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Collective Modes in a One-Dimensional Nonuniform Fluid Model

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A one-dimensional fluid with short-range repulsive interaction and one period of cosinusoidal attraction in a periodic container is transformed to a two-mode format. The system has both high-temperature single-phase regions and low-temperature two-phase regions with a very broad spatial interface that can be stabilized by a weak external field. The case of vanishing external field brings out properties of the mode amplitude dependence which one expects to extend to more complex systems.

KEY WORDS: Collective modes; one-dimensional fluid; two-phase interface; Kac–Siegert transformation.

1. INTRODUCTION

The existence of macroscopic modes supplies much of the interest—and much of the difficulty—in the analysis of microscopically defined many-particle systems. To the extent that they serve as perturbations of local properties, they fall under the rubric of hydrodynamic excitations, but naming them does not trivialize their treatment. Perhaps the cleanest physical context is that of thermally excited motion of the interface between defined fluids, basically a geometric object, and here it is not difficult to set up a phenomenological description. However, the task of producing it as a natural consequence of a microscopic analysis remains unfulfilled.

The special case in which the fluids in question are two phases of a single species is of obvious interest and importance, the autonomous inter-

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facial motions then being referred to as capillary waves. If one wants to establish control over the analytic structure of such a system, the first situation to be treated must surely be that of thermal equilibrium. There have of course been numerous studies along these lines. The general picture that emerged a long time ago(1) is that one can imagine an intrinsic interface, due to spontaneously broken translational symmetry of the uniform fluid, dynamically distorted on a scale which is determined by any constraining fields—gravitation, container, etc.—but which is large in comparison with interfacial thickness. The infinite-time average that defines thermal equilibrium then results in an extensive softening of the interfacial profile and an associated softening of the infinite-range transverse correlations that an actual plane interface would have. However, at a more detailed level, the internal flows associated with interface motion are not reliably known,(2) so that this picture does not provide precise quantitative accuracy.

From the point of view of theoretical analysis, a complex system is most effectively treated by providing a reference system or model which reproduces what are regarded as dominant characteristics, together with a well-defined perturbation method extending it to the system under scrutiny. One such model which has been suggested for capillary wave phenomena proceeds via effective replacement of particle coordinates by the potential field they create—the Kac–Siegert transformation.(3) The effective energy in the new configuration space is then expanded to second order about its minimum, leading to independent hydrodynamic excitations.(4) Higher order nonlinearity, mode coupling, etc., are thus neglected in this small-amplitude model, which, however, can in principle be corrected perturbationally.

When a two-phase system is considered in the grand ensemble, without which the formalism becomes extremely cumbersome, or even with periodic boundary conditions, the interface location is arbitrary in the absence of an external field, leading to a uniform density—the result of very large interfacial movements which are coextensive with the interfacial distortions. As an aid to developing suitable machinery to deal with very large fluctuations, we study in this paper a drastically oversimplified one-dimensional model fluid. Here, the particles in the fluid are coupled by very long-range cosinusoidal interaction, and one can therefore incite a phase transition by the van der Waals–Kac–Uhlenbeck(5) mechanism. The two phases have a very broad interface, which can be stabilized by a weak field, and whose fluctuations mimic those of capillary waves normal to an interface. We analyze this system—essentially exactly—from a point of view in direct analogy with the Kac–Siegert transformation, and conclude by suggesting how spatial fluctuations large in comparison with intrinsic spatial scale are to be managed in more complex situations.

2. BASIC FORMULATION

We consider a one-dimensional model of an interacting many-particle system with interaction potential given by

$$\phi(x_1,..., x_N) = \phi_0(x_1,..., x_N) - \frac{1}{2}\frac{A}{L} \sum \cos \gamma(x_i - x_j) + \sum u(\gamma x_i) \tag{1}$$

on a periodically bounded line of length L, where $\gamma = 2\pi/L$. The potential ϕ consists of a repulsive nearest neighbor potential ϕ_0 necessary for thermodynamic stability, and an attractive cosinusoidal potential of range L between all particles, with amplitude varying as $1/L$ to allow for a well-defined thermodynamic limit. There is in addition an external potential $u(\gamma x)$, similarly scaled. Since the interaction is itself size dependent, we will have to avoid thermodynamic identities involving volume derivatives.

