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An instability in a hard-disc system in a narrow box

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Abstract. It is shown that a system of N ($N \to \infty$) hard discs (of diameter σ) in a narrow box, of width D ($D < \sqrt{3}\sigma$) and length $L = Nl$, is unstable for a certain range of D and l when D is variable.

1. Introduction

It is well known (Van Hove 1949) that the second derivative of the Helmholtz free energy against volume for a system in the thermodynamic limit cannot be negative. In other words, the pressure–volume isotherm of such a system cannot include any part with a positive slope. However, it is also known (Alder and Wainwright 1960, Alder *et al* 1963, Hoover and Alder 1967) that van der Waals-like loops may occur in the equation of state of a small system (number of particles $N \sim 10^2$). This leads to the conclusion that the loop in the isotherm is connected with constraints imposed on a system by its boundaries (some configurations of molecules are excluded). Mayer and Wood (1965), studying periodic systems displaying a first-order phase transition in the thermodynamic limit, showed that the interfacial tension between two phases should give a loop in the equation of state at finite N. In this paper it is shown that a loop may be observed also in a system with infinitely large N if the system is a thin two-dimensional layer (strip). An example is the hard-disc system in a narrow box (Wojciechowski *et al* 1982) which is considered here. The box is a rectangle of width $D \leqslant \sqrt{3}\,\sigma$ parallel to the y axis and a length $L = Nl$ parallel to the x axis, periodic boundary conditions being imposed in the y direction. It is proved that if the two-dimensional volume of the box is changed keeping N, L and T (temperature), constant (that is only D is changed) then the transverse pressure p_{D} is an increasing function of the two-dimensional volume for a certain range of D and l (see the following section and Wojciechowski *et al* 1982).

2. Basic formulae

2.1. Preliminaries

The Helmholtz free energy per particle $\varphi(T; l; D)$ for a hard-disc system, contained in a narrow box of width D and length per particle l, has been calculated (Wojciechowski

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et al 1982). It is convenient to repeat this result:

$$\varphi(T;l;D)=k_BT\{g[l;s(l;D);D]-\ln(2\Lambda^2)\} \tag{1}$$

where the real and positive function $s_D=s(l;D)$ is given by

$$0=(\partial/\partial s)g(l;s;D)|_{s=s_D} \tag{2}$$

where s is in general complex and

$$\Lambda=(2\pi mk_BT/h^2)^{1/2} \qquad g(l;s;D)=h(s;D)-ls \tag{3}$$

$$h(s;D)=-\ln[R_0(s;D)/s] \tag{4}$$

$$R_i\equiv R_i(s;D)=\int_0^{D/2}(\sigma^2-x^2)^{i/2}\exp[-s(\sigma^2-x^2)^{1/2}]\,\mathrm{d}x. \tag{5}$$

Equation (2) can be written in the form

$$l=s_D^{-1}+R_1(s_D;D)/R_0(s_D;D) \tag{6}$$

since $s_D=f_L/k_BT$, where f_L is the force elongating the box ('longitudinal' force). Equation (6) will then express the force in terms of other parameters in the system, that is T, l, D. For simplicity we will write s in place of s_D bearing in mind that s is now real and positive. It is clear from the form of (6) that it would be convenient to treat s as an independent variable. This can be achieved when, instead of the Helmholtz free energy $\varphi(T,l;D)$, one introduces an analogue of the Gibbs free energy (free enthalpy) $\psi(T;s;D)$:

$$\psi(T;s;D)=\varphi[T;l(s;D);D]+k_BTsl(s;D)=k_BT[h(s;D)-\ln(2\Lambda^2)]. \tag{7}$$

This change enables one to find other properties of the system easily. For example, the transverse force per particle f_D (widening the box) can be calculated as†

$$f_D=-\partial\varphi/\partial D=-\partial\psi/\partial D=-k_BT\,\partial h/\partial D=\tfrac{1}{2}k_BT\exp[-s(\sigma^2-x^2)^{1/2}]/R_0(s;D). \tag{8}$$

