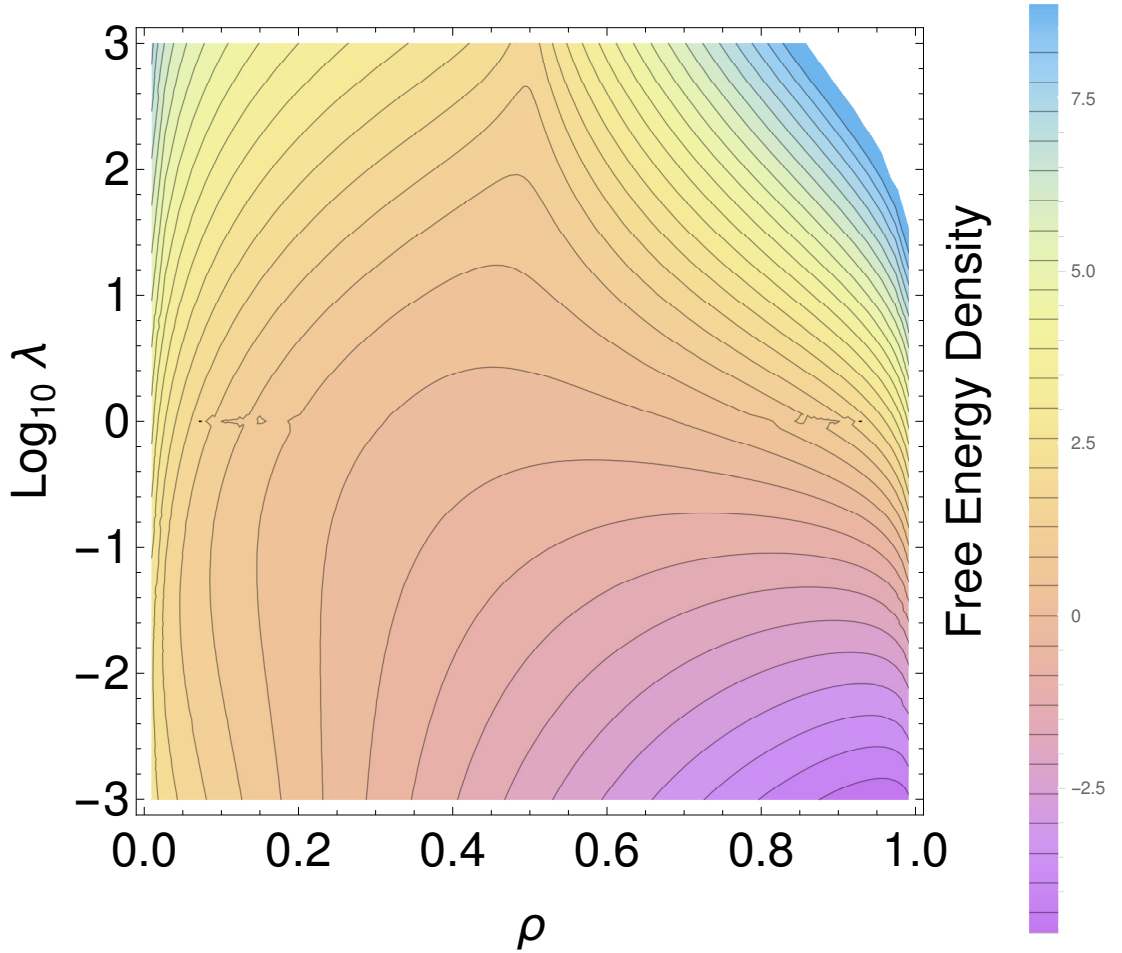
and a little analysis reveals that it is indeed a maximum, as required for the use

