RIGOROUS TREATMENT OF SYSTEMS WITH LONG RANGE

POTENTIALS AND OTHER TOPICS[*,+]

by

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A. RIGOROUS TREATMENT OF SYSTEMS WITH LONG-RANGE POTENTIALS

I. Equilibrium States

Rigorous upper and lower bounds were obtained[1] for the thermo-dynamic free-energy density $a(\rho,\gamma)$ of a classical system of particles with two-body interaction potential $q(\underline{r}) + \gamma^{\nu}\varphi(\gamma\underline{r})$ where ν is the number of space dimensions and ρ the density, in terms of the free-energy density $a^{0}(\rho)$ for the corresponding system (reference system) with $\varphi(\underline{x}) \equiv 0$. When $\varphi(\underline{x})$ belongs to a class of functions, which includes those which are non-positive and those whose ν-dimensional Fourier transforms are non-negative, the upper and lower bounds coincide in the van der Waals limit $\gamma \to 0$ and $\lim_{\gamma \to 0} a(\rho,\gamma) = CE\{a^{0}(\rho) + \tfrac{1}{2}\alpha\rho^{2}\}$:
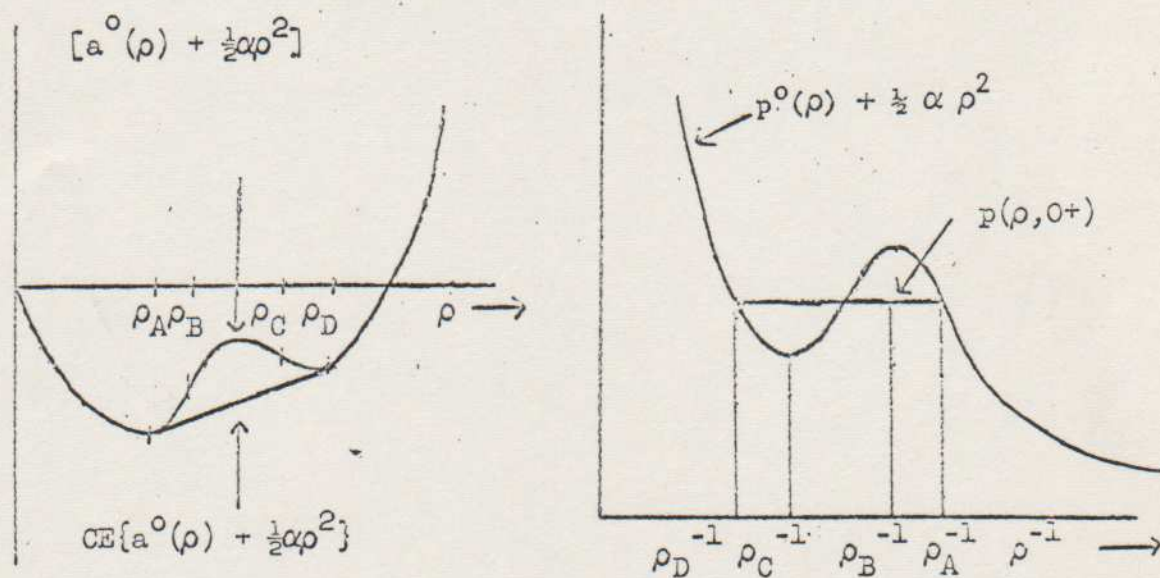
the maximal convex function of ρ not exceeding $a^{0}(\rho) + \tfrac{1}{2}\alpha\rho^{2}$, where $\alpha \equiv \int \varphi(\underline{x})d\underline{x}$. The corresponding equation of state is given by Maxwell's equal-area rule applied to the function $\qquad p^{0}(\rho) + \tfrac{1}{2}\alpha\rho^{2}$ where $p^{0}(\rho)$ is the pressure of the reference system for which $\varphi(\underline{x}) \equiv 0$. If

$a^0(\rho) + \frac{1}{2}\alpha\rho^2$ is not convex the behavior of the limiting free energy indicates a first-order phase transition.

