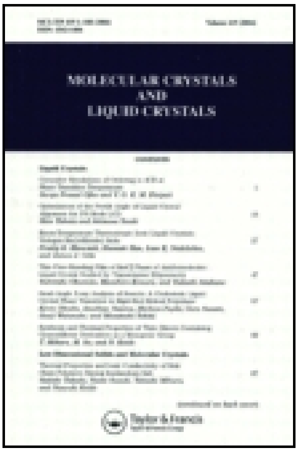

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

A Counterexample Concerning to the Phase Space Multi-Histogram Method

Hitomi Nomura [a], Tomonori Koda [a], Akihiro Nishioka [a] & Ken Miyata [a]

[a] Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata, 992-8510, Japan

Version of record first published: 18 Apr 2012.

To cite this article: Hitomi Nomura, Tomonori Koda, Akihiro Nishioka & Ken Miyata (2012): A Counterexample Concerning to the Phase Space Multi-Histogram Method, Molecular Crystals and Liquid Crystals, 558:1, 140-147

To link to this article: http://dx.doi.org/10.1080/15421406.2011.654182

Mol. Cryst. Liq. Cryst., Vol. 558: pp. 140–147, 2012

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.654182

A Counterexample Concerning to the Phase Space Multi-Histogram Method

HITOMI NOMURA,* TOMONORI KODA,
AKIHIRO NISHIOKA, AND KEN MIYATA

Graduate School of Science and Engineering, Yamagata University,
4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan

The phase space multi-histogram method is a new technique to study phase transitions in hard particle systems. The method constrains the phase space using a Monte Carlo approach by smoothly varying a potential between the ideal gas and the hard particle limit. Using a small sphere system, we give an example of computing chemical potential at the liquid state. However, we find that the method fails for a dense sphere system at the coexisting liquid-solid state. We conclude that the method is appropriate for dilute hard particle systems, but it fails when the volume fraction of the system is too high.

Keywords Chemical potential; Monte Carlo simulations; phase space multi-histogram method; phase transition

1. Introduction

Recently, we proposed the phase space multi-histogram (PSMH) method to compute the chemical potential of a hard particle system [1]. The PSMH method is a variant of the multi-canonical Monte Carlo (MC) method [2,3], and we also applied the PSMH method employed with the re-weighting histogram technique [4] to study the isotropic-nematic phase transition of a monodispersed infinitely thin square platelet system. Previously, a simulation study of the monodispersed infinitely thin platelet systems was carried out by Bates with grand canonical ensemble MC method to examine the isotropic-nematic phase transition of suspensions of sterically stabilized gibbsite platelets [5].

Traditionally speaking, thermodynamic integration [6] and Widom's method [7–9] are well-known to compute chemical potential on the basis of statistical mechanics, and they have been proved to be equivalent [10]. Nevertheless, the thermodynamic integration cannot be used in the case where there is a discontinuity in the phase transition between the ideal gas state and a desirable state in question. Our recent finding has shown that Bates' result with the use of the grand canonical method in chemical potential is comparable to ours with the PSMH method [1]. In the present paper; however, we give a counterexample where the PSMH method is not applicable. More precisely, we shall show that the PSMH

---

*Address correspondence to Hitomi Nomura, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan. E-mail: tmc27563@st.yamagata-u.ac.jp method works in the liquid phase of a monodispersed sphere system but not in the coexisting liquid-solid phase where a volume fraction (density) is high as shown in [11].

2. The PSMH Method and Our Model

Consider a pairwise repulsive potential ϕ_{ij} acting on a system of N hard spheres confined in a periodic box of volume V. It takes ∞ if two spherical particles indexed i, j ($i \neq j$) intersect and 0 otherwise. Each singular value of ϕ_{ij} is essentially responsible for determining their equilibrated structure. A unique feature of the PSMH method is an interpolation parameter h dependent potential, U_h defined by

$$U_h \equiv \frac{hn_c}{\beta}, \tag{1}$$

where

$$n_c = \sum_{i<j} \begin{cases} 1 & \text{if the ith and jth particles overlap,} \\ 0 & \text{otherwise.} \end{cases} \tag{2}$$

to transform between hard particles and the corresponding ideal gas. Here, notice that the total potential of the system can be equivalently written as $U_{h=\infty} \equiv \sum_{i<j}\phi_{ij}$.

