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Metastable States in the van der Waals–Maxwell Theory

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A slight modification of the recent Penrose and Lebowitz treatment of thermodynamic metastable states is presented. For the case of periodic boundary conditions, this modification allows the condition of metastability to be extended to all the metastable states in the van der Waals–Maxwell theory of the liquid–vapor phase transition, that is, for all states satisfying

$$f_0(\rho) + \tfrac{1}{2}\alpha\rho^2 > f(\rho, 0+)$$

and

$$f_0''(\rho) + \alpha \geqslant x > 0$$

where $f(\rho, 0+)$ is the (stable) Helmholtz free energy density of the generalized van der Waals–Maxwell theory and $f_0(\rho)$ is the Helmholtz free energy density of a reference system with no long-range interaction. α is a "mean field"-type term arising from a long-range Kac interaction, ρ is the overall mean particle density, and x is any positive number. For the case of rigid-wall boundary conditions, a more restrictive condition is placed on x.

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A recent article by Penrose and Lebowitz[1] presents a rigorous treatment of the metastable states in the van der Waals–Maxwell theory of the liquid–vapor phase transition. They consider a classical system contained in a

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ν-dimensional cube Ω, with a pair potential of the form $q(r) + \gamma^\nu \phi(\gamma r)$, where $q(r)$ is a short-range interaction and $\gamma^\nu \phi(\gamma r)$ is a long-range Kac interaction. The term γ represents an inverse range parameter. The domain Ω is divided into M cells each with volume $|\omega|$. A restricted region R of phase space is defined by requiring that the number of particles n_k in the kth cell satisfy the relation

$$\rho^- |\omega| < n_k < \rho^+ |\omega|, \qquad k = 1, 2, \ldots, M \tag{1}$$

where ρ^- and ρ^+ are to be specified. This restricted region of phase space is said to correspond to a metastable state in the following sense: If the maximum rate λ of phase points leaving R, given an ensemble of systems initially ($t = 0$) confined to R, can be made arbitrarily small, then we say that the region R corresponds to a thermodynamic metastable state.

Penrose and Lebowitz derive the rigorous upper bound on λ given by expression[3] [PL(30)]

$$\lambda \leqslant M(kT/2\pi m)^{1/2}\, 2\nu\, |\omega|^{1-(1/\nu)}\, \rho_{\max}\{\mathrm{Max}_i\, \mathrm{prob}(n_i = n^+ \text{ or } n^-)\} \tag{2}$$

This bound is obtained from a kinetic theory argument where k is Boltzmann's constant, T is the absolute temperature, and m is the mass of a particle. $\rho_{\max}$ is an upper bound on the density and $\{\mathrm{Max}_i\, \mathrm{prob}(n_i = n^+ \text{ or } n^-)\}$ is the maximum over i ($i = 1, 2, \ldots, M$) of the probability that the ith cell initially ($t = 0$) have either n^+ or n^- particles.[4] For a restricted portion of the metastable states in the van der Waals–Maxwell theory [see PL (10), (81), and (82)], Penrose and Lebowitz show that $\lambda \to 0$ under the limit

$$|\Omega| \gg \gamma^{-\nu} \gg |\omega| \gg r_0^{\,\nu} \ln |\Omega| \tag{3}$$

where r_0 is a length characterizing the potential $q(r)$. We note that the crucial property to show[5] is

$$\{\mathrm{Max}_i\, \mathrm{prob}(n_i = n^+ \text{ or } n^-)\} \leqslant \exp\{-|\omega|[C + o(1)]\} \tag{4}$$

where C is a positive number. If (4) is satisfied, then $\lambda \to 0$ under the limit given by (3).

Below, we show that for the case of periodic boundary conditions, a slight modification of the Penrose–Lebowitz procedure yields $\lambda \to 0$ for all

[3] Equations referring to Ref. 1 will be denoted by [PL ( )].

[4] n^+ and n^- are integral solutions of [PL (31)], $n^+ < \rho^+ |\omega| \leqslant n^+ + 1$ and $n^- > \rho^- |\omega| \geqslant n^- - 1$.