The 'longitudinal' and 'transverse' pressures p_L and p_D are defined as

$$p_L=f_L/D \qquad p_D=f_D/l \tag{9}$$

and the thermodynamic pressure p is given by

$$p=\tfrac{1}{2}(p_L+p_D). \tag{10}$$

2.2. *Second derivatives*

In this section second derivatives of the Helmholtz free energy against two-dimensional volume are analysed for the following three simple cases:

(*a*) $D=$ constant, l variable;
(*b*) D variable, $l=$ constant;
(*c*) $\alpha=l/D=\sqrt{3}/2$, $a=lD$ variable.

A negative value of the derivative for some range of l and D is equivalent to the existence of a 'loop' in the pressure–volume isotherm.

† Symbols of partial derivatives without brackets mean differentiation against direct arguments of a function. For example, $\partial\varphi/\partial D$ means $(\partial\varphi/\partial D)_{l,T}$ and $\partial\psi/\partial D$ means $(\partial\psi/\partial D)_{s,T}$. See also Wojciechowski *et al* (1982).

In case (a) for $s \in (0; \infty)$ one obtains

$$\left(\frac{\partial^2\varphi}{\partial a^2}\right)_{D,T} = -\left(\frac{\partial p_L}{\partial a}\right)_{D,T} = -\frac{1}{D^2}\left(\frac{\partial f_L}{\partial l}\right)_{D,T} = -\frac{k_B T}{D^2}\left(\frac{\partial l}{\partial s}\right)^{-1}$$
$$= \frac{k_B T}{D^2}\left(\frac{1}{s^2}+\frac{R_0R_2-R_1^2}{R_0^2}\right)^{-1} > 0. \tag{11}$$

The last inequality results from

$$0 < \tfrac{1}{2}\int_0^{D/2} \mathrm{d}x \int_0^{D/2} \mathrm{d}y [(\sigma^2-x^2)^{1/2}-(\sigma^2-x^2)^{1/2}]^2 \exp\{-s[(\sigma^2-x^2)^{1/2}+(\sigma^2-y^2)^{1/2}]\}$$
$$= R_0R_2-R_1^2. \tag{12}$$

In case (b) the following equalities hold:

$$\left(\frac{\partial^2\varphi}{\partial a^2}\right)_{l,T} = -\left(\frac{\partial p_D}{\partial a}\right)_{l,T} = -\frac{1}{l^2}\left(\frac{\partial f_D}{\partial D}\right)_{l,T} = -\frac{1}{l^2}\left[\left(\frac{\partial f_D}{\partial D}\right)_{f_L,T} + \left(\frac{\partial f_D}{\partial f_L}\right)_{D,T}\left(\frac{\partial f_L}{\partial D}\right)_{l,T}\right]$$
$$= \frac{k_B T}{l^2}\left[\frac{\partial^2 h}{\partial D^2}+\frac{\partial^2 h}{\partial s\,\partial D}\left(\frac{\partial s}{\partial D}\right)_l\right] = \frac{k_B T}{l^2}\left[\frac{\partial^2 h}{\partial D^2}+\left(\frac{\partial^2 h}{\partial s\,\partial D}\right)^2\left(-\frac{\partial l}{\partial s}\right)^{-1}\right]. \tag{13}$$

In view of (11) and since for $s \in (0; \infty)$

$$\frac{\partial^2 h}{\partial s \partial D} = -\frac{1}{2}\frac{\partial}{\partial s}[r(s;D)/R_0] = \frac{r(s;D)}{2R_0^2}[R_0(\sigma^2-D^2/4)^{1/2}-R_1]$$
$$= \frac{r(s;D)}{2R_0^2}\int_0^{D/2}[(\sigma^2-D^2/4)^{1/2}-(\sigma^2-x^2)^{1/2}]\exp[-s(\sigma^2-x^2)]\,\mathrm{d}r < 0 \tag{14}$$