The PSMH method calculates the volume of the phase space (a set of classical states) of a hard particle system by shrinking that of the ideal gas state lying in the 6N dimensional space. The first step of the PSMH method is to perform a usual isobaric MC simulation for hard particles. For each reduced pressure, about up to 50000 MC steps were generated for equilibration followed by additional 50000 MC steps were used for statistical analysis. After equilibrating, we obtain a reduced pressure versus density plot. Next, we carry out an isochoric MC simulation with relaxing the constraint of non-overlapping of the particles (i.e. we perform an isochoric MC simulation with the Boltzmann weight factor $\exp(-\beta U_h)$. Here, β is the inverse temperature defined by $\beta = 1/(k_B T)$, where k_B is Bolzmann's constant.) Denote the number of microstates such that there are n_c pair contacts in each microstate by $w(n_c)$. The isochoric MC simulation data enable us to construct the following apparent distribution $\psi_h(n_c)$ for each h:

$$\psi_h(n_c) = C_h w(n_c) \exp(-\beta U_h), \tag{3}$$

where C_h is a normalization constant. For each isochoric MC simulation, we required at least another 200000 MC steps to obtain an apparent distribution.

Since n_c takes an integer value, we rename it by the alphabets j, k, l. A straightforward sequence of algebraic manipulations leads us to

$$\log w(k) = \log \psi_{h=0}(k) \; - \log C_0, \; k = j, j-1, j-2, \ldots, l, l < j \tag{4}$$

when $h = 0$, and

$$\log w(l-1) = \log \psi_h(l-1) \; - \; \log \psi_h(l) \; + \; \log w(l) + h \tag{5}$$

when $h \neq 0$. Here,

$$C_0^{-1} = \sum_{n_c} w(n_c). \tag{6}$$

The Helmholtz free energy F, the Gibbs free energy G, and chemical potential μ of the N hard particles are

$$\beta \mathrm{F} \approx -\log \mathrm{w}(0) + \log \mathrm{C}_0, \mathrm{G} = \mathrm{F} + \mathrm{pV} \tag{7}$$

and

$$\beta\mu = \beta \mathrm{G}/\mathrm{N} = \frac{\beta \mathrm{F}}{\mathrm{N}} + \frac{\mathrm{p} * \mathrm{V}}{\mathrm{ND}^3}, \tag{8}$$

where for a given pressure p, the reduce pressure is

$$\mathrm{p}^* \equiv \mathrm{D}^3 \beta \mathrm{p}, \tag{9}$$

and D is the unit length in simulation. The value of C_0 is estimated by

$$\mathrm{C}_0 = \frac{\mathrm{N}!\Lambda^{3\mathrm{N}}}{(4\pi \mathrm{V})^{\mathrm{N}}}, \tag{10}$$

where Λ is the thermal de Broglie wavelength. In particular, for the system of N spherical particles, a volume fraction η are computed by

$$\eta \equiv \frac{ND^3\pi}{6V}, \tag{11}$$

where D is the diameter of spheres, and V is the volume of a periodic simulation box.

We test the PSMH to an N = 108 (3 × 3 × 3 unit cells) monodispersed sphere system. A crystal with a cubic periodic condition is taken as its initial configuration. The type of crystal structure was taken as face-centered cubic (FCC) packing since it has the highest density of any sphere packing. An excluded volume repulsion drives the solid-liquid phase transition of the system. In our simulation, the density (volume fraction) dependence of the pressure for the liquid-crystal phase transition is described by two branches, LC and CL branches. The LC (or CL) branch is obtained via compression (or expansion) from the liquid (or crystal) phase to the crystal (or liquid) phase. The FCC packing was taken to be a starting point for the CL branch.