A classical canonical equilibrium ensemble is defined via the weight

$$w(x_1,..., x_N) = w_0(x_1,..., x_N) \exp\left[\frac{1}{2}\beta\frac{A}{L}\sum \cos \gamma(x_i - x_j)\right] \exp\left[-\beta \sum u(\gamma x_i)\right] \tag{2}$$

where β denotes reciprocal temperature. Since the long-range interaction

$$\sum_{i,j} \cos \gamma(x_i - x_j) = \left(\sum_i \cos \gamma x_i\right)^2 + \left(\sum_i \sin \gamma x_i\right)^2 \tag{3}$$

depends only upon the combinations $\sum \cos \gamma x_i$ and $\sum \sin \gamma x_i$, it makes sense to treat these combinations separately. They can be extracted either via δ-functions or—since they occur quadratically in the energy—via suitable Gaussians. To implement the latter approach, we introduce the decomposition of unity

$$\frac{\beta A/L}{2\pi} \iint dq_c\, dq_s \exp\left[-\beta\frac{A}{2L}\left(q_c + \sum \cos \gamma x_i\right)^2\right] \times \exp\left[-\beta\frac{A}{2L}\left(q_s + \sum \sin \gamma x_i\right)^2\right] = 1 \tag{4}$$

so that Eq. (2) becomes[6]

$$w(x_1,..., x_N) = \frac{\beta A/L}{2\pi} \iint dq_c\, dq_s \exp\left[-\beta\frac{A}{2L}(q_c^2 + q_s^2)\right] \times \left(\exp\left\{-\beta\left[\frac{A}{L} q_c \sum \cos \gamma x_i + \frac{A}{L} q_s \sum \sin \gamma x_i + \sum u(\gamma x_i)\right]\right\}\right) \times w_0(x_1,..., x_N) \tag{5}$$

Our system has now been reinterpreted as one with $N+2$ coordinates, N particles interacting via nearest neighbor repulsive cores, and under the influence of a true external field $u(\gamma x)$, which we control, as well as

$$v_q(\gamma x) = \frac{A}{L}\,(q_c \cos \gamma x + q_s \sin \gamma x) \tag{6}$$

which is controlled by the two mode coordinates q_c and q_s. The latter in turn contribute quadratically and independently to the energy of the extended system. This kind of transformation is in fact a special case of the more general Kac–Siegert transformation⁽⁴⁾ which can be carried out for any system with appended negative-definite pair interaction.

Rescaling the mode coordinates, $q_c \to Lq_c$, $q_s \to Lq_s$, we can now write the grand partition function for our system as

$$\Xi[\mu - u] = \frac{\beta AL}{2\pi} \iint dq_c\, dq_s \left\{ \exp\left[-L\left(\frac{\beta A}{2}\right)(q_c^2 + q_s^2)\right]\right\} \Xi_0[\mu - u - v_q] \tag{7}$$

where

$$\begin{aligned} \Xi_0[\mu - u - v_q] = \sum_N \frac{1}{N!} \exp(\beta N \mu) \int \cdots \int dx_1 \cdots dx_N\, w_0(x_1,\ldots, x_N) \\ \times \exp\left[-\beta A \left(q_c \sum \cos \gamma x_i + q_s \sum \sin \gamma x_i \right)\right] \\ \times \exp\left[-\beta \sum u(\gamma x_i)\right] \end{aligned} \tag{8}$$

In the thermodynamic limit with the ranges of both trigonometric and external potentials going to infinity with the size of the system, we can work in the local thermodynamic approximation (see, e.g., ref. 6)

$$\Xi_0[\mu - u - v_q] = \exp\left[\beta \int P_0(\mu - u(\gamma x) - v_q(\gamma x))\, dx \right] \tag{9}$$

where $P_0(\mu)$ is the pressure of the bulk core system. Defining $\theta = \gamma x$, we now have for the grand partition function

$$\begin{aligned} \Xi[\mu - u] = \frac{\beta AL}{2\pi} \iint dq_c\, dq_s \exp\left[-\frac{L\beta A}{2}(q_c^2 + q_s^2)\right] \\ \times \exp\left\{ \frac{\beta L}{2\pi} [P_0(\mu - q_c A \cos\theta - q_s A \sin\theta - u(\theta)]\, d\theta \right\} \end{aligned} \tag{10}$$

which one can regard as a partition function in mode space, with effective mode Hamiltonian given by

$$H_{\text{eff}}(q_c, s_s) = L\left[\frac{A}{2}(q_c^2+q_s^2)-\frac{1}{2\pi}\int_0^{2\pi} P_0(\mu - q_c A\cos\theta - q_s A\sin\theta - u(\theta))\,d\theta\right] \tag{11}$$

Here we can imagine that the thermodynamic limit is being taken in the sense of Kac and Hemmer: the volume of the system in θ space remains fixed, but the particle size $2\pi a/L$ goes to zero, while $\gamma n(\theta/\gamma) \to n(\theta)$ becomes the scaled particle density, the volume of particles per unit volume remaining fixed as well.