These results are easily generalized to lattice gases and thus apply also to Ising spin systems. This was used[2] incidently to test an idea of Fisher's that in comparing the specific heats of lattice gases with continuum fluids near the critical point it should be done on the basis of their value per unit volume per particle at close packing $C*(T) = \rho \, C_{conf}^{(T)}/\rho_{max}$, where C_{conf} is the configurational specific heat per particle and $\rho = \rho_{critical}$ along the critical isochore. Using then for our reference system an 'ideal' lattice gas $q(\underline{r}) = \{^{\infty,\ \underline{r}\ =\ 0}_{0,\ \underline{r}\ \neq\ 0}$ or a continuum system of hard rods, discs or spheres we find the following results for the specific heat discontinuity at the critical point (using Pade equations of state for $\nu = 2,3$)

	Lattice gas		Continuum	
	$\nu = 1,2,3$	$\nu = 1$	$\nu = 2$	$\nu = 3$
ρ_c/ρ_{max}	.5	1/3	.233	.176
$\Delta C*/k$	1.5	1.5	1.465	1.480
$(\frac{\beta p}{\rho})_c$	.386	.376	.366	.359

The constancy of $\Delta C*$ is remarkable and unexplained.

The generalization of our results to quantum systems[3] requires only very mild additional assumptions. This permits[4] explicit calculations of the properties and critical parameters of a one dimensional quantum system of hard rods with long range attraction, i.e. $q(r) = \{^{\infty,\ r\ <\ a}_{0,\ r\ >\ a}$. The behavior of the critical temperature, pressure and density as a function of the quantum parameter λ, the ratio of the de Broglie wave length to the interparticle separation evaluated at the classical critical point

show surprising similarity to that found for real fluids expected to obey the law of corresponding states, i.e. the critical temperature and critical density decrease rapidly with λ (in almost identical manner) while the critical ratio is almost independent of λ.

II. Metastable States

In considering the equilibrium properties of these systems no meaning at all is attached to that part of the curve $a^o(\rho) + \frac{1}{2}\alpha\rho^2$ which lies above the curve $CE\{a^o(\rho) + \frac{1}{2}\alpha\rho^2\}$ or to the corresponding part of the pressure curve $p^o(\rho) + \frac{1}{2}\alpha\rho^2$. Traditionally however the parts of these curves (actually of similar curves obtained from the original van der Waals-Maxwell theory) are assumed to represent the properties of metastable states of uniform density corresponding to the supercooled vapour and the superheated liquid respectively. It is possible[5] to give a rigorous meaning to these states by considering the properties of our system when it is confined to a restricted region of the configuration space. This is done by a simple extension of the method used to obtain bounds on the equilibrium free energy. The cubical box of volume Ω to which our system consisting of N particles is confined is divided up into M cells of volume ω. We can now restrict the configuration space of our system by imposing restrictions on the densities $\rho_i \equiv N_i/\omega$ of the various cells: $N_i = N$, $i = 1, \ldots M$. The simplest such restriction is

$$\rho_- \leq \rho_i \leq \rho_+$$

where $\rho_- \leq \rho \leq \rho_+$. Let $R = R(\Omega, \omega; \rho_-, \rho_+)$ the region in configuration
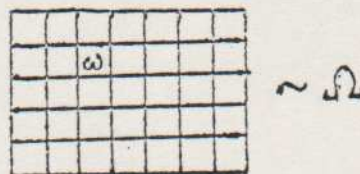
space where these restrictions are satisfied and $a'(\rho,\gamma:\omega,\mathcal{R})$ the corresponding free energy per unit volume (in the thermodynamic limit $\Omega \to \infty$, ρ fixed). When $\rho_- = 0$, $\rho_+ = \infty$, $\mathcal{R}$ coincides with the whole configuration space and $a' = a(\rho,\gamma)$ while letting ρ_- and ρ_+ approach ρ corresponds to restricting the system to be completely uniform on the scale of ω. It is then shown[5] that in the limit $\gamma \to 0$ <u>followed</u> by the limit $\omega \to \infty$, i.e. the cell size $\omega^{1/\nu} \ll \gamma^{-1}$ the range of $\varphi(\gamma_r)$,