3. Results and Discussion

In Fig. 1, a crystal phase of the system of 108 hard spheres is displayed. h = ∞ was used in the isobaric MC simulation of Fig. 1. In Fig. 2, a reduced pressure versus volume

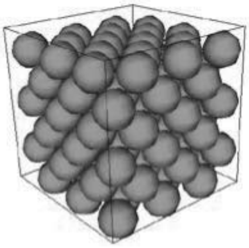

Figure 1. An FCC crystal packing of 108 hard spheres.

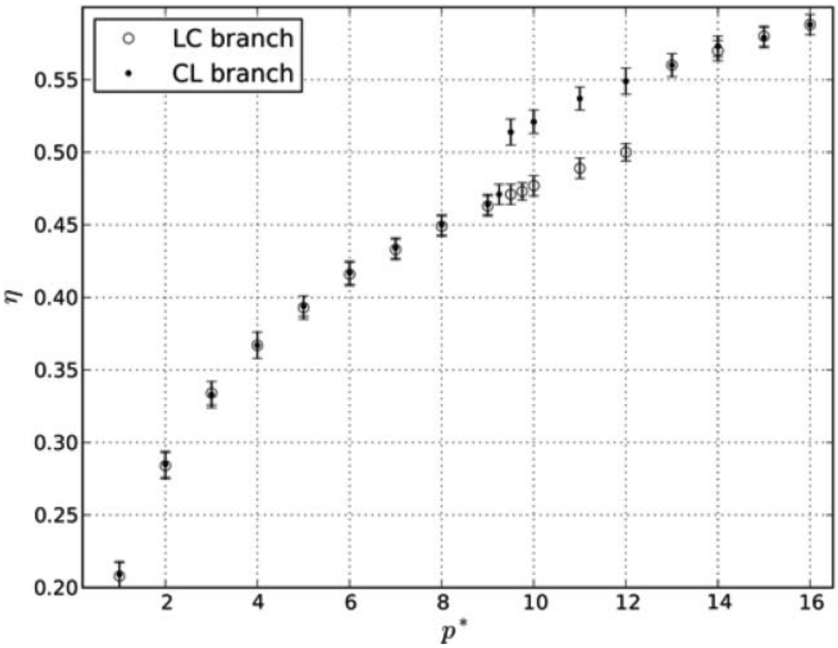

Figure 2. A reduced pressure p*-volume fraction η plot. Each vertical error bar indicates the standard deviation.

fraction plot is shown. A hysteresis in volume fraction between the LC and CL branches was detected around $p^* = 11$.

The potential employed in the isochoric MC simulation is repulsive but not hard, with a typical value of h ranging from 0 to 9. In Fig. 3, a snapshot of the hard spheres at $p^* = 1.0$, $h = 0.1$ is shown.

As expected, we observed that the spheres intersected each other. The PSMH method was successfully applied in the liquid state ($p^* = 1.0$ of the LC branch) of the hard spheres since multi-histograms overlapped within full width at half maximum over the range $n_c = [0, 129]$. (See Fig. 4). Each step size of h was chosen to makes sure that two neighboring histograms overlap within full width at half maximum. Typically, we use a step size of 0.1.

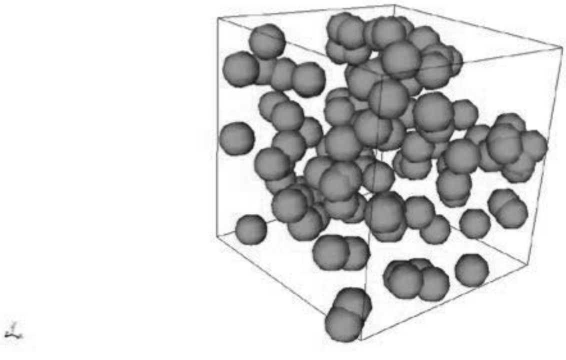

Figure 3. A snapshot of the hard sphere system at $p^* = 1.0$, $h = 0.1$ of the LC branch. Some of spheres intersected each other.