[5] The order symbol means: If $x = o(1)$, then $\lim x = 0$.

the metastable states in the van der Waals–Maxwell theory; that is, for all states satisfying

$$f_0(\rho) + \tfrac{1}{2}\alpha\rho^2 > f(\rho, 0+) \tag{5a}$$

and

$$f_0''(\rho) + \alpha \geqslant x > 0 \tag{5b}$$

where $f(\rho, 0+)$ is the Helmholtz free energy density acted on by the limiting process (3) which is given by[1,2]

$$f(\rho, 0+) = \text{C.E.}\{f_0(\rho) + \tfrac{1}{2}\alpha\rho^2\}. \tag{6}$$

The term C.E.{ } is the convex envelope of the function in the bracket. $f_0(\rho)$ is the Helmholtz free energy density (evaluated in the thermodynamic limit) for a reference system with short-range interactions but no long-range interactions. f_0'' denotes the second derivative of f_0 and is assumed to be continuous. The term α ($\alpha < 0$) is a "mean field"-type term arising from the long-range Kac interaction and x is any positive number. For the case of rigid-wall boundary conditions, a more restrictive condition is placed on x.

We establish a bound on the probability $p_i(n^+)$ that the ith cell has n^+ particles given an ensemble of systems confined to R. A similar argument leads to bounds on $p_i(n^-)$. A bound for $p_i(n^+)$ is given by [PL (49)], which should read[6]

$$p_i(n^+) \leqslant \exp\Big\{\Big[\mu(n^+ - \bar{n}) - F_0(n^+, \omega) + F_0(\bar{n}, \omega') - (n^+ - \bar{n}) \sum_j n_j w(\mathbf{k}_{ij}) + o(|\,\omega\,|)\Big]\Big/kT\Big\} \tag{7}$$

where $w(\mathbf{k}_{ij})$ is a "characteristic" long-range Kac interaction between cells i and j,

$$F_0(n, \omega) = |\,\omega\,|[f_0(n/|\,\omega\,|) + o(1)] \tag{8}$$

and $\bar{n}$ is any integer such that $n^- < \bar{n} < n^+$. The choice of $\bar{n}$ is specified below. Inequality (7) can now be written as

$$p_i(n^+) \leqslant \exp\Big\{\Big[|\,\omega\,|/kT\Big]\Big[\mu(\rho^+ - \bar{\rho}) - f_0(\rho^+) + f_0(\bar{\rho}) - (\rho^+ - \bar{\rho}) \sum_j n_j w(\mathbf{k}_{ij}) + o(1)\Big]\Big\} \tag{9a}$$

where[7]

$$\bar{\rho} = \bar{n}/\,|\,\omega\,| \tag{9b}$$

[6] Note that there is a misprint in [PL (49)]. The n^- terms should be $\bar{n}$.

[7] Note that at this point we do not place any conditions on $\bar{\rho}$ other than requiring $\rho^- < \bar{\rho} < \rho^+$.

Using [PL (9)], which relates the chemical potential μ to the overall mean density $\rho(\rho^- < \rho < \rho^+)$ by

$$\mu = f_0'(\rho) + \alpha\rho \tag{10}$$

in (9a) we obtain

$$p_i(n^+) \leqslant \exp\left\{-\frac{(\rho^+ - \bar{\rho})|\,\omega\,|}{kT}\left[\frac{f_0(\rho^+) - f_0(\bar{\rho})}{\rho^+ - \bar{\rho}} - f_0'(\rho) + \sum_j n_j w(\mathbf{k}_{ij}) - \alpha\rho + o(1)\right]\right\} \tag{11}$$

We now assume that

$$w(\mathbf{k}_{ij}) \leqslant 0 \tag{12}$$

for all i and j. Since all n_j must be less[4] than $\rho^+ |\,\omega\,|$, we obtain [PL (54)]

$$\sum_j n_j w(\mathbf{k}_{ij}) \geqslant n^+ \sum_j w(\mathbf{k}_{ij}) = \rho^+[\alpha + o(1)] \tag{13}$$

This inequality is valid independent of the system being described by periodic or rigid-wall boundary conditions [see PL(54) and (80)]. Inequality (11) can now be written as

$$p_i(n^+) \leqslant \exp\left\{-\frac{(\rho^+ - \bar{\rho})|\,\omega\,|}{kT}\left[\frac{f_0(\rho^+) - f_0(\bar{\rho})}{\rho^+ - \bar{\rho}} - f_0'(\rho) + \alpha(\rho^+ - \rho) + o(1)\right]\right\} \tag{14}$$