When it is necessary to be explicit, we will choose P_0 in the simplest possible way consistent with thermodynamic stability and appropriate limiting behavior in low-density and close-packing limits. Thus, we mimic the ideal lattice gas and write

$$\beta P_0 = -\tfrac{1}{2}\ln(1-na) \tag{12}$$

where a is the core size and n the number density. For this equation of state, all thermodynamic variables have simple algebraic expressions in terms of all others. In particular, it is easily seen that

$$\begin{aligned}
\beta P_0(\mu) &= \frac{1}{2}\ln(1+ae^{\beta\mu}) \\
P_0'(\mu) &= n_0(\mu) = e^{\beta\mu}/(1+ae^{\beta\mu}) \\
P_0''(\mu) &= n_0\frac{\partial n_0}{\partial P_0}(\mu) = \frac{\beta e^{\beta\mu}}{(1+ae^{\beta\mu})^2}
\end{aligned} \tag{13}$$

3. UNIFORM FLUID

Let us start by specializing to the case of zero external field. Then (on rotating θ), Eq. (11) becomes a function of $Q=(q_c^2+q_s^2)^{1/2}$ alone,

$$\begin{aligned}
H_{\text{eff}}(u) &= -LP(Q) \\
P(Q) &= -\frac{A}{2}Q^2+\frac{1}{2\pi}\int_{-\pi}^{\pi} P_0(\mu - QA\cos\theta)\,d\theta
\end{aligned} \tag{14}$$

In the thermodynamic limit $L \to \infty$, we will thus have for the equation of state

$$\begin{aligned} P &= \lim_{L \to \infty} \frac{1}{\beta L} \ln \left(\frac{\beta A L}{2\pi} \int e^{\beta L P(Q)} 2\pi Q \, dQ \right) \\ &= \max_{Q} P(Q) \end{aligned} \tag{15}$$

The properties of

$$f(Q) = \frac{1}{2\pi} \int_{-\pi}^{\pi} P_0(\mu + QA \cos\theta) \, d\theta \tag{16}$$

are crucial. In particular, we note that

$$\begin{aligned} f'(Q) &= \frac{A}{2\pi} \int_{-\pi}^{\pi} n_0(\mu + QA\cos\theta) \cos\theta \, d\theta \\ &= \frac{A}{2\pi} \int_{-\pi/2}^{\pi/2} [n_0(\mu + QA\cos\theta) - n_0(\mu - QA\cos\theta)] \cos\theta \, d\theta \geqslant 0 \\ f''(Q) &= \frac{A^2}{2\pi} \int_{-\pi}^{\pi} n_0'(\mu + QA\cos\theta) \cos^2\theta \, d\theta \geqslant 0 \end{aligned} \tag{17}$$

the inequalities depending only upon monotonicity of $n_0(\mu)$. Thus, for $0 \leqslant Q < \infty$, $f'(Q)$ is a positive, monotonically increasing function of Q, linear with slope $f''(0) = \frac{1}{2}A^2 n_0'(\mu)$ at small Q, and reaching the constant value $f'(\infty) = A/2a$ at close-packing density $n_{\text{cp}} = 1/a$.

Since $P'(0) = 0$, there is always a stationary value of $P(Q)$ at $Q = 0$. However, if $P''(0) = -A + \frac{1}{2}A^2 n_0'(\mu) > 0$, this is a minimum, and since $P(\infty) = -\infty$, there will be an absolute maximum at some $\bar{Q} \neq 0$. For reasons to be seen later, we refer to $\bar{Q} \neq 0$ as the two-phase case:

$$\begin{aligned} &\text{two-phase:} \qquad n_0'(\mu) > 2/A \\ &P = P(\bar{Q}) \qquad \text{where} \quad f'(\bar{Q}) = A\bar{Q} \end{aligned} \tag{18}$$

If $P''(0) < 0$, $Q = 0$ is a maximum, and if an absolute maximum, we have the one-phase case in which $\bar{Q} = 0$:

$$\begin{aligned} &\text{one-phase:} \qquad n_0'(\mu) < 2/A \\ &P(Q) < P(0), \qquad P = P(0) = P_0(\mu) \end{aligned} \tag{19}$$

Here, uniformity is so stable against fluctuations that the cosinusoidal interaction simply cancels out in all thermodynamic energies.