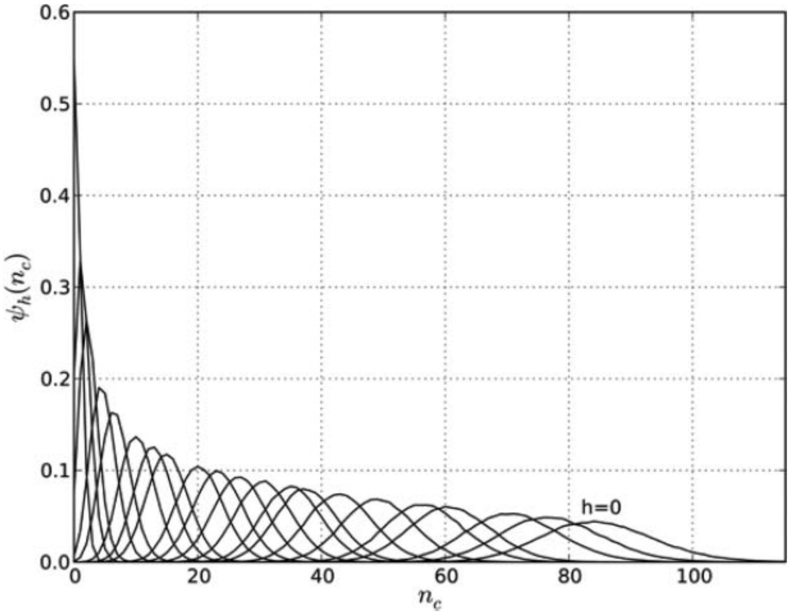

Figure 4. A plot of multi-histograms $\psi_h(n_c)$ for h ranged in [0, 6]. The LC branch at $p^* = 1.0$ was taken.

Figure 5 shows n_c versus $-\log w(n_c)$ plot at $p^* = 1.0$ of the LC branch. In order to compute free energy and chemical potential of the liquid state of the hard sphere system, we need to know the value of $-\log w(0)$. By Equations (4) and (5), the principle of going from one histogram to the next neighboring one found that $-\log w(0) = 192.76$, and our result in

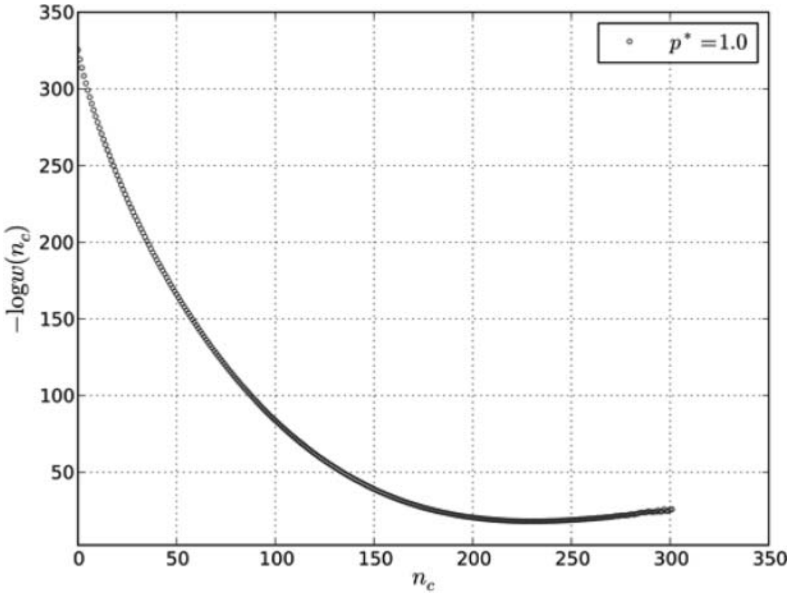

Figure 5. n_c vs. $-\log w(n_c)$.