where $r(s;D) = \exp[-s(\sigma^2-D^2/4)^{1/2}]$, then the second term in the square brackets in (13) is always positive. On the other hand, the first term

$$\partial^2 h/\partial D^2 = -\tfrac{1}{2}(\partial/\partial D)[r(s;D)/R_0] = \tfrac{1}{4}[r(s;D)/R_0^2][r(s;D)-\tfrac{1}{2}sD(\sigma^2-D^2/4)^{-1/2}R_0] \tag{15}$$

is positive for $s \to 0_+$, while for $s \to \infty$ it becomes negative. The last conclusion can be drawn from analysis of the asymptotic expansion (see Fedorjuk 1977 p 35)

$$R_0(s;D) \simeq \frac{1}{s}r(s;D)\left(\frac{2}{D}(\sigma^2-D^2/4)^{1/2}+\frac{8}{D^3}\frac{1}{s}+\ldots\right). \tag{16}$$

The region in which expression (15) is negative is shown in figure 1. From a formal point of view one can say that $D < \sigma$ in figure 1 (see Wojciechowski *et al* 1982) negates the hard-disc concept. It is worth noting, however, that a hard-disc system in a y periodic box of width $D (D \leqslant \sqrt{3})$ is very similar to a hard-disc system in a y hard-wall box of width $D' = \sigma + D/2$. The similarity is clearly visible when one analyses close-packed structures of both systems and their thermodynamic properties in the one-dimensional limit, that is $D \to 0$, $D' \to \sigma$.

Since, as mentioned above, the second term in the square brackets in (13) is positive, the region in which the whole bracket is negative is reduced considerably (see figure 2). Plots of $(\partial^2\varphi/\partial a^2)_{l,T}$ and p_D against D for $l = 1.5\sigma$ are presented in figure 3. The positive slope of the latter for $D > D^*$ is clearly visible.

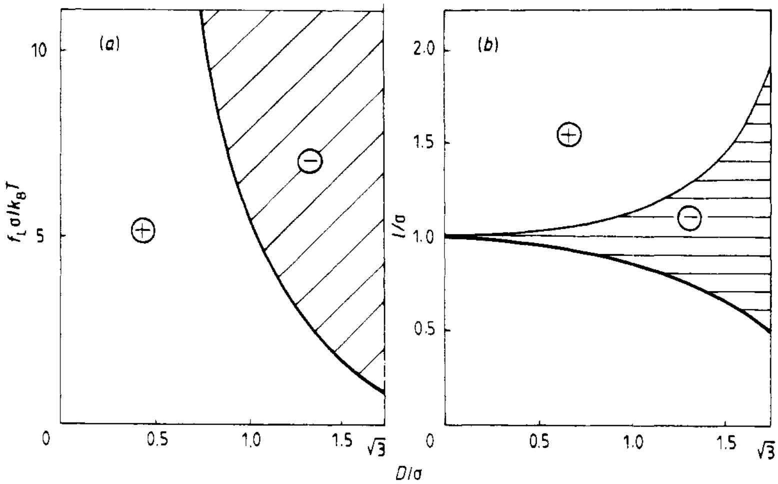

Figure 1. Diagram of the sign of $\partial^2 h/\partial s^2$: (*a*) D–s diagram; (*b*) D–l diagram. The thick curve in (*b*) represents the closest packing limit—states below this line are not accessible for the system.

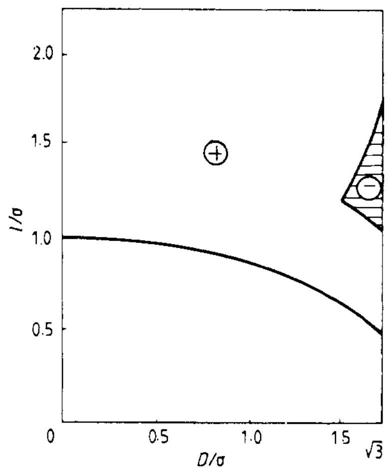

Figure 2. Region of negativity of $(\partial^2\varphi/\partial a^2)_{l,T}$. The thick curve represents the closest packing limit.