$$\lim_{\omega \to \infty} \lim_{\gamma \to 0} a'(\rho,\gamma:\omega,\mathcal{R}) \equiv a'(\rho,0+:\mathcal{R}) = \mathcal{CE}\{a^0(\rho) + \tfrac{1}{2}\alpha\rho^2 + g(\rho)\} \qquad (2)$$

where

$$g(\rho) = \begin{cases} 0, & \rho_- \le \rho \le \rho_+ \\ \infty, & \text{otherwise} \end{cases} \qquad (3)$$

Thus if $a^0(\rho) + \tfrac{1}{2}\alpha\rho^2$ is convex in the interval $\rho_- \le \rho \le \rho_+$, a' coincides with $a^0(\rho) + \tfrac{1}{2}\alpha\rho^2$. This will be true when ρ and the interval (ρ_-,ρ_+) surrounding it is confined to the stable and/or 'metastable' parts of the graph $a^0(\rho) + \tfrac{1}{2}\alpha\rho^2$; e.g., $0 \le \rho_- \le \rho \le \rho_+ \le \rho_B$ or $\rho_C \le \rho_- \le \rho \le \rho_+ \le \infty$ in Fig.1. The precise value of ρ_- and ρ_+ are then not important, and the interval can be shrunk to the point ρ, i.e. the system will actually be in a completely uniform state. When ρ is however, in the unstable part of the graph of $a^0(\rho) + \tfrac{1}{2}\alpha\rho^2$; i.e. $\dfrac{d^2}{d\rho^2}\left[a^0(\rho) + \tfrac{1}{2}\alpha\rho^2\right] \le 0, \rho_B < \rho < \rho_C$ in Fig.1, then $a'(\rho;\mathcal{R})$ coincides with $a^0(\rho) + \tfrac{1}{2}\alpha\rho^2$ <u>only</u> when the interval (ρ_-,ρ_+) is shrunk to a point. We thus see, as expected, that the uniform state coincides with a minimum (maximum) of the constrained free energy in the metastable (unstable) region of $a^0(\rho) + \tfrac{1}{2}\alpha\rho^2$. (In the stable region where $a^0(\rho) + \tfrac{1}{2}\alpha\rho^2$ coincides with $\mathcal{CE}\{a^0(\rho) + \tfrac{1}{2}\alpha\rho^2\}$, $0 \le \rho \le \rho_A$ or $\rho_D \le \rho \le \infty$, in Fig. 1, the uniform state is, of course, the state of minimum free energy).

III. Metastable States for $\gamma \neq 0$

We have seen that in the van der Waals limit, $\gamma \to 0$, when the range of the potential becomes infinite it is possible to give a complete physical characterization of the metastable state. This state also coincides with the analytic continuation of the equilibrium isotherm in the p-ρ plane. We could also construct a restricted grand partition function $\Xi'(z,\gamma,\Omega,\omega,\aleph)$, where z is the fugacity, obtaining in the triple limit

$$\beta p'(z;\aleph) = \lim_{\omega \to \infty} \lim_{\gamma \to 0} \lim_{\Omega \to \infty} \ln \Xi'/\Omega \qquad (4)$$

the analytic continuation of the equilibrium pressure into the meta-stable region. (There is a singularity of $p'(z;\aleph)$ at the end of the metastable region where the uniform state is no longer stable against small perturbations).

The question arises however, of whether there is any way of defining metastable states for systems with realistic (non infinite-range) potentials, i.e., $\gamma \neq 0$. It seems quite possible[6] (on the basis of the droplet model) that for such potentials the isotherm $p(\rho)$ (and $p(z)$) has an essential singularity at the onset of condensation $\rho = \rho_A$. It is however, possible that there might still be some sort of analytic continuation which will define the metastable state[7]. Even if this were the case there would still be the question of how to characterize the metastable state physically, i.e. how to define a region $\aleph$ in configuration space in which the metastable state would be a local minimum for the free energy.