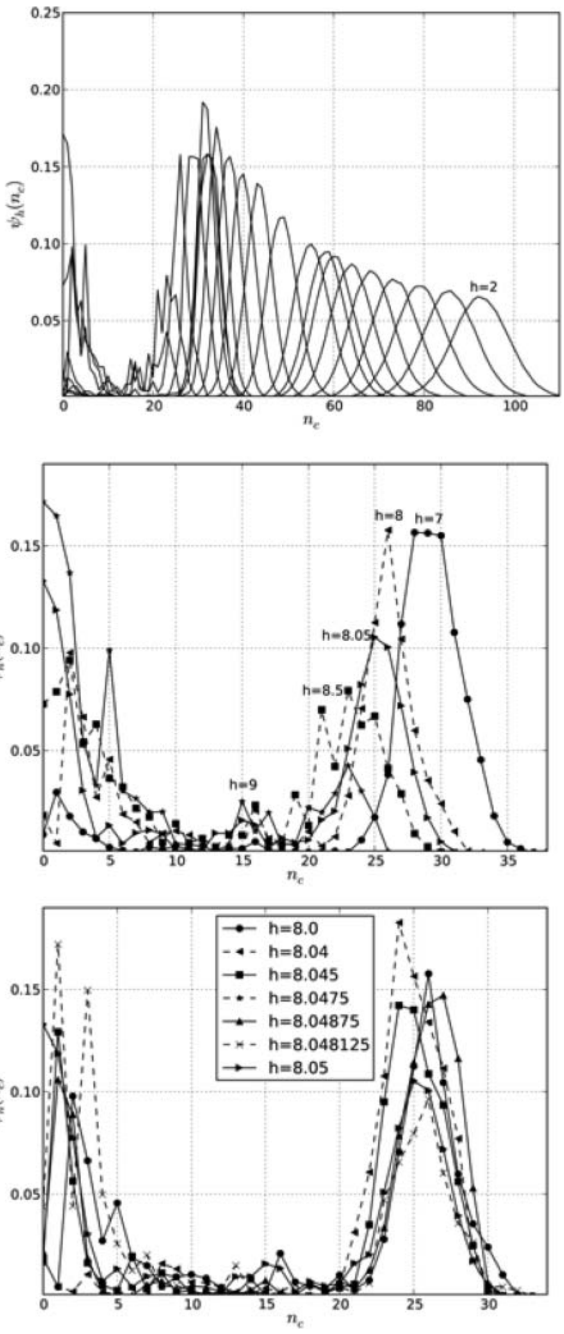

Figure 6. (top) A plot of histograms $\psi_h(n_c)$ for h ranged in [2,9]. The CL branch at $p^* = 12$ was taken. (middle) A zoomed-in histograms $\psi_h(n_c)$ plot for h ranged in {7, 8, 8.05, 8.5, 9}. (bottom) A further zoomed-in histograms $\psi_h(n_c)$ plot for h ranged in {8, 8.04, 8.045, 8.0475, 8.04875, 8.048125, 8.05}. Despite of the smaller step size near the gap in the histograms, we found no improvement.