of Laplace's Method. Therefore, we find that

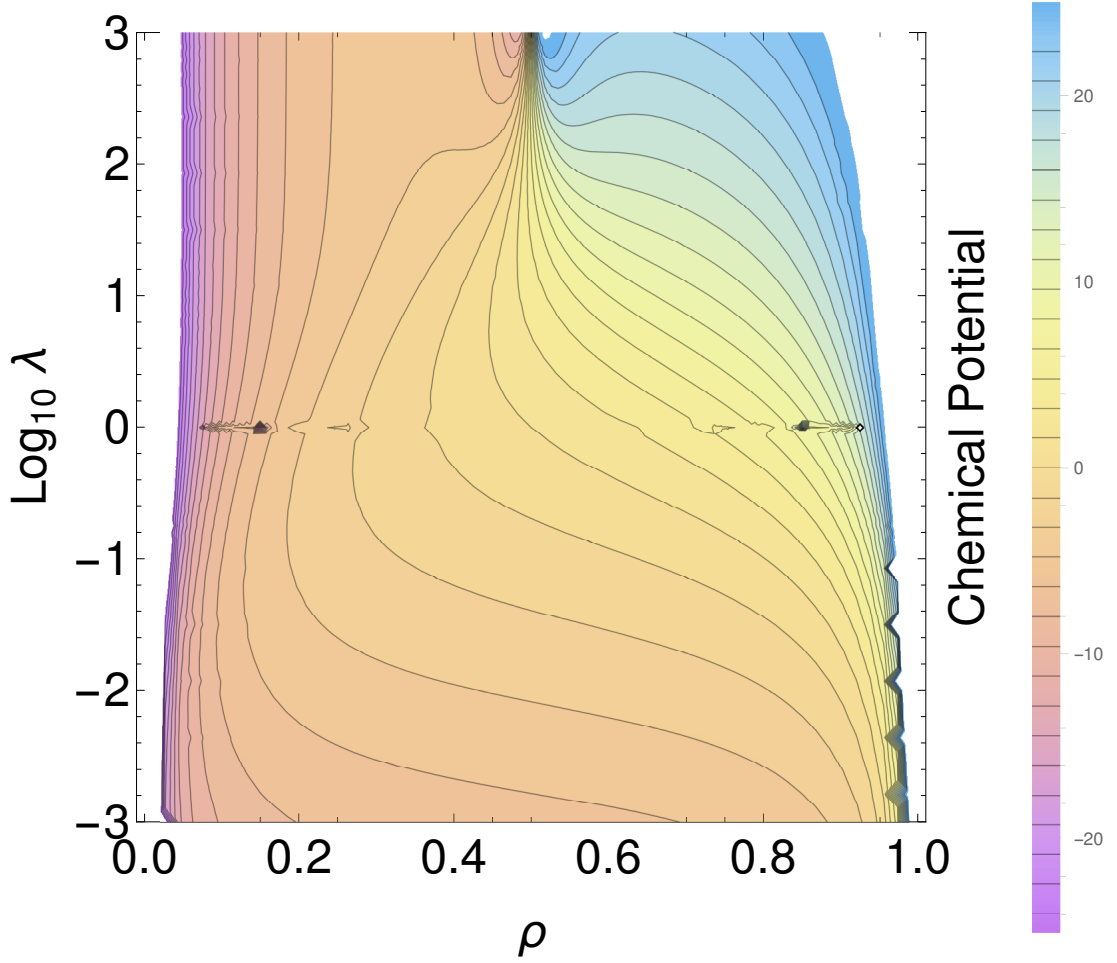
$$\begin{aligned} \sqrt[L]{Z_L(\lambda, \rho)} &\sim \sqrt{2\pi} \frac{(1-\rho)^{1-\rho} \rho^\rho}{m_+^{2m_+} (\rho - m_+)^{\rho-m_+} (1-m_+-\rho)^{1-m_+-\rho}} \\ &\times \sqrt{\frac{m_+ (\rho - m_+) (1 - m_+ - \rho)}{2(1-\rho)\rho - m_+}} \lambda^{m_+-\rho}. \end{aligned} \quad (2.16)$$

From here one can use computer algebra to obtain the free energy density  $F(\rho, \lambda) = -\frac{\log Z_L}{L}$  (Fig. 2.2) and chemical potential  $\mu(\rho, \lambda) = \frac{\partial F}{\partial \rho}$  (Fig 2.3) of the SPM system.