However, even if $n_0'(\mu) < 2/A$, $Q = 0$ need not be an absolute maximum. To see how this may come about, we need only examine the putative transition line region, i.e., that in the vicinity of $P''(0) = 0$. Expanding about $\bar{Q} = 0$, we have

$$P(Q) = P_0(\mu) + \frac{Q^2}{2}\left[-A + \frac{A^2}{2} n_0'(\mu) \right] + \frac{Q^4}{24} \frac{3A^4}{8} n_0'''(\mu) + \cdots \qquad (20)$$

Clearly, if $n_0'''(\mu) > 0$ [indeed $n_0'''(\mu) = \beta^3 (1 - ae^{\beta\mu})^2/(1 + ae^{\beta\mu})^4$ for the model (13)], then $\bar{Q} = 0$ will not be the absolute maximum when $n_0'(\mu) = 2/A$, and hence in some region of $n_0'(\mu) < 2/A$ as well. Of course, even if $n_0'''(\mu) < 0$, $\bar{Q} = 0$ need not be the absolute maximum—the phase diagram is capable of some complexity. But it is not hard to show, e.g., for (12), that at sufficiently high temperature, $P(Q)$ of (14) necessarily satisfies $P(Q) < P(0)$ for $Q \neq 0$, allowing only a one-phase state.

4. APPLIED EXTERNAL FIELD

The thermodynamic behavior of the model suggests a spatial structure which, however, can be evoked only by application of an external field. From (10), and with the notation of (11), the resulting density is then

$$\begin{aligned} n(\theta) &= -\frac{\gamma}{\beta} \frac{\delta}{\delta u(\theta)} \ln \Xi[\mu - u] \\ &= \frac{\beta A L}{2\pi} \iint dq_c \, dq_s \, n_0(\mu - q_c A \cos\theta - q_s A \sin\theta - u(\theta)) \\ &\quad \times \exp[-\beta H_{\text{eff}}(q_c, q_s)]/\Xi[\mu - u] \end{aligned} \qquad (21)$$

A cosinusoidal potential

$$u(\theta) = -gA\cos\theta \qquad (22)$$

is particularly easy to incorporate into our discussion, and will be quite sufficient for our purposes. Letting $L \to \infty$, Eq. (21) then tells us that

$$n(\theta) = n_0(\mu - A(\bar{q}_c - g)\cos\theta - A\bar{q}_s \sin\theta)$$

at maximum

$$\begin{aligned} P(\bar{q}_c, \bar{q}_s) &= -\frac{1}{L} H_{\text{eff}}(\bar{q}_c, \bar{q}) = -\frac{A}{2}(\bar{q}_c^2 + \bar{q}_s^2) \\ &\quad + \frac{1}{2\pi} \int_{-\pi}^{\pi} P_0(\mu + [(\bar{q}_c - g)^2 + \bar{q}_s^2]^{1/2} A \cos\psi) \, d\psi \end{aligned} \qquad (23)$$

The zero-field maximum point $\bar{Q}$ of (15) now attains direct physical meaning: the stationary pair $(\bar{q}_c, \bar{q}_s)$ is determined by

$$\begin{aligned} 0 &= -\bar{q}_c + \frac{\bar{q}_c - g}{[(\bar{q}_c - g)^2 + \bar{q}_s^2]^{1/2}} \frac{1}{2\pi} \\ &\quad \times \int_{-\pi}^{\pi} n_0(\mu + [(\bar{q}_c - g)^2 + \bar{q}_s^2]^{1/2} A \cos\psi) \cos\psi \, d\psi \\ 0 &= -\bar{q}_s + \frac{\bar{q}_s}{[(\bar{q}_c - g)^2 + \bar{q}_s^2]^{1/2}} \frac{1}{2\pi} \\ &\quad \times \int_{-\pi}^{\pi} n_0(\mu + [(\bar{q}_c - g)^2 + \bar{q}_s^2]^{1/2} A \cos\psi) \cos\psi \, d\psi \end{aligned} \tag{24}$$

readily seen to be equivalent to

$$\bar{q}_s = 0, \quad \bar{q}_c = \operatorname{sgn}(\bar{q}_c - g) \frac{1}{2\pi} \int_{-\pi}^{\pi} n_0(\mu + |\bar{q}_c - g| \, A \cos\psi) \cos\psi \, d\psi \tag{25}$$