chemical potential at the liquid state was $\beta\mu = 2.48$ by using Equation (8). In contrast, the PSMH method failed at the coexisting liquid-solid state ($p^* = 12$ of the CL branch) of the hard sphere system because there was an unfillable gap to overlap two histograms around $n_c = 15$. We did not examine for a larger number of cycles more than 200000 MC steps, but we tested for smaller step sizes down to $\Delta h = 0.000625$, but we still could not generate overlapping multi-histograms when $p^* = 12$ of the CL branch. (See Fig. 6.) This stemmed from an enormous free energy barrier between the solid phase and the liquid phase, and it was impossible to go from one phase to another. Furthermore, those two pinpointed checks whether the PSMH method works or not give us more information without further calculations. For example, we can guess that the PSMH will be applicable to calculate free energy at $p^* = 1$ of the CL branch where the volume fraction is low. According to [11], we can also expect that the PSMH (or MC) method will fail at $p^* = 12$ and $p^* = 15$ of the LC branch where the volume fraction is high. We attempt three additional free energy calculations at those $p^* = 1$ of the CL branch, $p^* = 12$ and $p^* = 15$ of the LC branch, and we found the results as we predicted.

Previously, we showed that the PSMH method works in the nematic phase of the infinitely thin square platelet system [1]. Why does it work for infinitely thin platelets and not for spheres? The sphere has a volume, but the platelets do not. The volume fraction of openings for the sphere system is at most 0.26 since the volume fraction of sphere packing with a close-packed structure is 0.74 [12].

When the volume fraction of openings for the sphere system approaches to 0.26, it is difficult for two spheres to find an opening to separate each other. However, in the case of infinitely thin platelets, there are plenty of openings due to the fact that they are a two dimensional object confined in the three dimensional box. Therefore, we could generate overlapping multi-histograms, and the PSMH method worked [1]. We anticipate that there is a break down of applying the PSMH method as we increase thickness to the platelets. It is because of a free energy barrier around the phase transition prevents us from going from one phase to another.

4. Conclusion and Prospects

We tried to apply the phase space multi-histogram (PSMH) method to study the phase transition of the system of hard spheres. The PSMH method worked in the liquid state where the volume fraction is low; however, the method failed at coexisting liquid-solid state where the volume fraction is high. This shows a counterexample of applying the method. In that case, other methods such as grand canonical and Gibbs ensemble Monte Carlo methods also expexct to fail. Nonetheless, the advantage of the PSMH method is that the idea of the method, shrinking the volume of a phase space, is handy and easily understood. The prospective studies would be to classify what kinds of hard particles can be applicable to the PSMH method. To find the upper bound of the thickness of the platelets and test the method to two dimensional irregular objects would be the first step.

Acknowledgment

A part of this work was supported by Grant-in-Aid for Scientific Research on Priority Areas, Matter Physics from the Ministry of Education, Culture, Sports, Science and Technology, Japan. I wish to thank Jun-ichi Takimoto, Ben R. Gannet, and Sathish K. Sukumaran for their helpful discussions. I would also like to thank an anonymous reviewer for thoughtful comments.

References

[1] Nomura, H., Koda, T., Nishioka, A., & Miyata, K. Submitted to *J. Phys. Soc. Jpn*, 81, 014001-014001.5 (2012).

[2] Berg, B. A., & Neuhaus, T. (1991). *Phys. Lett. B*, *267*, 249.

[3] Berg, B. A., & Neuhaus, T. (1992). *Phys. Rev. Lett.*, *68*, 9.

[4] Ferrenberg, M., & Swendsen, H. (1988). *Phys. Rev. Lett.*, *61*, 2635.

[5] Bates, M. A. (1999). *J. Chem. Phys.*, *111*, 1732.

[6] Frenkel, D., & Smit, B. (2002). *Understanding Molecular Simulation: From Algorithms to Applications*, Academic Press: San Diego, USA.

[7] Widom, B. (1963). *J. Chem. Phys.*, *39*, 2808.

[8] Widom, B. (1978). *J. Stat. Phys.*, *19*, 563.

[9] Widom, B. (1982). *J. Phys. Chem.*, *86*, 869.

[10] Koda, T., & Ikeda, S. (2002). *J. Chem. Phys.*, *116*, 5825.

[11] Fixman, M. (1983). *J. Chem. Phys.*, *78*, 4223.

[12] http://en.wikipedia.org/wiki/Sphere_packing