We may gain some insight into this problem by considering the case of very small γ, i.e. $\gamma^{-1} \gg r_o$ where r_o is the effective range of $q(r)$.

Making the dimensions of the cell ω of $O(\gamma^{-1+\delta})$, $0 < \delta < 1$, we then

have from our inequalities[1] that

$$a(\rho,\gamma) = CE\{a^o(\rho) + \tfrac{1}{2}\alpha\rho^2\} + \delta(\gamma) \tag{5}$$

while

$$a'(\rho,\gamma;\omega,R) = a^o(\rho) + \tfrac{1}{2}\alpha\rho^2 + o(\gamma) \tag{6}$$

where ρ_- and ρ_+ are again chosen in such a way that $a^o(\rho) + \tfrac{1}{2}\alpha\rho^2$ is

convex in that interval. It is thus seen that if ρ is in the

metastable portion of $a^o(\rho) + \tfrac{1}{2}\alpha\rho^2$, (for $\gamma = 0$), then for sufficiently

small γ, and hence $\omega^{1/\nu} \gg r_o$, restricting the system to a region in

configuration space where it cannot be very non-uniform on the scale

of γ^{-1} leads to a free energy per unit volume very close to that of

van der Waals, $\gamma = 0$, metastable value, corresponding to the system

being uniform. The free energy for the unrestricted system $a(\rho,\gamma)$

will, on the other hand, be close to the flat portion of the curve,

corresponding to the system being in two phases. This is true both

in one and higher dimensions. In the latter case, we expect the system

to have a first order phase transition even for finite γ while a one

dimensional system will not have a phase transition[8] for $\gamma \neq 0$. The

difference between (5) and (6) in one dimension thus indicates a tend-

ency to form clusters on the scale of γ^{-1}, with densities close to

those of liquid and vapour phases (something found numerically by

Andrews[8]). The fact that in one dimension $a(\rho,\gamma)$ is a

differentiable function[7] of ρ for $\gamma \neq 0$ (at least for some forms of q

and φ) also indicates that the 'metastable' or uniform state for

finite γ cannot come from simple analytic continuation in ρ of the equilibrium

uniform state, i e. while $a'(\rho,\gamma;\omega,R)$ is 'close' to $a(\rho,\gamma)$ for $\rho < \rho_A$
it is not close for $\rho_A < \rho < \rho_B$ to an analytic continuation of $a(\rho,\gamma)$
as would be the case in the limit $\gamma \to 0$ where $a'(\rho,0+;R)$ is the anaytic
continuation of $a(\rho,0+)$. This would be consistent with the conjecture[5,6]
that in higher dimensions also (where there is a phase transition for
finite γ) the metastable state is not a simple analytic continuation of
the equilibrium state. It is however possible, and even probable, that
$a'(\rho,\gamma:\omega,R)$ is analytic for $\rho < \rho_B$ or $\rho > \rho_c$.

These considerations, while suggestive of the meaning of the
metastable state for very small but finite γ are not entirely
satisfactory in that a' depends somewhat on the choice of ω which is
not an intrinsic parameter of the problem (simple considerations seen
to indicate that the choice $\omega^{1/\nu} \sim \gamma^{-\frac{1}{2}}$ gives the best bounds for a' in
(5)). There are two possible ways which occur to me about how it might
be possible to 'uniquely' define the metastable state:

(1) Let $\gamma^{\nu}\varphi(\gamma r) = \alpha\,\gamma^{\nu}\psi(\gamma r)$ with $\int\psi(y)dy = 1$ and $\psi(y)$ independent of
α and satisfying the conditions, $\psi(k) \geq 0, \underset{k}{\text{Max}}\,\widetilde{\psi}(\underline{k}) = \psi(0)$, where $\widetilde{\psi}(k)$ is the
Fourier transform of $\psi(y)$ e.g., $\psi(y)=(2\pi)^{-\nu/2}\ell^{-\frac{1}{2}y^2}$. Then in the limit $\gamma \to 0$ the
metastable (and unstable) state for $\alpha < \alpha_0$ 0 is the analytic continuation of the
equilibrium state for $\alpha > \alpha_0$. It is now <u>possible</u> that for $\gamma \neq 0$ there might
also be an analytic continuation in the complex α-plane from $\alpha > \alpha_0$ to
$\alpha < \alpha_0$ for the metastable state. (We are assuming here throughout that
$a^0(\rho)$ does not have a phase transition in the range of densities of
interest). This is suggested in part by considering 'formal' expansions[10]
in powers of γ of $a(\rho,\gamma)$ (or correlation functions). The coefficients
of this expansion which are functions of ρ and α appear to behave well

for the stable _and_ metastable states, the zero order term being $a^o(\rho) + \frac{1}{2}\alpha\rho^2$, diverging however at the unset of the unstable region.

2) Another possibility which is in principle applicable also to systems with short range potentials is to consider regions R not in configuration space but in the function space of possible correlation functions a la Ruelle[10]. The metastable state might then be character- ized as the state of minimum free energy in the restricted region where the pair distribution function $n_2(\underline{r}_1, \underline{r}_1, +\underline{r})$ approaches ρ^2 asymptotically.

Using the results of reference 1 it is indeed possible to show (c.f. also ref. 11) that when the free energy of the reference system $a^o(\rho)$ (where $q(r)$ is 'essentially' stable potential and contains a hard core or $q(r) \geq 0$) is strongly convex in an interval surrounding ρ (e.g. $\frac{d^2 a^o(\rho)}{d\rho^2} > 0$ in $(\rho-\delta, \rho+\delta)$) then

$$\lim_{\gamma \to 0} \lim_{\Omega \to \infty} \frac{\gamma^\nu}{\Omega} \iint \psi(\gamma r) [n_2^c(\underline{r}_1, \underline{r}_1 + \underline{r}; \rho, \Omega) - \rho^2] d\underline{r}_1 d\underline{r} = 0 \qquad (7)$$

where $\psi(y)$ satisfies the conditions of the last paragraph. Eq. (7) follows from the inequality (sec. VIII, ref. 1).

$$a(\rho, \gamma) \leq a^o(\rho) + \frac{1}{2}\alpha\rho^2 + \frac{1}{2}\alpha\gamma^\nu \lim_{\Omega \to \infty} \frac{1}{\Omega} \iint \psi(\gamma r)[n_2^o(\underline{r}_1, \underline{r}_1 + \underline{r}; \rho, \Omega) - \rho^2] d\underline{r}_1 d\underline{r} \qquad (8)$$

which holds for all α and ψ. Now taking the limit $\gamma \to 0$ we have, under the above conditions on ψ that

$$CE\{a^o(\rho) + \frac{1}{2}\alpha\rho^2\} \leq a^o(\rho) + \frac{1}{2}\alpha\rho^2 + \frac{\alpha}{2} \lim_{\gamma \to 0} \lim_{\Omega \to \infty} \frac{\gamma^\nu}{\Omega} \iint \psi(\gamma r)[n_2^o - \rho^2] d\underline{r}_1 d\underline{r} \qquad (9)$$

However under the condition on $a^o(\rho)$ mentioned before $CE\{a^o(\rho) + \frac{1}{2}\alpha\rho^2\} = a^o(\rho) + \frac{1}{2}\alpha\rho^2$ for sufficiently small (but finite) $|\alpha|$, (since $a^o(\rho)$ is convex). Q.E.D.