In case (*c*) the derivative $(\partial^2\varphi/\partial a^2)_{\alpha,T}$ is calculated. In view of the relations

$$a = lD = \alpha D^2 \tag{17}$$

$$\left(\frac{\partial f_{\mathrm{L}}}{\partial D}\right)_{\alpha,T} = -\left(\frac{\partial \alpha}{\partial D}\right)_{f_{\mathrm{L}},T}\left(\frac{\partial \alpha}{\partial f_{\mathrm{L}}}\right)_{D,T} = k_{\mathrm{B}}T\left(\alpha - \frac{\partial l}{\partial D}\right)\left(\frac{\partial l}{\partial s}\right)^{-1} \tag{18}$$

$$\left(\frac{\partial f_{\mathrm{D}}}{\partial f_{\mathrm{L}}}\right)_{D,T} = -\frac{\partial^2 h}{\partial s\,\partial D} = -\frac{\partial l}{\partial D} \tag{19}$$

$$\left(\frac{\partial f_{\mathrm{D}}}{\partial D}\right)_{\alpha,T} = \left(\frac{\partial f_{\mathrm{D}}}{\partial D}\right)_{f_{\mathrm{L}},T} + \left(\frac{\partial f_{\mathrm{D}}}{\partial f_{\mathrm{L}}}\right)_{D,T}\left(\frac{\partial f_{\mathrm{L}}}{\partial D}\right)_{\alpha,T} \tag{20}$$

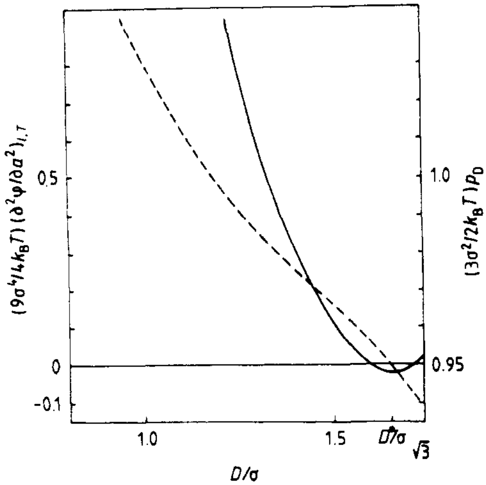

Figure 3. p_D (full curve) and $(\partial^2\varphi/\partial a^2)_{l,T} = -(\partial p_D/\partial a)_{l,T}$ (broken curve) against D at constant $l = 1.5\sigma$.

one obtains, after simple calculations,

$$\left(\frac{\partial^2\varphi}{\partial a^2}\right)_{\alpha,T} = -\left(\frac{\partial p}{\partial a}\right)_{\alpha,T} = \frac{p}{2a} + \frac{k_BT}{4l^2}\left[\frac{\partial^2 h}{\partial D^2} - \left(\alpha - \frac{\partial l}{\partial D}\right)^2\left(\frac{\partial l}{\partial s}\right)^{-1}\right]. \tag{21}$$

A graph of the function at $\alpha = \sqrt{3}/2$ is shown in figure 4. It is clear that in this case (as in case (a)) the derivative is positive.

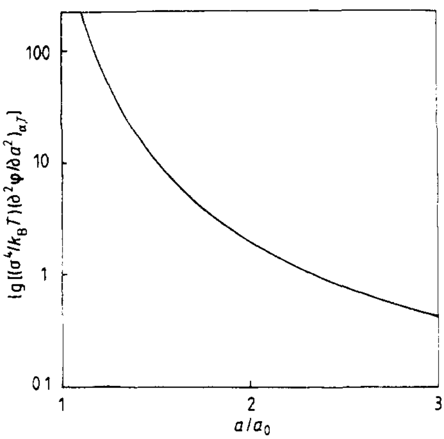

Figure 4. $(\partial^2\varphi/\partial a^2)_{\alpha,T}$ against two-dimensional volume a for $\alpha = \frac{1}{2}\sqrt{3}$ $(a_0 = \frac{1}{2}\sqrt{3}\sigma^2)$.