**Figure 2.2** *The variation of the SPM free energy density on a large closed ring as a function of particle density and stickiness parameter  $\lambda$ . The patches on the line  $\lambda = 1$  are due to the way that  $m_+$  is calculated; although a little analysis reveals that it is in fact a well-behaved removable singularity, numerical errors cause the plotting numerics to behave badly in places.*



**Figure 2.3** *The variation of the SPM chemical potential on a large closed ring as a function of particle density and stickiness parameter  $\lambda$ . Again, we see some bad behaviour at  $\lambda = 1$ , for the same reasons as before.*



Of course, in thermodynamic equilibrium a system generally attempts to lower its total free energy to the lowest value allowed by the constraints. If we hold  $\lambda$  constant whilst allowing  $\rho$  to vary, this corresponds to the curve  $\mu(\rho, \lambda) = 0$ , which one can follow on Fig. 2.3; a glance at Fig. 2.2 confirms that this is indeed a minimum. Thus we should expect that a very large system connected to a particle reservoir would tend towards having a total density such that  $\mu = 0$ , regardless of the particle density in the reservoir, as the particle density in the system would only be pinned to that of the reservoir near to the boundary. Therefore, at large  $\lambda$  we would see systems tend towards a density of  $\rho_{\frac{1}{2}}$ , whereas for small  $\lambda$  the system would tend to fill. Of course, if we were to hook a system up to two different boundaries and cause a current to flow, as we have done many times in the course of this project, that might change things, as now the system would

be in a nonequilibrium steady state as opposed to a thermodynamic equilibrium, and those are not quite the same beast.

## 2.3 Using the Mean-Field Approximation on the SPM

For the reasons discussed in Sec. ??, we do not possess an analytic solution for the SPM on a nonperiodic bounded domain. Such a solution might exist, but we will proceed on the assumption that the model is not analytically solvable. Therefore, it would be useful to at least possess approximate analytic solutions, as this can help us by giving us something to test our numerics against, and point us in the direction of interesting behaviours which might occur. We will start by deriving the MFT on a lattice, and will then take the continuum limit (as the lattice spacing tends to zero relative to our scale of interest), as that should predict the dominant behaviour on the macroscopic scale.

### 2.3.1 Lattice MFT Derivation

As usual, in an MFT approximation, we will be saying that the equal-time probability of the  $(i + 1)^{\text{th}}$  site being occupied is independent of the probability that the  $i^{\text{th}}$  site is occupied. More formally, let us denote the mean occupation of the  $i^{\text{th}}$  site at time  $t$  by  $\rho_i(t)$ . When we invoke the mean-field approximation, we say that the mean occupations of sites at equal times are independent; thus, the probability that site  $j \neq i$  occupied given that site  $i$  is occupied is  $\rho_j(t)$ . We can use this to calculate the rate at which  $\rho_i(t)$  increases and decreases, and so obtain a system of coupled ODEs for  $\rho_i(t)$ .

Let us first consider the situation where the  $i^{\text{th}}$  site is unoccupied. The probability of this being the case is  $(1 - \rho_i(t))$ . A particle could move from site  $(i - 1)$  or site  $(i + 1)$ , but only if those sites are currently occupied. Assuming that site  $(i - 1)$  is occupied (occurring with probability  $\rho_{i-1}$  in MFT), the rate at which it would jump to site  $i$  would depend on the occupation of site  $(i - 2)$ , as it would be 1 if it was unoccupied and  $\lambda$  if it was occupied. Phrasing this in MFT terms, and suppressing  $t$ -dependence for brevity, the rate at which  $\rho_i(t)$  is increased by