B. OTHER TOPICS

    I. Kinetic Equations and Density Expansions: Exactly Solvable

        One Dimensional System

We have made a tetailed study of the time evolution of the distri-
bution function $f(q,v,t)$ of a labelled (test) particle in a one-dimensional
system of hard rods of diameter a. The system has a density ρ and is in
equilibrium at $t=0$. (Some properties of this system were studied earlier
by Jepsen.) When the distribution function f at $t=0$ corresponds to a delta
function in position and velocity, then $f(q,v,t)$ is essentially the time-
displaced self distribution function f_s. This function f_s (which can be
found in an explicit closed form), and all of the system properties which
can be derived from it, depend on ρ and a only through the combination
$n = (\rho/(1-\rho a))$. In particular, the diffusion constant D is given by
$D^{-1} = \lim_{s\to 0} [\tilde{\psi}(s)]^{-1} = (2\pi\beta m)^{\frac{1}{2}}n$, where $\tilde{\psi}(s)$ is the Laplace transform of
the velocity auto-correlation function $\psi(t) = \langle v(t)v \rangle$. An expansion of
$[\tilde{\psi}(s)]^{-1}$ in powers of n on the other hand has the form $\Sigma B_\ell n^\ell/s^{\ell-1}$, leading
to divergence of the density coefficients for $\ell \geq 2$ when $s \to 0$. This is
similar to the divergences found in higher dimensional systems. Similar
results are found as well in the expansion of the collision operator
describing the time evolution $f(q,v,t)$. The lowest order term in the
expansion is the ordinary (linear) Boltzmann equation, while higher terms
are $O(\rho^\ell t^{\ell-1})$. Thus any attempt to write a Bogoliubov, Choh-Uhlenbeck type
of Markoffian kinetic equation as a power series in the density leads to
divergence in the terms beyond the Boltzmann equation. A Markoffian
collision operator can however be constructed, without using a density
expansion, which e.g. describes the stationary distribution of a charged

test particle in the system in the presence of a constant electric field. The distribution of the test particle in the presence of an oscillating external field is also found. Finally, the short and long time behavior of the self-distribution is examined.

II. Properties of a Harmonic Crystal in a Stationary Non-Equilibrium State

The stationary nonequilibrium Gibbsian ensemble representing a harmonic crystal in contact with several idealized heat reservoirs at different temperatures is shown to have a Gaussian Γ-space distribution for the case where the stochastic interaction between the system and heat reservoirs may be represented by Fokker-Planck type operators. The covariance matrix of this Gaussian is found explicitly for a linear chain with nearest neighbor forces in contact at its ends with heat reservoirs at temperatures T_1 and T_N, N being the number of oscillators. We also find explicitly the covariance matrix, but not the distribution, for the case where the interaction between the system and the reservoirs is represented by very 'hard' collisions. This matrix differs from that for the previous case only by a trivial factor. The heat flux in the stationary state is found, as expected, to be proportional to the temperature difference (T_1-T_N) rather than to the temperature gradiant $(T_1-T_N)/N$. The kinetic temperature of the jth oscillator $T(j)$ behaves, however, in an unexpected fashion. $T(j)$ is essentially constant in the interior of the chain <u>decreasing</u> exponentially in the direction of the <u>hotter</u> reservoir rising only at the end oscillator in contact with that reservoir (with corresponding behavior at the other end of the chain). No explanation is offered for this paradoxical result.

III. A Note on the Ensemble Dependence of Fluctuations with Application
      to Machine Computations

The Standard theory of fluctuations in thermodynamic variables in various ensembles is generalized to non-thermodynamic variables: e.g., the mean square fluctuations of the kinetic energy K in a classical micro-canonical ensemble at fixed energy E is given for large systems by $\langle (\delta K)^2 \rangle / \langle K \rangle = T(1 - 3/2C)$ where T is the temperature (corresponding to the energy E) and C is the specific heat per particle (in units of Boltzmann's constant). The general results may be expressed in terms of the asymptotic behavior of the Ursell functions in various ensembles. Applications are made to molecular dynamic computations where time averages correspond (via ergodicity) to phase averages in an ensemble with fixed energy and momentum. The results are also useful for time dependent correlations.

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