Hence in the limit $g \to 0$, the profile is stabilized at

$$n(\theta) = n_0(\mu - \bar{Q}A \operatorname{sgn}(g) \cos\theta) \tag{26}$$

where

$$\bar{q}_s = 0, \qquad \bar{q}_c = -\bar{Q} \operatorname{sgn}(g)$$

$$\bar{Q} = \frac{1}{2\pi} \int_{-\pi}^{\pi} n_0(\mu + \bar{Q}A \cos\psi) \cos\psi \, d\psi$$

$\bar{Q}$ is precisely that which maximizes (15). The signs used in (26) arise from the requirement that the Jacobian matrix of (24) at $\bar{q}_s = 0$ be negative at a maximum:

$$J = \begin{pmatrix} \begin{aligned} &-1 + \frac{A}{2\pi} \int_{-\pi}^{\pi} n_0'(\mu + \bar{Q}A \cos\psi) \\ &\quad \times \cos^2\psi \, d\psi \end{aligned} & 0 \\ 0 & \begin{aligned} &-1 + \frac{1}{|\bar{q}_c - g|} \frac{1}{2\pi} \int_{-\pi}^{\pi} n_0(\mu + \bar{Q}A \cos\psi) \\ &\quad \times \cos\psi \, d\psi \end{aligned} \end{pmatrix} \tag{27}$$

Here, by virtue of (25),

$$J_{22} = \frac{g}{\bar{q}_c - g} \tag{28}$$

whose negativity requires $\bar{q}_c/g < 1$, and thereby from (24), $\bar{q}_c/g < 0$ as well.

The "one-phase, two-phase" terminology thus appears meaningful. If the $g = 0$ maximum occurs at $\bar{Q} = 0$, then the system becomes uniform, $n(\theta) = n_0(\mu)$ when g approaches zero, the cosinusoidal internal forces averaging out completely. On the other hand, if $\bar{Q} > 0$, then in the $g \to 0^+$ limit, a varying density profile results, a broken symmetry which may be regarded as representing two phases with a very broad interface. Indeed, the locations of the phases interchange if $g \to 0^-$ instead.

5. LARGE-FLUCTUATION REGIONS

The continued stabilization of the two-phase profile as $g \to 0$ is a limiting result, $L \to \infty$ already having been taken. It is clear that as $g \to 0$ with $\bar{Q} \neq 0$, the vanishing of J_{22} of (2.8) will produce an arbitrarily large fluctuation in q_s, eventually exceeding any finite value of L. Indeed, it is a comparison with L that is relevant to capillary wave analogies, since the thickness of the "intrinsic interface" in this model is measured by L. A strong hint as to how to proceed under these circumstances is given by (14), where we see that *at* $g = 0$, H_{eff} depends only upon Q, so that in (21), now appearing as

$$n(\theta) = n = \frac{\beta A L}{2\pi} \iint Q\, dQ\, d\phi\, n_0(\mu - QA\cos(\theta - \phi)) \\ \times \exp\left[-\beta H_{\text{eff}}(Q)\right] / \Xi[\mu] \tag{29}$$

the conjugate angle $\phi = \tan^{-1} q_s/q_c$ is simply integrated out. It is the variable ϕ, then, which is free in the $g = 0$ limit at finite L and which therefore must be recognized as the appropriate variable in this regime.

How, then, are the variable ϕ and associated order parameter Q to be recognized *ab initio*? The key, of course, is to be found in the $g \to 0$ limit, where $\bar{Q}$ is independent of how the limit is approached, whereas $\bar{\phi}$ is totally labile. Here, since only two mode amplitudes are in question, it suffices to apply

$$u(\theta) = g(\cos\alpha\cos\theta + \sin\alpha\sin\theta) \tag{30}$$

the parameter α allowing for the full roster of fundamental wavelength applied potentials of amplitude g. As $g \to 0^+$, we find as in (26) that

$$\bar{q}_c = q \cos \alpha, \qquad \bar{q}_s = q \sin \alpha \tag{31}$$

where q is fixed by thermodynamics. Thus,

$$\partial \bar{Q}/\partial \alpha = 0, \qquad \partial \bar{\phi}/\partial \alpha = 1 \tag{32}$$

determine the natural coordinates $\bar{Q} = (\bar{q}_c^2 + q_s^2)^{1/2}$, $\bar{\phi} = \tan^{-1} \bar{q}_s/\bar{q}_c$. Extension to multiple modes is in principle direct, and will be treated in work to follow.

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