3. Discussion and conclusions

The necessary condition of mechanical internal stability of a bulk system is a positive value of the second derivative of its Helmholtz free energy against volume. This follows immediately from the second law of thermodynamics (see for example, Guggenheim 1967) when one assumes that the Helmholtz free energy of the system is an additive function of volume. The last assumption means that if the system is divided into two macroscopic parts, the sum of the free energies of both sub-systems is equal to the free energy of the whole, that is a correction caused by interaction of both parts can be neglected. This assumption is not generally true for thin layers (strips). Only when a layer (strip) is divided in parts transversely (the cut dividing the layer (strip) is parallel to its thickness (width)) the interaction of both parts can be neglected. Then following Guggenheim one obtains $(\partial^2\varphi/\partial a^2)_{D,T} > 0$ for the system studied here (case (a)). When a layer (strip) is divided 'longitudinally' (the cut is perpendicular to the thickness (width)) the correction arising from interactions of both sub-systems, being proportional to the area (length) and, hence, to N, cannot be neglected. Thus the Helmholtz free enegy is not additive and the previous (Guggenheim) discussion (which would give $(\partial^2\varphi/\partial a^2)_{l,T} > 0$ for the system studied) is useless. Calculations performed in case (b) showed that the derivative $(\partial^2\varphi/\partial a^2)_{l,T}$ is indeed negative in a certain range of D and l.

Results obtained in § 2.2 proved that if the width D of the box is variable and can be changed independently of the length l, the system will be unstable for certain D and l (case (b)). The necessity of changeability of D and independency of D on l results from cases (a) and (c): firstly at fixed D the system is stable (case(a)) and secondly at constant ratio $l/D = \sqrt{3}/2$ it is also stable (case (c)). The size of domains representing unstable states in the l–D diagram depends on external conditions to which the system is subjected. Figure 2 shows the domain of unstable states at fixed length of the box and controlled force f_{D}. The case when, instead of the length l, the force f_{L} is fixed and f_{D} is controlled is shown in figure 1(b).

The van der Waals-like loop (see figure 3) appearing in the hard-disc system in the narrow box has its source in restrictions imposed on possible configurations of particles by boundary conditions. The main restrictions, that is firstly the condition of the same width D along all the box and secondly limited y component of the distance of interacting particles, are common for both periodic and hard-wall boundary conditions. These restrictions are also substantial (at finite temperatures) for less artificial potentials of interactions and in three-dimensional systems. This provides the suggestion that the loop may occur in three-dimensional layers. It should not be difficult to examine this possibility by performing computer simulations. The existence of the loop would also be visible in experiments with latexes (Pieranski 1980) both in two-dimensional and three-dimensional cases if particles were between parallel lines and plates, respectively.

In a system containing large planar molecules dispersed among small spherical ones the instability might manifest itself as clustering of planar molecules. At small external pressure (the systems out of the instability region) the distances of planar molecules are almost equal. At higher pressure (the system in the instability region) the distances cannot be equal because such a state is thermodynamically unstable. There will be two most probable distances between nearest plates: the larger one which is equal to the distance between clusters, and the smaller one which is equal to the intermolecular distance in a cluster. The dimensions of clusters should be finite because the system is close to being one-dimensional with nearest-neighbour interaction and the latter does not show any phase transitions (Takahashi 1942).

After submitting this paper we received a communication (Antonchenko *et al* 1982) about computer simulations of hard-sphere three-dimensional thin layers with hard walls. The pressure on the wall shows some oscillations when the width of the layer increases (density is taken as constant). It supports our suggestion that the instability analysed here may occur in three dimensions and for other boundary conditions. Because oscillations (and not only one loop) are observed, one can suspect that some (not only two) most probable distances will be observed in the system of large planar molecules.

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