We observe that $\alpha(\rho^+ - \rho)$ is negative and independent of the choice of $\bar{\rho}$. However, since $f_0(\rho)$ is a convex function,[3]

$$\Delta = \frac{f_0(\rho^+) - f_0(\bar{\rho})}{\rho^+ - \bar{\rho}} - f_0'(\rho) \tag{15}$$

is positive provided $\rho < \bar{\rho} < \rho^+$. In fact, Δ must increase as $\bar{\rho}$ becomes closer to ρ^+. By the mean value theorem, (15) can be written as

$$\Delta = f_0'(\rho_1) - f_0'(\rho) \tag{16}$$

where ρ_1 is contained in $[\bar{\rho}, \rho^+]$. Again using the mean value theorem, we obtain

$$\Delta = f_0''(\rho_2)(\rho_1 - \rho) \tag{17}$$

where ρ_2 is contained in $[\rho, \rho_1]$. We now assume (5b) is satisfied for all values of the argument in the interval $[\rho^-, \rho^+]$. Equation (17) can then be bounded below by

$$\Delta \geqslant (x - \alpha)(\rho_1 - \rho) \geqslant (x - \alpha)(\bar{\rho} - \rho) \tag{18}$$

provided $\rho < \bar{\rho} < \rho^+$.

Using (15) and (18) in (14), we find

$$p_i(n^+) \leqslant \exp\{-[(\rho^+ - \bar{\rho})|\,\omega\,|/kT][x(\bar{\rho} - \rho) + \alpha(\rho^+ - \bar{\rho}) + o(1)]\} \quad (19)$$

We desire an upper bound on $p_i(n^+)$ which is of the form given in (4), i.e.,

$$p_i(n^+) \leqslant \exp\{-\,|\,\omega\,|[C + o(1)]\} \quad (20)$$

where C is a positive number. This can always be accomplished by using (19) and defining

$$C = [(\rho^+ - \bar{\rho})/kT][x(\bar{\rho} - \rho) + \alpha(\rho^+ - \bar{\rho})]$$

provided we choose $\bar{\rho}$ such that

$$(x\rho - \alpha\rho^+)/(x - \alpha) < \bar{\rho} < \rho^+ \quad (21)$$

Any $\bar{\rho}$ so chosen[8] yields a bound on $p_i(n^+)$ as given by (20).

For the case of periodic boundary conditions, a similar analysis for $p_i(n^-)$ yields the desired bound provided that for this case $\bar{\rho}'$ is chosen such that

$$\rho^- < \bar{\rho}' < (x\rho - \alpha\rho^-)/(x - \alpha) \quad (22)$$

which is always satisfied for any $x > 0$. For the case of rigid-wall boundary conditions, the analysis[9] for $p_i(n^-)$ yields the desired bound provided $\bar{\rho}'$ is chosen such that

$$\rho^- < \bar{\rho}' < (\rho x - \rho^-\alpha')/(x - \alpha) \quad (23)$$

where α' is given by [PL (80)]

$$\alpha' = \text{limit of Min}_i\,|\,\omega\,|\sum_j w(\mathbf{k}_{ij}) = 2^{-\nu}\alpha \quad (24)$$

Unlike (22), (23) is not satisfied for any $x > 0$. There are, however, two possible ways of using (23). One way is to choose $\rho^- = 0$. Then, (23) reduces to

$$0 < \bar{\rho}' < \rho x/(x - \alpha) \quad (25a)$$

which is valid for any $x > 0$. However, since we have required (5b) to be satisfied in the interval $[\rho^-, \rho^+]$, the choice of $\rho^- = 0$ must be coupled with the condition

$$f_0''(y) + \alpha > 0, \qquad y \in [0, \rho^+] \quad (25b)$$

[8] Note that $\rho < (x\rho - \alpha\rho^+)/(x - \alpha) < \rho^+$ for any $x > 0$.

[9] For this case the inequality corresponding to (13) is $\sum_j n_j w(\mathbf{k}_{ij}) \leqslant n^- \sum_j w(\mathbf{k}_{ij}) \leqslant \rho^-\alpha'$.

The other way of using (23) is to choose

$$x > [\rho^{-}/(\rho - \rho^{-})][-\alpha + \alpha'] \tag{26}$$

Expression (23) can be satisfied for any x consistent with (26).

The main departure from the Penrose and Lebowitz work is in choosing the appropriate $\bar{\rho}$ as specified by (21)–(23), instead of choosing $\bar{\rho} = \rho$. Simply stated, the choice of $\bar{\rho}$ as presented here allows the replacement of 2α by α in [PL (10), (81), and (82)].

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